



UNIVERSITY OF SILESIA
IN KATOWICE

Institute of Physics

Faculty of Science and Technology

DOCTORAL THESIS

**Molecular Dynamics and Specific Interactions in Soft Glass Formers:
3-Phenylpropanal with Weak Hydrogen Bonding and Cyclic Dimethylsila
Crowns under Elevated Pressure and Nanoscale Spatial Confinement**

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Chorzów 2026

Acknowledgments

After four years, as I reach the end of my PhD journey, I look back with deep gratitude. These years have been scientifically challenging, personally transformative, and, despite many difficult moments, truly meaningful. This thesis would not have been possible without the support, guidance, patience, and kindness of many people, whom I would like to acknowledge sincerely.

First and foremost, I would like to express my deepest gratitude to my supervisor, **Prof. dr hab. Kamil Kamiński**. I started working with him during the second year of my PhD, and from the moment I joined his group, he was always there for me, not only as an exceptional scientist and mentor but also as someone who created a sense of belonging and support. His scientific knowledge, experience, and critical insight were essential for shaping this dissertation and for developing my understanding of molecular dynamics. Beyond science, his care, fairness, and positive attitude toward every member of the group helped me grow not only as a researcher but also as a more confident person.

I am also sincerely grateful to **dr. hab. Magdalena Tarnacka, Prof. US**. Despite her many responsibilities, she always found time to teach me how to work with scientific equipment and approach experimental problems with patience and precision. Also, I extend my gratitude towards **Prof. dr hab. Ewa Kamińska**, and **dr hab. Barbara Hachula, Prof. US**, for their constant support and guidance throughout my scientific journey.

I would also like to thank my **colleagues** and **friends**, with whom, over time, the laboratory became much more than just a workplace. My sincere thanks for their help in overcoming scientific obstacles, for everyday support, and for making life far from home much easier. I am grateful to the staff and faculty of the **Doctoral School** and to the staff of the Chorzów campus for their administrative support, technical assistance, and for providing a cooperative academic environment.

My heartfelt gratitude goes to my **parents, brother**, and **friends** in India. Thank you for understanding my absence and for supporting me through every difficult moment and every new beginning. Without your love, patience, and faith in me, I would not have reached this point. I would also like to thank **Ms. Ania Wilczek** and family for caring for me and giving me a sense of home while I was far from my own. I would also like to thank my partner, **Mr. Hemanth Pillai**, for choosing to stand beside me and for constantly encouraging me to continue.

Finally, I thank the Almighty for being my invisible support throughout this path. I am also grateful to every person who, in any way, extended a helping hand during my scientific and academic life here.



NATIONAL SCIENCE CENTRE
POLAND

The research conducted for the purposes of this doctoral thesis was financed by the National Science Centre under the OPUS 24 project entitled "The Study of molecular dynamics and specific interactions in soft materials infiltrated within nanostructured mesoporous membranes"; Grant No: 2022/47/B/ST4/00236.

Abstract

Molecular dynamics in soft glass-forming systems are often discussed mainly in terms of temperature-dependent slowing down; however, temperature alone does not fully explain how molecular architecture, specific intermolecular interactions, density changes, and nanoscale environments control relaxation behavior. This issue is particularly relevant for weakly associating molecular liquids and cyclic glass formers, whose response to high pressure and nanoconfinement remains less understood than that of classical hydrogen-bonded liquids, linear polymers, or simple molecular glass formers. This dissertation addresses this gap by investigating selected soft molecular glass formers, namely 3-phenylpropanal and cyclic dimethylsila crowns, as model systems for understanding how different molecular architectures and interaction motifs influence dielectric relaxation dynamics. Broadband dielectric spectroscopy (BDS) was used as the principal experimental method, supported by differential scanning calorimetry, Fourier-transform infrared and Raman spectroscopy, X-ray diffraction, atomic force microscopy, and molecular dynamics simulations. A central idea of the thesis was to use BDS not only to determine individual relaxation times, but also to examine the relationships between different modes of molecular mobility, especially the coupling or separation between structural α - and secondary β -relaxation, as well as between α - and Debye-like processes related to collective dipolar or supramolecular dynamics. Within this framework, thermal studies first established the basic relaxation landscape and dominant interaction motifs of the investigated systems, particularly near the glass transition temperature, T_g . High-pressure measurements then showed that compression provides a non-equivalent route to slowing down molecular dynamics. In weakly associating aldehyde systems, pressure modified the Debye-like response and its separation from the α -process, indicating changes in collective dipolar organization and supramolecular association. In cyclic dimethylsila crowns, compression revealed topology-dependent differences in the pressure sensitivity of α - and β -relaxations, activation volume, pressure coefficient of T_g , cooperative length scale, and Coupling Model (CM) analysis. Nanoconfinement introduced a further level of control by combining spatial restriction with interfacial effects. In confined DMS17C6, surface-sensitive investigations provided a different perspective from that suggested by macroscopic wettability alone, showing that local molecule–surface interactions play a decisive role in confined dynamics. The results further indicate that nanoroughness does not necessarily suppress the formation of an interfacial dynamic fraction, as previously suggested for some linear systems, but may act differently in cyclic molecular liquids. This was accompanied by a confinement-induced modification of the

α - β relationship, where the secondary process deviated from the bulk CM expectation. This peculiar behavior of β -relaxation under nanoconfinement remains an open question and requires further systematic investigation in additional glass-forming systems. Overall, thermal cooling, compression, and nanoconfinement emerge as complementary but non-equivalent pathways for probing glassy dynamics. They are connected by changes in molecular packing, density fluctuations, and available free volume, while each pathway affects intermolecular interactions, supramolecular organization, and correlations between different relaxation processes in the studied systems in a distinct manner.

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List of Abbreviations

3P1Pal – 3-Phenyl-1-propanal

3P1Pol – 3-Phenyl-1-propanol

AAO – anodic aluminium oxide

AFM – atomic force microscopy

BDS – broadband dielectric spectroscopy

CC – Cole-Cole (function)

CD – Cole-Davidson (function)

CM – coupling model

Const – constant

C_p – heat capacity at constant pressure

CRR – cooperatively rearranging regions

D – Debye/ Debye-like (process)

DFT – density functional theory

DGEBA - diglycidyl ether of bisphenol A

DMS11C4 – dimethylsila 11 crown 4

DMS14C5 – dimethylsila 14 crown 5

DMS17C6 – dimethylsila 17 crown 6

DSC – differential scanning calorimetry

dT_g/dp – pressure coefficient of glass transition temperature

E – electric field

E_a – activation energy

E_p – activation energy at constant pressure

Eq. – equation

E_v – activation energy at constant volume

f – frequency

Fig. – figure

FTIR – Fourier-transform infrared spectroscopy

g_k – Kirkwood correlation factor

HB – hydrogen bond

HN – Havriliak-Negami function
 HP – high pressure
 JG – Johari Goldstein
 KWW – Kohlrausch- William- Watts function
 MD – molecular dynamics (simulations)
 Modul - modulated
 NCL – nearly constant loss
 NM – normal mode
 NMR – nuclear magnetic resonance
 P – polarization vector
 p – pressure
 p_g – glass transition pressure
 RDF – radial distribution function
 S_c – configurational Entropy
 T – temperature
 t – time
 T_g – glass transition temperature
 T_m – melting temperature
 TPS – temperature- pressure-superposition
 V – volume
 V_f – free volume
 VFT – Vogel- Fulcher- Tammann
 XRD – X-ray diffraction
 Z^* - number of molecules involved in CRR
 α -, β - - relaxation processes
 γ – density scaling exponent
 γ_{SL} – Interfacial Energy
 $\Delta V^\#$ - activation volume
 $\Delta\epsilon$ – dielectric strength
 ϵ^* - complex dielectric permittivity

ε' – real part of the complex dielectric permittivity

ε'' – imaginary part of the complex dielectric permittivity (dielectric loss)

ε_r – relative permittivity

ε_s – static permittivity

ε_∞ - high frequency permittivity

η – viscosity

ζ – correlation / cooperative length scale

$\tau_\alpha, \tau_D, \tau_\beta, \tau_0$ – relaxation times

ω – angular frequency

χ_e - electric susceptibility

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1. Introduction

1.1. Glass-forming liquids

The glass transition is one of the most intriguing and still not fully understood phenomena in condensed matter physics. For a long time, it was often discussed in analogy to a second-order phase transition because some macroscopic quantities, such as volume and entropy, change continuously at the glass-transition temperature, T_g , whereas the heat capacity exhibits a step-like discontinuity. Despite this phenomenological similarity, the glass transition does not fully satisfy the thermodynamic criteria for an equilibrium phase transition [1–3].

One important feature of T_g is that it is not a unique thermodynamic temperature, but an operational quantity that depends on the experimental time scale. Faster cooling shifts the

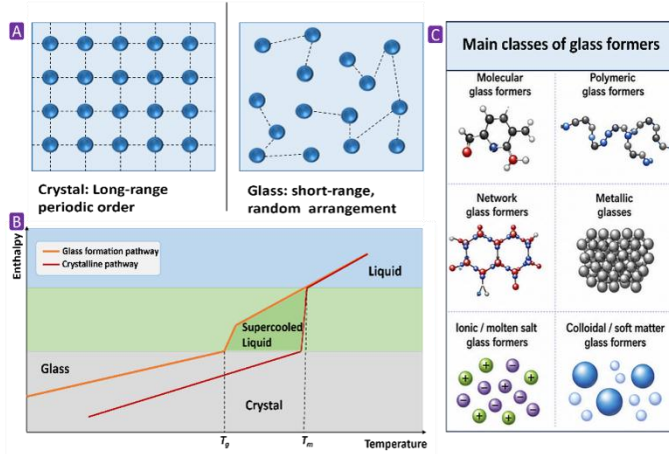


Figure 1: Schematic representation of: (A) structural ordering in crystals and glasses, (B) thermal pathways leading to glass formation or crystallization, and (C) classes of commonly studied glass formers.

glassy state. Above T_g , the supercooled liquid remains in metastable equilibrium on the experimental time scale, whereas below T_g it falls out of equilibrium and becomes an amorphous solid whose properties slowly evolve with time (Fig. 1). This physical aging is reflected in gradual changes in volume, density, enthalpy, dielectric response, conductivity, and relaxation times, showing that the glass transition marks the crossover from a metastable supercooled liquid to a non-equilibrium glass [2,4]. Thus, the glass transition is best described as a kinetic arrest of molecular motion rather than a classical thermodynamic phase transition.

The main dynamic signature of vitrification is the sharp increase in the structural α -relaxation time, and viscosity, η , upon cooling toward T_g . This slowing down is universal in glass-forming liquids, but its steepness and temperature dependence vary from nearly Arrhenius to strongly super-Arrhenius behavior, reflecting the progressive loss of molecular mobility and the growing cooperativity of structural rearrangements near T_g [1–3].

apparent T_g to a higher temperature (T) because molecular rearrangements cannot keep pace with the imposed cooling rate, whereas slower cooling allows the liquid to remain equilibrated for longer and results in a lower T_g [3]. Thus, T_g reflects the point at which the structural relaxation time (τ_α) becomes comparable to the experimental observation time. Another key feature is the non-equilibrium nature of the

A major explanation for this slowdown was proposed by Adam and Gibbs, who related the increase in structural relaxation time to the decrease in configurational entropy, S_c , upon cooling [5]. This relation is commonly expressed as:

$$\tau_\alpha = \tau_0 \exp \left(\frac{C}{TS_c} \right) \quad (1)$$

where τ_0 is the high-temperature limiting relaxation time, C is a material-dependent constant associated with the free-energy barrier for cooperative rearrangement, T is temperature, and $S_c(T)$ is the configurational entropy. As S_c decreases on cooling, τ_α increases rapidly, reflecting the growing difficulty of structural rearrangement.

Here, the central concept is the cooperatively rearranging region, CRR, defined as the smallest region able to undergo structural rearrangement independently of its surroundings. The number of molecules involved in a CRR, z^* , is inversely related to the S_c :

$$z^*(T) \propto \frac{1}{S_c(T)} \quad (2)$$

Thus, as S_c decreases upon cooling, z^* increases, leading to a larger activation barrier and a more cooperative α -relaxation near T_g .

A second classical phenomenological explanation is the free-volume concept developed by Cohen and Turnbull, which relates the slowing down of molecular motion to the reduction of available volume required for rearrangements [6]. Upon cooling, molecular packing becomes denser, free volume decreases, and translational or orientational motions become increasingly restricted. Hence, the structural relaxation time can be expressed as:

$$\tau_\alpha = \tau_0 \exp \left(\frac{B}{v_f} \right) \quad (3)$$

where v_f is the free volume, and B is a material-dependent constant. Thus, the rapid increase in τ_α near T_g is attributed to the progressive loss of free volume needed for molecular rearrangement.

Several other theoretical frameworks have also been proposed to explain the slowing down of molecular dynamics in the vicinity of T_g . The potential-energy landscape approach describes cooling as the progressive exploration of deeper metastable minima separated by higher energy barriers [7]. Mode-coupling theory explains the initial slowdown through the increasing coupling of density fluctuations and predicts a dynamic crossover above T_g [8]. More recent concepts, such as dynamic facilitation and random first-order transition theory, emphasize spatially heterogeneous dynamics, cooperativity, and growing dynamic length scales [9]. Despite their different assumptions, these approaches share a common central idea:

near T_g , molecular rearrangements become slow, cooperative, and strongly constrained by the surrounding structure.

1.2. Broadband dielectric spectroscopy as a probe of molecular dynamics

The glass transition and molecular dynamics of glass-forming systems are investigated using a range of complementary techniques, including mechanical spectroscopy, dynamic light scattering, X-ray and neutron scattering and diffraction methods, infrared and Raman spectroscopy, calorimetry, nuclear magnetic resonance (NMR), and Atomic Force Microscopy (AFM). Each method probes different aspects of soft matter, such as mechanical response, density fluctuations, local structure, molecular vibrations, intermolecular interactions, or changes in ordering near T_g [2,3,10]. Molecular dynamics (MD) simulations provide an additional and highly important source of information about the dynamics and microscopic properties of liquids. They offer a microscopic perspective by giving direct access to local structure, intermolecular correlations, conformational changes, cluster formation, and the relationship between molecular architecture and dynamics [11,12]. Thus, MD simulations can support experimental results by revealing structural and dynamical details that are not directly accessible through macroscopic measurements.

However, the interpretation of such microscopic insight must take into account the limited time scales accessible to simulations. Conventional MD simulations usually capture fast processes on pico- to nanosecond scales, whereas relaxation processes relevant to the glass transition may extend from microseconds to hundreds of seconds near T_g . This timescale mismatch makes direct comparison with experimentally measured slow α -relaxation difficult. Therefore, MD simulations should be regarded as a powerful complementary tool that helps interpret experimental trends, rather than replacing techniques that probe slow supercooled-liquid dynamics. Together, experiments and simulations enable a more complete description of dynamic properties, static structure, intermolecular interactions, and microscopic organization near T_g . Among the methods mentioned above, broadband dielectric spectroscopy (BDS) is one of the most powerful techniques for studying soft matter close to the glass transition [13–15].

The major strength of BDS lies in its exceptionally broad frequency (f) and time window. As shown schematically in **Fig. 2**, it can probe molecular mobility from fast local motions to slow α -relaxation processes approaching the experimental glass transition. This makes it particularly powerful for glass-forming liquids, where τ_α may change by many orders of magnitude upon cooling.

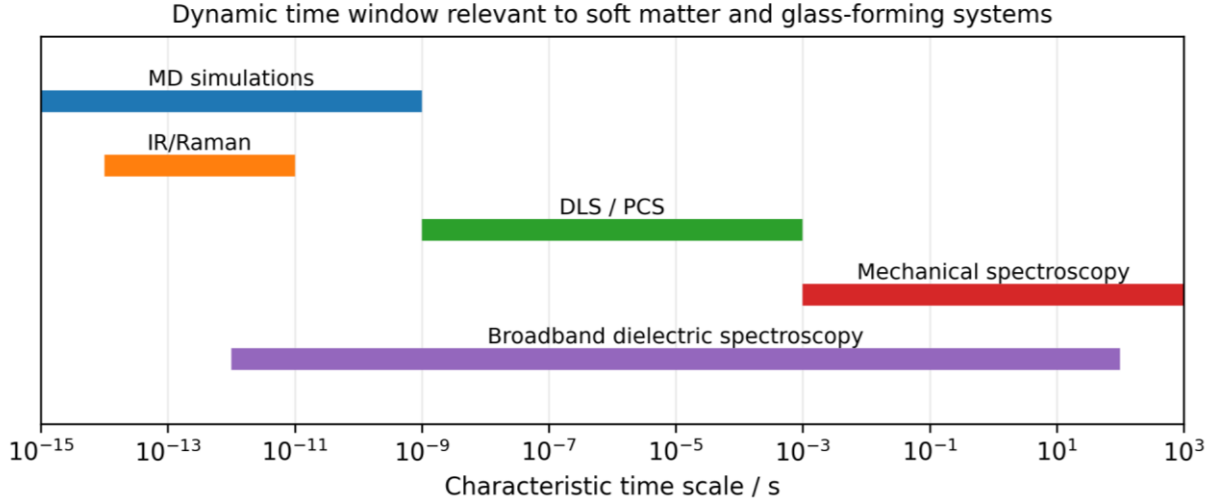


Figure 2. Schematic illustration of the broad dynamic time window accessible to BDS compared with selected complementary experimental methods and molecular dynamics simulations. (Here, DLS and PCS denote Dynamic Light Scattering and Photon Correlation Spectroscopy, respectively, which are synonymous techniques used to evaluate relaxation dynamics.)

BDS is also experimentally versatile because it requires only a small amount of material, which is particularly important for thin films, confined systems, and nanoporous samples. A limiting example was reported by Tress et al. in *Science*, who demonstrated that the dielectric response can be measured even for condensed isolated polymer chains [16]. This sensitivity makes BDS especially useful in nanoconfinement studies, where the signal from the confined phase is often weak.

Another advantage is its nondestructive character, since the sample is usually exposed only to a weak alternating electric field and can later be used for complementary measurements. Moreover, BDS can be combined with high-pressure cells, temperature-controlled chambers, light irradiation, and nanostructured templates [13,17]. This makes it suitable not only for equilibrium relaxation studies, but also for monitoring time-dependent processes involving changes in dipole moment, such as polymerization, crystallization, conformational or isomeric transformations, phase transitions, and changes in supramolecular organization.

The physical basis of dielectric spectroscopy is the interaction between electric dipoles and an external electric field. When a sample is placed between the electrodes of a capacitor and subjected to a sinusoidally varying electric field, the charges and dipoles within the material respond to the applied perturbation. The time-dependent electric field can be expressed as

$$E(t) = E_0 \exp(i\omega t), \quad (4)$$

where E_0 is the amplitude of the electric field, t denotes time, and $\omega = 2\pi f$ is the angular frequency of the applied field, with f being the frequency. The use of the complex exponential

notation is mathematically convenient and represents a harmonic oscillation of the electric field.

In a linear, isotropic dielectric, the electric displacement field, D , is related to the electric field, E , and the polarization, P , by

$$D = \varepsilon_0 E + P \quad (5)$$

where ε_0 is the vacuum permittivity. The polarization is the dipole moment per unit volume and, in the linear regime, is given by

$$P = \varepsilon_0 \chi_e E \quad (6)$$

where χ_e is the electric susceptibility. Combining these relations gives

$$D = \varepsilon_0 \varepsilon_r E \quad (7)$$

where $\varepsilon_r = 1 + \chi_e$ is the relative permittivity. In an alternating field, the response is generally delayed with respect to the applied field, and the relative permittivity becomes a complex quantity:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad (8)$$

Here, ε' describes the energy stored by the material, whereas ε'' describes dielectric losses associated with molecular relaxation and charge transport.

Several polarization mechanisms contribute to the dielectric response. Electronic polarization results from the displacement of the electron cloud relative to the nuclei and is extremely fast. Atomic or ionic polarization arises from the relative displacement of atoms or ions in a molecule or lattice

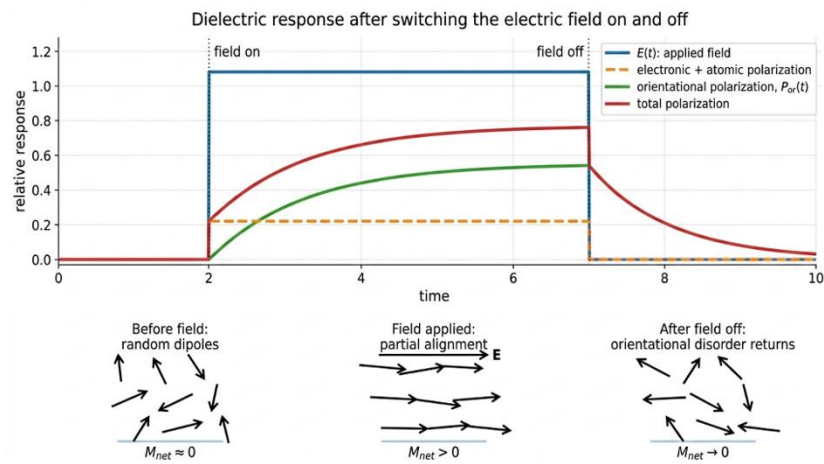


Figure 3. Schematic representation of the dielectric response after switching an external electric field on and off. The electronic and atomic contributions appear almost instantaneously after the field is applied and disappear immediately after it is removed. The orientational polarization, associated with dipolar alignment and the net dipole moment of the sample, builds up and decays on a characteristic relaxation time scale.

[13]. Orientational polarization is slower and results from the reorientation of permanent dipole moments in the direction of the applied electric field. It is this orientational contribution that is especially important in dielectric studies of molecular dynamics, because its characteristic time scale reflects molecular mobility[18].

In this context, Debye introduced the simplest description of dielectric relaxation for a system of non-interacting dipoles characterized by a single relaxation time. In this ideal case, the complex permittivity is given by

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+i\omega\tau_D} \quad (9)$$

where ε_∞ is the high-frequency permittivity, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric strength, ε_s is the static permittivity, τ_D is the Debye relaxation time. The dielectric loss maximum occurs when $\omega_{\max}\tau_D = 1$ or, equivalently, $\tau_D = 1/(2\pi f_{\max})$. The Debye model predicts a symmetric loss peak on a logarithmic frequency scale and represents the limiting case of a single exponential relaxation process [13].

However, most glass-forming liquids, polymers, and confined systems deviate from ideal Debye behavior. Their relaxation peaks are broadened and often asymmetric, which reflects a distribution of relaxation times, dynamic heterogeneity, intermolecular correlations, or overlapping molecular processes. Therefore, empirical non-Debye functions are widely used to describe dielectric loss ε'' spectra. The most general of these commonly used functions is the Havriliak-Negami (HN) equation, often supplemented with an additional term describing the dc conductivity:

$$\varepsilon(\omega)'' = \frac{\sigma_{dc}}{\varepsilon_0\omega} + \varepsilon_\infty + \text{Im} \sum_{i=1}^n \left(\frac{\Delta\varepsilon_i}{[1+(i\omega\tau_{HN,i})^{\alpha_{HN,i}}]^{\beta_{HN,i}}} \right) \quad (10)$$

where σ_{DC} is the DC-conductivity, τ_{HN} is the characteristic HN time, while α_{HN} and β_{HN} are shape parameters describing the width and asymmetry of the relaxation peak [19]. The Debye, Cole-Cole (CC), and Cole-Davidson (CD) functions are limiting cases of this expression. For $\alpha_{HN} = 1$ and $\beta_{HN} = 1$, the Debye equation is recovered. For $0 < \alpha_{HN} < 1$ and $\beta_{HN} = 1$, the expression reduces to the CC function, which describes a symmetrically broadened relaxation peak. For $\alpha_{HN} = 1$ and $0 < \beta_{HN} < 1$, it becomes the CD function, which accounts for asymmetric broadening. When both α_{HN} and β_{HN} differ from unity, the full HN function describes a broad and asymmetric non-Debye response (see **Fig. 4**) [20,21].

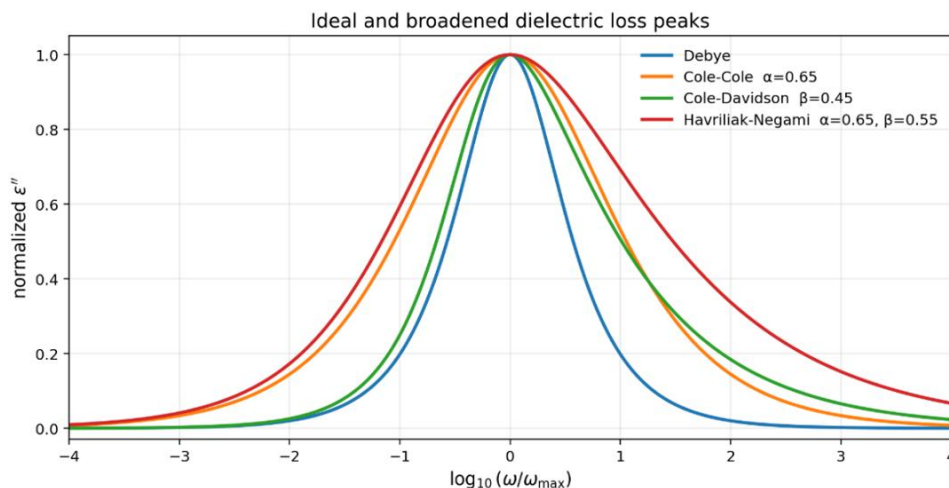


Figure 4. Schematic comparison of Debye and non-Debye dielectric loss peaks described by CC, CD, and HN type functions.

Thus, BDS provides direct access to molecular and supramolecular dynamics through the frequency-dependent dielectric response. In the context of glass-forming systems, it is particularly valuable because the structural α -relaxation, secondary relaxations, conductivity, interfacial polarization, and time-dependent transformations can often be followed within the same experimental platform. This makes BDS a central tool for connecting macroscopic dielectric response with molecular mobility, cooperative dynamics, and changes in intermolecular organization near the glass transition.

1.3. Dielectric relaxation processes in glass-forming systems

BDS does not provide a single relaxation time, but a relaxation spectrum in which different molecular, supramolecular, and polymer-specific processes may appear. Their assignment is essential because individual dielectric modes probe different length scales of motion, from local intramolecular fluctuations and cooperative structural rearrangements to segmental polymer dynamics, global chain motion, or collective fluctuations of supramolecular aggregates.

a) Structural α -relaxation

The α -relaxation is the central dynamic process of glass formation in molecular liquids. It reflects cooperative molecular rearrangements responsible for the liquid-to-glass transformation. In dielectric spectra, the α -process usually appears as a broad, asymmetric, non-Debye loss peak and is therefore often described using empirical functions such as the CD or HN equations, as described in the previous section using **Eq. 10** [2,3].

As noted above, the temperature dependence of τ_α is usually non-Arrhenius, meaning that the apparent activation energy (E_a) increases upon cooling toward T_g . In practice, calorimetric T_g often corresponds approximately to the temperature at which τ_α reaches about 100 s, although this value depends on the experimental definition and time scale as mentioned in **section 1.1**. This temperature dependence of τ_α is commonly used to classify glass formers as strong or fragile [1]. The kinetic fragility index, m , is defined as:

$$m = \left[\frac{d \log_{10} \tau_\alpha}{d(T_g/T)} \right]_{T=T_g} \quad (11)$$

or analogously using viscosity.

b) Segmental relaxation in polymers

In polymers, the counterpart of the structural α -relaxation is referred to as the segmental relaxation. It originates from cooperative conformational rearrangements of short portions of the polymer backbone, typically involving several repeating units, rather than from the motion of the entire macromolecule [22]. This process determines the glass transition of polymers because, when the segmental relaxation time exceeds the experimental observation window, the polymer falls out of equilibrium and enters the glassy state, similar to the α -relaxation in molecular glass formers.

Dielectrically, segmental relaxation is observed when the polymer contains dipoles along and perpendicular to the chain contour or when local conformational changes produce fluctuations of the dipole moment. Similar to the α -relaxation in small-molecular glass formers, the segmental process is broad, non-Debye in shape, and strongly temperature dependent, often described by the Vogel-Fulcher-Tammann (VFT) equation [23–25].

$$\tau_\alpha = \tau_\infty \exp \left(\frac{D_T T_0}{T - T_0} \right) \quad (12)$$

where τ_∞ is the relaxation time in the high temperature limit, T_0 represents the ideal glass transition temperature corresponding to the extrapolated divergence of τ_0 , and D_T is the strength parameter. The broadness of the segmental relaxation reflects the distribution of local environments and relaxation times arising from chain connectivity, packing constraints, intermolecular interactions, and dynamic heterogeneity.

The segmental process controls the onset of large-scale mobility in polymers because any long-range chain displacement requires local conformational rearrangements of the backbone. Therefore, it provides the elementary dynamic step that enables larger-scale chain motions. Segmental relaxation determines the glass transition and local viscoelastic response of polymers, while terminal flow emerges only when these local segmental motions are coupled over progressively larger portions of the chain [22,26].

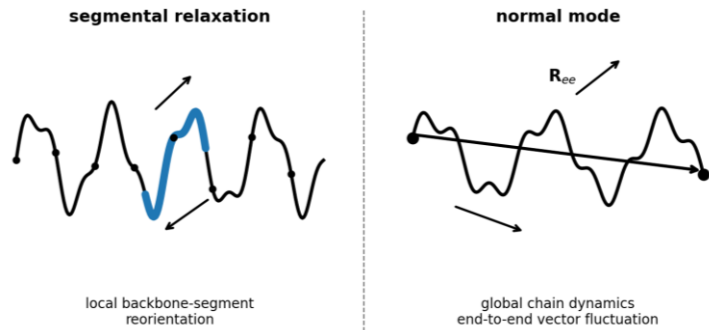


Figure 5. Schematic representation of polymer segmental relaxation and NM relaxation.

c) Secondary relaxations, including the Johari-Goldstein process

Secondary relaxations (such as β -, γ -, and higher-order processes) are usually observed below T_g , although in many systems they may also enter the experimental frequency window above T_g [13,27]. Below T_g , temperature dependences of secondary relaxation times (τ_x) are commonly described by the Arrhenius equation:

$$\tau_x = \tau_\infty \exp\left(\frac{E_a}{RT}\right) \quad x = \beta, \gamma, \dots \quad (13)$$

where E_a is the activation energy, and R is the gas constant. Unlike the α -relaxation, these processes usually exhibit an approximately constant E_a . Their molecular origin may involve local intramolecular motions of polar side groups or molecular fragments, such as ester, amino, hydroxymethyl, or other dipolar units [28]. Such relaxations, typically having low E_a values, around 10–30 kJ/mol, are weakly sensitive to density changes, and often show very small activation volumes ($\Delta V^\ddagger$), close to 0 cm³/mol [17].

A distinct class of secondary relaxations is the Johari-Goldstein (JG) β -relaxation, commonly regarded as a precursor of the structural α -relaxation. Unlike purely intramolecular motions, the JG process has an intermolecular character and is often interpreted as a local motion of the whole molecule within the cage formed by its neighbors. JG relaxations usually have higher activation energies, often around 50-90 kJ/mol, and are sensitive to pressure and density. Therefore, their activation volume is non-zero, and their relaxation time shifts measurably under compression.

One useful criterion for distinguishing JG-like from purely intramolecular secondary processes is the Coupling Model (CM) proposed by Ngai [29]. In this model, the non-

exponential α -relaxation is described by a coupling parameter n , related to the stretching exponent (β_{KWW}) of the Kohlrausch–Williams–Watts (KWW) function:

$$\Phi(t) = \exp \left[- \left(\frac{t}{\tau_\alpha} \right)^{\beta_{KWW}} \right] \quad (14)$$

by $n = 1 - \beta_{KWW}$ [30]. The primitive relaxation time is estimated from the α -relaxation time as:

$$\tau_0 = t_c^n \tau_\alpha^{1-n} \quad (15)$$

where t_c is a microscopic crossover time, typically of the order of 1-2 ps for many molecular glass formers. If the experimentally observed secondary relaxation time, usually τ_β , is close to the calculated primitive relaxation time τ_0 , the process is often considered JG-like. This agreement is not an absolute proof, but it supports the assignment when combined with pressure dependence, $\Delta V^\ddagger$, and molecular-structure arguments.

d) Debye-like processes in associating liquids

A characteristic slow Debye-like (D-) process is frequently observed in dielectric spectra of associating liquids, especially monohydroxy alcohols, but also in amides, amines, carboxylic acids, and selected pharmaceutical glass formers such as ibuprofen [31–33]. It often appears as a more intense and narrower peak at lower frequencies than the α -process. Importantly, the D-process should not be understood as an ideal Debye relaxation of independent, freely rotating dipoles. Instead, it reflects a collective dielectric response generated by transient supramolecular organization.

In monohydroxy alcohols, this behavior is commonly described by the transient chain model proposed by Gainaru and co-workers [34]. According to this model, alcohol molecules form temporary hydrogen-bonded chain-like aggregates, and the fluctuations of their end-to-end dipole moment are reflected as the D-process. The relaxation does not require rigid rotation of the whole aggregate, but may occur through molecular attachment and detachment, hydrogen-bond (HB) breaking and reformation, and reorganization of the supramolecular structure [34,35]. This explains why the D-process is slower than the α -relaxation and why its strength depends strongly on the topology of H-bonded aggregates.

More recent studies have refined the interpretation of the dielectric Debye peak by showing that it may arise not only from self-reorientation of individual molecules, but also from cross-correlations between different molecular dipoles. Since dielectric spectroscopy probes fluctuations of the total dipole moment, the measured response contains both single-dipole reorientation terms and correlated orientational motions of neighboring dipoles. In transient supramolecular structures, H-bonded clusters, or locally correlated polar domains, these cross-

correlations can become sufficiently slow and intense to generate an additional Debye-like contribution to the dielectric spectrum [35,36].

Thus, the D-process should not be viewed only as a signature of a specific aggregate geometry, such as a simple H-bonded chain, but more broadly as a manifestation of collective dipolar organization. Its dielectric strength reflects the extent and intensity of orientational dipole–dipole correlations, whereas its time scale is related to the lifetime and reorganization of the correlated supramolecular structure. Consequently, changes in Debye strength or in the separation between D- and α -relaxation times can serve as sensitive indicators of changes in supramolecular topology, cluster compactness, and molecular association [34,35]. The D-process often shows a more Arrhenius-like temperature dependence than the structural α -relaxation [37].

e) Normal mode in type-A polymers

The dielectric normal mode is observed in Stockmayer type-A polymers, where the dipole moment has a component parallel to the chain contour [38]. It originates from fluctuations of the end-to-end vector (see **Fig. 5**) and therefore probes global chain dynamics rather than local segmental motion. Its relaxation time depends on molecular weight, chain stiffness, architecture, and entanglements, and is closely related to the longest chain relaxation time. Accordingly, rheological and dielectric studies often show comparable temperature dependences of the NM relaxation and terminal relaxation, confirming its connection with large-scale chain dynamics [39,40].

f) Sub-Rouse modes

Sub-Rouse modes are relaxation processes typically slower than the segmental α -relaxation but faster than the full-chain normal mode or terminal relaxation. They are observed in some polymers and reflect motions on length scales larger than a segment but smaller than the entire chain. Importantly, they do not satisfy the strict criteria for the dielectric NM, which is limited to type-A polymers according to the Stockmayer classification [41,42]. Sub-Rouse processes are therefore useful for identifying intermediate chain dynamics, particularly in systems where specific interactions, architecture, or confinement modify the usual hierarchy of polymer relaxation modes.

g) Excess wing

The excess wing is a weak, power-law-like contribution on the high-frequency flank of the α -relaxation, commonly observed when a distinct secondary peak is not resolved. It has been interpreted either as an intrinsic part of the broad, heterogeneous α -response or as the unresolved high-frequency side of a hidden β -relaxation, often of JG character. Aging

experiments below T_g and high-pressure (HP) studies frequently support the latter view, since the wing may evolve into a shoulder or separate β -peak when the α -process shifts away [27,43]. Therefore, the excess wing should be assigned cautiously and, whenever possible, supported by temperature-, pressure-, or aging-dependent measurements.

h) Nearly constant loss

At frequencies higher than the α -process and secondary relaxations, many glass-forming systems show a nearly constant loss (NCL). In dielectric loss spectra, it appears as a very weak frequency dependence, often approximated by $\varepsilon''(f) \propto f^{-c}$ with c close to zero, for example, around 0.1 [27,44]. The NCL is usually associated with very fast, localized, cage-rattling dynamics, where molecules or molecular fragments perform small-amplitude motions inside cages formed by their neighbors. Thus, it reflects the fast vibrational or anharmonic dynamics of the glassy or deeply supercooled state rather than a complete structural rearrangement.

1.4. Temperature- and pressure-dependent BDS studies of glass-forming systems

Most studies of glass-forming liquids have traditionally been performed at atmospheric pressure by varying temperature. These measurements established the basic phenomenology of structural relaxation and led to the Angell classification, in which strong glass formers show a nearly Arrhenius temperature dependence of the structural or segmental relaxation time,

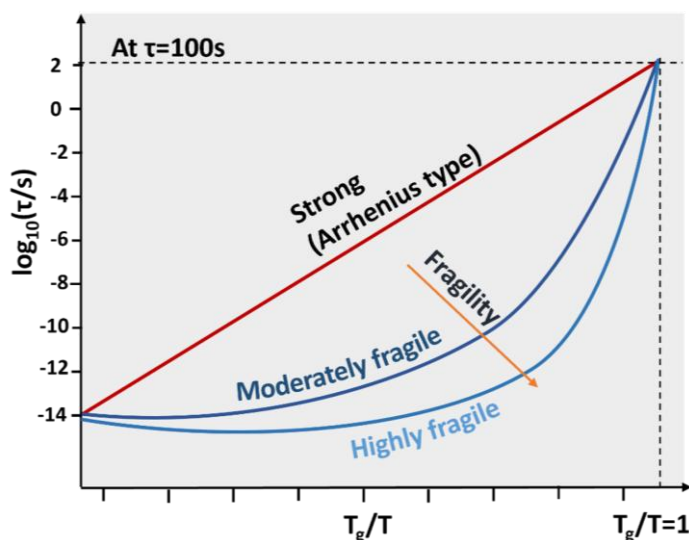


Figure 6. The Angell representation showing the difference between strong and fragile glass formers.

whereas fragile systems exhibit a steep super-Arrhenius slowdown near T_g (Fig. 6). The fragility index, m (Eq. 11), therefore quantifies how rapidly the dynamics slow down when approaching the glass transition, as discussed in the previous sections [1].

In general, network-forming systems often display lower fragility than typical van der Waals liquids, but this trend is not

universal. The final value of m depends not only on the dominant intermolecular interactions but also on molecular architecture, packing efficiency, conformational flexibility, and possible changes in supramolecular organization. Plastic crystals, in which translational crystalline order

coexists with orientational disorder, are often relatively strong glass formers; however, fragile plastic crystals have also been reported, showing that orientational disorder alone does not uniquely determine the steepness of structural slowdown [45].

Temperature-dependent studies also revealed important empirical correlations between fragility and the spectral shape of the structural relaxation. Böhmer *et al.* showed that, for many glass formers, more fragile systems tend to exhibit more non-exponential α -relaxation [46]. In the time domain, the α -relaxation is often represented by the KWW function (**Eq. 14**) [30].

Lower values of the stretching exponent (β_{KWW}) correspond to broader relaxation-time distributions and stronger deviations from Debye behavior. The empirical Böhmer relation, $m \approx 250(\pm 30) - 320\beta_{KWW}$, indicates that fragile liquids generally display broader and more stretched α -relaxation peaks [46]. Nevertheless, this relation should be treated as a useful empirical trend rather than a universal law, because orientational glasses, monohydroxy alcohols, strongly associating liquids, and systems with overlapping relaxation processes may deviate from it.

Temperature-dependent dielectric studies have also shown that the apparent spectral shape of the α -relaxation can be strongly influenced by molecular polarity. Paluch and co-workers demonstrated that liquids with larger dielectric relaxation strength often exhibit narrower, less stretched dielectric α -peaks [47]. This effect arises because BDS probes fluctuations of the total dipole moment of the sample and therefore contains not only self-correlation terms related to single-molecule reorientation but also cross-correlation terms associated with correlated orientational motion of neighboring dipoles. In polar and associating liquids, these dipole–dipole correlations can significantly modify the apparent shape and intensity of the measured relaxation peak.

Thus, a more Debye-like dielectric α -response in highly polar liquids does not necessarily mean that the underlying structural relaxation is intrinsically homogeneous or Debye-like. Rather, the measured spectrum reflects both the distribution of molecular relaxation times and the degree of collective dipolar organization. This distinction is particularly important for monohydroxy alcohols, where BDS detects not only the structural α -relaxation but also an intense and slower Debye-like process [34,48]. Comparative studies using dielectric spectroscopy together with techniques such as photon correlation spectroscopy and NMR have shown that this slow D-process does not represent ordinary α -relaxation of individual molecules. Instead, the α -process reflects the structural dynamics of the liquid matrix, whereas the D-mode is associated with fluctuations of transient H-bonded supramolecular structures [34,37,49].

Comparison between BDS and techniques more sensitive to local or self-reorientational dynamics is essential for separating α -relaxation from dielectric contributions arising from intermolecular dipolar correlations [49]. This distinction is important not only for monohydroxy alcohols but also for polar glass-forming liquids in general, because the shape, amplitude, and time scale of a dielectric peak may reflect both molecular mobility and dipolar organization.

Moreover, temperature-dependent BDS also enables the relationship between α -relaxation and secondary dynamics to be examined. Secondary relaxations are usually most clearly resolved below T_g , although they may persist above T_g and overlap with the α -process. As discussed above, the CM proposed by Ngai provides a useful framework for relating the JG-relaxation to the primitive relaxation preceding cooperative α -dynamics. Together with studies of the excess wing and nearly constant loss, this shows that secondary processes may contain important information about cage dynamics and cooperativity, and some of them, especially JG relaxations, may act as precursors of structural relaxation. However, at atmospheric pressure, distinguishing a true intermolecular JG process from an intramolecular secondary relaxation can be difficult because different mechanisms may appear in a similar frequency range.

Introducing pressure as an additional thermodynamic variable provides deeper insight into glassy dynamics. In isobaric temperature-dependent experiments, cooling simultaneously changes thermal energy, density, packing, free volume, and intermolecular correlations. HP BDS, especially when combined with pressure-volume-temperature (PVT) data or an equation of state, helps separate these contributions by allowing relaxation times to be analyzed under different thermodynamic pathways, such as isobaric, isothermal, isochoric, or isochronal conditions [17,50,51].

The relative roles of temperature and volume can be quantified using the apparent activation energies determined at constant pressure and constant volume[51,52]:

$$E_p = R \left[\partial \ln(\tau_\alpha) / \partial \left(\frac{1}{T} \right) \right]_p \quad (16)$$

$$E_v = R \left[\partial \ln(\tau_\alpha) / \partial \left(\frac{1}{T} \right) \right]_v \quad (17)$$

The ratio E_v/E_p estimates the relative contribution of thermal energy to the structural slowdown. Values close to unity indicate predominantly temperature-controlled dynamics, whereas lower values reflect a stronger influence of volume or density. In many van der Waals

liquids and polymers, density changes play a major role, while in strongly associating systems, especially those governed by directional hydrogen bonding, temperature-dependent changes in the interaction network may become more important.

A particularly important outcome of HP studies is thermodynamic, or density, scaling. For many glass-forming liquids and polymers, structural relaxation times measured at different combinations of temperature and pressure can be superimposed onto a single master curve using a scaling variable that combines temperature and volume [53]:

$$\tau_{\alpha} = F(1/(TV^{\gamma})) \quad (18)$$

where V is the specific volume, γ is the density-scaling exponent, and F is a material-specific function. Equivalently, the scaling can be written as $\tau_{\alpha} = F(\rho^{\gamma}/T)$, where $\rho = 1/V$. The exponent γ reflects the relative importance of density or volume compared with thermal energy and is often related to the steepness of the effective repulsive part of the intermolecular potential. Thus, pressure-dependent measurements of $\tau_{\alpha}(T,p)$, combined with volumetric data, provide insight into how intermolecular packing controls structural dynamics.

HP BDS has also shown that, for many van der Waals liquids, the shape of the α -relaxation peak is governed mainly by the τ_{α} itself rather than by T or p separately. Dielectric loss spectra measured at different T and p , but at the same τ_{α} , often superimpose after normalization. This behavior, known as time-temperature-pressure superposition (TPS), indicates that along an isochronal path, the distribution of relaxation times and the α -relaxation mechanism remain nearly unchanged [17,54,55]. It is also consistent with the isomorph theory for Roskilde-simple liquids, i.e., liquids in which structure and dynamics remain approximately invariant along specific temperature–density pathways because thermal and density effects are strongly correlated [56].

Associating liquids often deviate from this simple TPS rule because p and T can change not only density, but also the topology, lifetime, and dipolar organization of supramolecular structures [33]. Therefore, two state points with the same τ_{α} may still differ in spectral shape, dielectric strength, or relaxation-mode separation, indicating that pressure can reorganize molecular association rather than merely slow down dynamics [57].

HP BDS also provides a stricter test of secondary relaxations. At ambient pressure, agreement between the experimental β -relaxation time and the CM primitive time may suggest JG-like behavior, but this criterion is not conclusive. Under compression, a β -process coupled to structural dynamics should show measurable pressure sensitivity, whereas more local intramolecular motions are usually much less affected and exhibit smaller $\Delta V^{\#}$ [58].

Pressure studies are equally useful for collective dielectric modes. In associating liquids, changes in D-strength, Kirkwood correlation factor, and D/α time-scale separation reveal modifications in supramolecular size, topology, and stability [35,59]. In type-A polymers, comparison of segmental and normal-mode relaxations shows whether local backbone mobility and global chain dynamics remain coupled under densification [60]. Thus, temperature- and pressure-dependent BDS provides more than a simple shift of relaxation peaks. It separates thermal and density effects, tests spectral-shape invariance through TPS, and probes the coupling between structural, secondary, supramolecular, and polymer-specific relaxation modes.

Overall, combined temperature- and pressure-dependent BDS provides a richer picture of glassy dynamics than temperature-dependent measurements alone. It helps separate thermal and density contributions, quantify packing effects through E_V/E_P and density scaling, test spectral-shape invariance through time-temperature-pressure superposition, and examine the coupling between structural, secondary, supramolecular, and polymer-specific relaxation modes. In this sense, pressure acts not only as a way to slow dynamics, but also as a probe of intermolecular interactions, cooperative motion, and the hierarchy of molecular mobilities in soft matter.

1.5. Nanoconfinement effects in glass-forming liquids and polymers

Temperature- and pressure-dependent studies have shown how structural, secondary, supramolecular, and polymer-specific relaxations respond to changing thermodynamic conditions. Nanoconfinement provides a complementary approach by placing glass-forming liquids or polymers in restricted geometries, such as controlled-pore glasses, silica matrices, anodic aluminum oxide (AAO) membranes, thin films, or nanoporous templates. This allows one to examine how molecular dynamics is modified when the confining length scale becomes comparable to molecular dimensions, interfacial layers, or cooperative length scales. One of the original motivations for confinement studies was to test whether the dramatic slowing down of structural relaxation near T_g is connected with the growth of CRRs. In the Adam-Gibbs theory, the decrease in S_c upon cooling leads to an increase in the size of the cooperatively rearranging region (Eq. 2). If a liquid is confined within pores whose diameter is comparable to the expected CRR size, typically of the order of a few nanometers, the growth of these regions may become geometrically restricted. Therefore, confinement offers an indirect but powerful test of whether the temperature dependence of τ_α is controlled by a growing cooperative length scale.

Early dielectric studies of low-molecular-weight glass formers confined in nanoporous materials provided important support for this idea. Arndt *et al.* showed that, when a glass-forming liquid was confined in controlled-pore glasses with pore diameters of only a few nanometers, the structural relaxation initially followed the bulk-like temperature dependence upon cooling, but below a certain temperature it deviated toward a more Arrhenius-like behavior [61]. This crossover was interpreted as an indication that the growth of the cooperative length scale was limited by the pore size. In this sense, nanoconfinement provided indirect evidence that the increase in τ_α near T_g may be related to the growth of CRRs, as anticipated by the Adam-Gibbs framework.

However, later studies showed that this interpretation is not complete. A major step forward came from combined dielectric spectroscopy and positron annihilation lifetime spectroscopy. Kipnusu and co-workers investigated confined 2-ethyl-1-hexanol and demonstrated that the confinement-induced acceleration of the α -relaxation correlates with an increase in effective free volume [62]. These results indicated that the deviation of confined dynamics from bulk behavior cannot be understood only as a geometrical limitation of CRR growth; it is also strongly connected with density and free-volume fluctuations inside the pores [63].

This interpretation was later refined by studies linking confined dynamics directly with pressure-dependent bulk behavior. During cooling in nanopores, the confined liquid may deviate from an ordinary isobaric path and approach quasi-isochoric conditions once the interfacial layer becomes dynamically arrested. In this regime, the temperature dependence of τ_α may resemble the isochoric relaxation behavior obtained from high-pressure bulk data extrapolated into the negative-pressure domain [64]. This behavior was rationalized by the development of negative pressure inside the pores, which compensates thermal contraction and maintains a quasi-constant volume during cooling. Equation-of-state analysis therefore provides a way to estimate this negative pressure and establish a direct connection between nanoconfinement effects and pressure-dependent bulk dynamics [64,65].

In this view, confinement-induced changes in α -relaxation are not simply finite-size effects. They arise from the interplay between pore geometry, interfacial interactions, density fluctuations, and the thermodynamic pathway imposed on the confined liquid. This concept was further supported by studies combining dielectric and calorimetric signatures of confined glass formers. In several systems, calorimetry revealed the double glass-transition events, commonly interpreted within a core-shell, or two-layer, model [66,67]. In this picture, the confined material contains dynamically distinct fractions: an interfacial shell strongly affected

by the pore wall and a core-like fraction whose dynamics are closer to the bulk liquid. Once the interfacial layer becomes dynamically arrested, it may impose volume or density constraints on the remaining mobile core fraction, so that the core dynamics can approach quasi-isochoric behavior rather than ordinary isobaric cooling [64]. Consequently, the apparent T_g , dielectric strength, and relaxation-time behavior measured under confinement reflect an average response of spatially heterogeneous molecular populations, whose relative contributions depend on pore size, surface interactions, and the core/interfacial volume ratio.

Despite this progress, the core-shell model alone does not fully explain why confinement-induced T_g shifts differ strongly among liquids and polymers. Floudas and co-workers addressed this issue for polymers confined in nanoporous alumina and showed that the depression of T_g relative to the bulk correlates with the polymer-alumina interfacial energy determined from contact-angle measurements on flat alumina surfaces [68]. This demonstrated that polymer-substrate interactions are an important parameter controlling segmental dynamics under nanoconfinement.

However, subsequent investigations showed that interfacial energy (γ_{SL}) alone is not always sufficient to describe confinement-induced shifts in T_g for different polymers and molecular liquids. Talik *et al.*, and later Zimny *et al.*, in studies on confined polymer systems, demonstrated that the pressure coefficient of the glass transition temperature (dT_g/dp) determined from bulk HP dielectric measurements, is also an important parameter [66,69]. Systems with a larger dT_g/dp are more sensitive to density fluctuations and pressure-like constraints; therefore, their dynamics may be more strongly affected by density perturbations generated under confinement. Thus, the confinement response is better described by considering both molecule-surface interactions and the intrinsic density sensitivity of the bulk material. Such an approach directly links nanoconfinement-induced changes in T_g with density-controlled dynamics known from HP experiments.

This observation creates a direct conceptual bridge between two apparently different experimental approaches: high-pressure studies of bulk materials and nanoconfinement studies in porous media. In both cases, density fluctuations play a central role. In HP experiments, density is controlled externally by hydrostatic compression. In confinement, density fluctuations are generated internally by interfacial interactions, capillary effects, incomplete thermal contraction, and the vitrification of the interfacial layer. Thus, nanoconfinement can mimic certain aspects of pressure-dependent dynamics, although the microscopic origin of the density perturbation is different.

Another important development was the recognition that confinement effects are not fixed, but can depend strongly on thermal history and equilibration. Adrjanowicz *et al.* showed by dielectric spectroscopy that confinement-induced deviations from bulk glass-transition dynamics can partially relax toward bulk-like behavior after appropriate thermal treatment, and related this recovery to very slow viscous flow in nanopores [70]. Similar conclusions were drawn from studies of diglycidyl ether of bisphenol A (DGEBA) confined in AAO templates, where dielectric and Raman measurements demonstrated that molecular dynamics above and below T_g depend on the previous thermal pathway and equilibration state inside the pores [71]. Recent work from the Floudas group has also emphasized that appropriate annealing protocols can strongly reduce, or even erase, apparent confinement effects in selected polymer systems. Therefore, confinement-induced deviations from bulk dynamics should be interpreted not only in terms of geometry and surface interactions, but also in terms of nonequilibrium interfacial states and thermal history [72].

A related route to controlling confined dynamics is modification of the interacting surface. This idea was first developed extensively in studies of thin polymer films, where it became clear that glass-transition dynamics cannot be determined by film thickness alone. For the same polymer and comparable film thickness, different T_g shifts, or even the absence of a measurable shift, may be obtained depending on the character of the substrate. Attractive, repulsive, hydrophilic, hydrophobic, polar, or specifically interacting surfaces can generate different mobility gradients across the film [73,74]. In addition, the quality of the interface, including roughness and nanoscale topography, may redefine the effective boundary condition experienced by polymer segments. Smooth and rough substrates may therefore produce different changes in T_g , fragility, and local segmental mobility, even when the nominal film thickness is the same [75].

It should be emphasized, however, that the experimental control and characterization of roughness are very different in thin films and in nanoporous templates. In thin-film studies, changing the roughness of a flat substrate is relatively straightforward, and the modified surface can usually be characterized directly by Atomic Force Microscopy (AFM) or related surface-sensitive techniques. In nanopores, the same procedure is much more difficult. The surface is strongly curved, hidden inside the membrane, and often accessible only indirectly. As a result, defining and quantifying roughness inside cylindrical or modulated nanochannels remains a nontrivial experimental and analytical problem. This difficulty is important because even small changes in nanoscale wall morphology may alter wetting, interfacial adhesion, and local density fluctuations, and therefore may strongly influence the dynamics of the confined material [76].

In nanopores, the confining surface should not be regarded as a passive geometrical boundary, but rather as an active interfacial environment that may either slow down or accelerate the dynamics of the infiltrated material. Changes in wall polarity, hydrophilicity, hydrophobicity, chemical coating, or specific dipolar and hydrogen-bonding interactions can alter the balance between interfacial and core-like molecular fractions. Consequently, the apparent T_g , τ_α distribution, and magnitude of confinement effects may change even for the same nominal pore diameter. Studies of polymers and molecular liquids confined in chemically modified alumina nanopores confirm that surface chemistry can tune the balance between bulk-like and interfacial dynamics in confined soft matter [77,78].

In this context, the work of Tarnacka and co-workers on alumina templates with a nanostructured interface provided an additional important step. The authors showed that not only chemical modification, but also physical modification of the pore-wall morphology can strongly affect confined dynamics [79,80]. By changing the nanoscale structure of the pore wall, it is possible to weaken, modify, or even nearly suppress the usual confinement-induced acceleration of segmental or structural relaxation. However, this tendency toward bulk-like behavior is not universal. In the confinement study of cyclic dimethylsila crowns, Kumari *et al.* indicated that, in nanostructured modulated membranes, the dynamics remained strongly affected by the combined influence of cyclic molecular topology and surface nanoroughness [76]. Thus, the behavior of liquids and polymers in nanopores is controlled by a combination of surface chemistry, surface roughness, pore morphology, wetting, density fluctuations, and thermal history rather than by pore size alone.

These results opened an important new direction in confinement research. Instead of treating nanoconfinement as a simple reduction of system size, it became necessary to consider it as a multidimensional perturbation involving pore diameter, curvature, roughness, surface chemistry, interfacial adhesion, wetting, density fluctuations, and thermal history. Depending on the balance between these factors, confined dynamics may be accelerated, slowed down, split into core and shell contributions, become quasi-isochoric, or recover bulk-like behavior. In summary, studies of low-molecular-weight glass formers and polymers under nanoconfinement have provided a complementary route to understanding glassy dynamics near T_g . Initially, confinement was used to test the idea of a growing cooperative length scale predicted by the Adam-Gibbs theory. Later, combined dielectric, calorimetric, positron annihilation, and high-pressure-inspired analyses revealed that density fluctuations, free volume, interfacial vitrification, and negative pressure play equally important roles. Current research shows that the dynamics of confined liquids are controlled by an interplay between

molecular mobility, interfacial interactions, pore geometry, and thermodynamic constraints. Importantly, there is now a clear link between confinement studies and HP studies of bulk materials: both probe how density and volume fluctuations influence structural relaxation. In this sense, the key connecting concept between these two fields is the density fluctuation induced either externally, by hydrostatic pressure, or internally, by confinement and molecule-wall interactions. Understanding this link is essential for interpreting the behavior of soft matter in nanoscale environments and for using confinement as a tool to probe the microscopic origin of the glass transition.

2. Research Objective

The primary objective of this doctoral study was to investigate the molecular dynamics, thermal properties, and specific interactions in selected soft molecular glass formers (3-Phenylpropanal and cyclic dimethylsila crowns) under different thermodynamic and spatially restricted conditions. This was achieved through complementary thermal, high-pressure, and nanoconfinement pathways, employing broadband dielectric spectroscopy (BDS) as the principal analytical technique (**Fig. 7**). The results were supported by DSC, FTIR, Raman spectroscopy, AFM, and MD simulations. Particular attention was devoted to understanding how molecular mobility, glass-transition behavior, α -relaxation, secondary relaxation processes, D-modes, and supramolecular association are governed by molecular architecture, intermolecular interactions, density changes, and spatial restrictions. The research was carried out in three complementary stages. Ambient-pressure studies were first used to establish the thermal behavior, relaxation map, and dominant interaction motifs of the selected systems. High-pressure measurements then examined how compression modifies their molecular dynamics and relaxation behavior. Finally, mesoporous confinement was applied to a selected cyclic system to probe the additional role of spatial restriction, pore morphology, and interfacial effects.

Within this framework, the dissertation aimed to answer the following research questions:

- What are the dominant intermolecular interactions and supramolecular motifs in the investigated systems near T_g ?
- How does hydrostatic pressure modify these interactions, and does time-temperature-pressure superposition remain valid for the α -D processes, or α - β processes under strong compression?
- Can pressure reorganize weak supramolecular associates, such as those formed in aldehyde systems, into different pressure-stabilized structures?
- Does the pressure sensitivity of cyclic molecules depend on ring size, molecular rigidity, and conformational flexibility?
- How are $\Delta V^\ddagger$, dT_g/dp , and cooperative length scale (ξ) related in cyclic glass-forming liquids, and do these relationships follow previously proposed correlations?
- Does the secondary β -relaxation in cyclic dimethylsila crowns follow the CM prediction under ambient and high-pressure conditions, or does pressure reveal a more local, topology-sensitive contribution?

- How do cyclic molecular liquids behave under mesoporous confinement, and do they differ from previously studied linear polymers and linear associating liquids?

By addressing these questions, the dissertation aims to provide a comparative view of how thermal cooling, hydrostatic pressure, and nanoconfinement affect molecular mobility, supramolecular organization, and the relationships between α -, β -, and D-like relaxation processes. The results show that these pathways are complementary but non-equivalent: they are linked by changes in molecular packing, density, and available free volume, while their differences reveal the roles of molecular architecture, specific interactions, cyclic topology, and interfacial effects. The confinement-induced modification of the α - β relationship further indicates that the nature and degree of coupling of secondary β -relaxation under spatial restriction require further systematic studies on additional glass-forming systems.

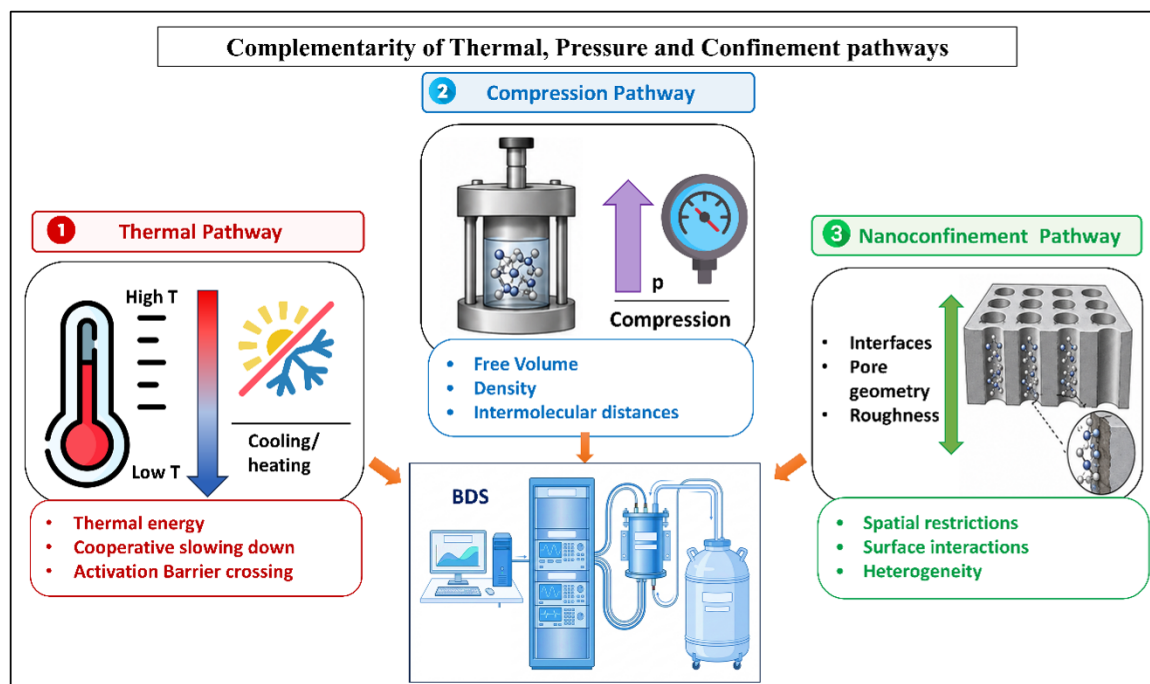


Figure 7. Schematic representation of the complementarity of the thermal, high-pressure, and nanoconfinement pathways using BDS to study the dynamics of glass-forming systems.

The names, chemical structures, and abbreviations of all investigated compounds are summarized in **Table 1**. The experimental techniques used and their role in this particular work are given in **Table 2**.

Table 1. Chemical structures and names of substances studied as part of the doctoral thesis.

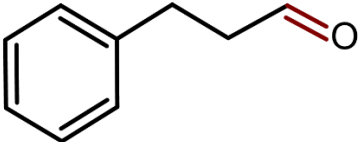
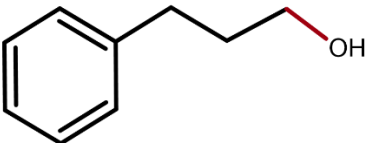
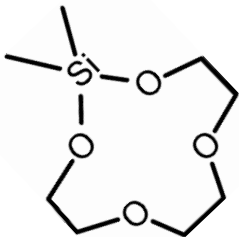
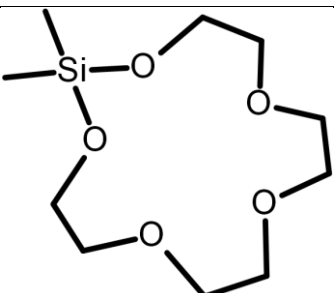
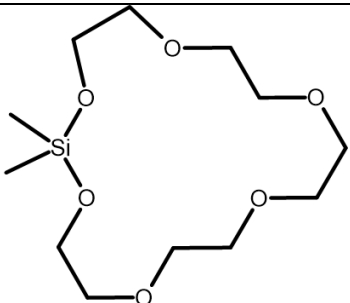
Name	Chemical structure	Abbreviation
3-Phenyl-1-propanal		3P1Pal
3-Phenyl-1-propanol		3P1Pol
Dimethylsila-11-crown-4		DMS11C4
Dimethylsila-14-crown-5		DMS14C5
Dimethylsila-17-crown-6		DMS17C6

Table 2. The experimental techniques used and their corresponding roles in this research work.

Technique	Abbreviations	Role in this dissertation
Broadband dielectric spectroscopy	BDS	Quantifies molecular mobility under temperature, pressure, and confinement
Differential scanning calorimetry	DSC	Determines glass-forming ability and T_g
Fourier-transform infrared spectroscopy	FTIR	Connects relaxation changes to structural/molecular reorganizations
Raman spectroscopy	-	Connects relaxation changes to structural/molecular reorganizations
X-ray diffraction	XRD	Relates relaxation changes to structural ordering/molecular reorganizations
Contact Angle measurements	-	Determine the wettability of the sample on the substrate
Atomic force microscopy	AFM	Provides microscopic insight into surface morphology and confinement effects
Molecular dynamics simulations and Density Functional Theory	MD simulations & DFT	Support the interpretation of the molecular origin and evolution of relaxation behaviour

The results of the experimental studies described in this dissertation were published in international peer-reviewed journals indexed in the Web of Science/Journal Citation Reports database. Collectively, these publications correspond to a total Journal Impact Factor (IF) of 20.4 and 500 points according to the Polish ministerial classification of scientific journals.

A1. A.K. Sudhakaran Nair Valsala Kumari, B. Hachuła, M. Tarnacka, E. Kamińska, J. Grelska, T. Lamrani, K. Jurkiewicz, P. Włodarczyk, K. Grzybowska, K. Kamiński, Specific interactions and mechanism of association in highly viscous aldehyde 3-phenylpropanal, J. Chem. Phys. 163 (2025). <https://doi.org/10.1063/5.0283944>. IF=3.1; Ministry points:100.

A2. A.K. Sudhakaran Nair Valsala Kumari, B. Hachuła, P. Włodarczyk, M. Tarnacka, K. Witkowicz, R. Wrzalik, E. Kamińska, K. Kamiński, Pressure-Induced Self-Assembly in 3-

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A3. A.K. Sudhakaran Nair Valsala Kumari, E. Kamińska, M. Tarnacka, K. Kamiński, The Role of Ring Geometry and Rigidity in the Glassy Dynamics of Cyclic Dimethylsila Crowns under Elevated Pressure, Phys. Chem. Chem. Phys. (2026), [DOI: 10.1039/D6CP00287K](https://doi.org/10.1039/D6CP00287K). IF=2.9; Ministry points: 100.

A4. A.K. Sudhakaran Nair Valsala Kumari, M. Tarnacka, E. Kaminska, M. Wojtyniak, M. Geppert-Rybczyńska, K. Bilska, A. Brzózka, K. Kamiński, Nanoscale dewetting and unpredictable dynamics of cyclic liquid in curved and rough nanochannels, J. Colloid Interface Sci. 704 (2026) 139390. <https://doi.org/10.1016/J.JCIS.2025.139390>. IF=9.7; Ministry points: 100.

3. Overview and Discussion of the research outcome

3.1. The study of molecular dynamics and specific interactions in 3-phenylpropanal: effect of isobaric cooling

A1. Specific interactions and mechanism of association in highly viscous aldehyde 3-phenylpropanal

J. Chem. Phys. 163 (2025) 104505

<https://doi.org/10.1063/5.0283944>

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This study aimed to determine the molecular origin of the D- relaxation observed in 3-phenylpropanal (3P1Pal) and to clarify whether a weakly associating aldehyde can form supramolecular structures in the highly viscous supercooled state. This question is relevant because slow D-modes are most often associated with liquids that exhibit a pronounced tendency toward supramolecular association, such as monohydroxy alcohols, amines, amides, and carboxylic acids, where they are usually linked to H-bonded supramolecular clusters [34,35,48,81,82]. Aldehydes, by contrast, are generally considered weakly associating systems. Therefore, the appearance of a Debye-like process in 3P1Pal required a molecular-level explanation. To address this issue, 3P1Pal was compared with the structurally related alcohol 3-phenyl-1-propanol (3P1Pol), using BDS, DSC, XRD, FTIR, Raman spectroscopy, density functional theory (DFT) calculations, and MD simulations. This comparison was particularly useful because both molecules share a similar phenylpropyl framework but differ in the terminal functional group, allowing the effect of strong O–H hydrogen bonding to be separated from weaker aldehyde-specific interactions.

The first stage of the work established the thermal and dielectric behavior of both compounds. The DSC measurements demonstrated that both 3P1Pal and 3P1Pol are good glass formers, since no crystallization or melting events were detected during cooling and subsequent heating. Only a single heat-capacity step related to the glass transition was observed on both runs. However, the glass transition temperature (T_g) of 3P1Pol was significantly higher than that of 3P1Pal, with values of approximately 182 K and 165 K, respectively (insets of **Fig. 1**, in **A1**). This difference was interpreted as evidence of stronger intermolecular association in

the alcohol, where classical O–H···O hydrogen bonds dominate, compared with the aldehyde, where interactions are weaker and more complex.

The dielectric results were particularly important. In 3P1Pal, two relaxation processes were identified above T_g : a faster structural α -relaxation associated with cooperative molecular motions responsible for vitrification, and a slower D-like process (**Fig. 8a**). Since aldehydes are usually treated as weakly associating molecular liquids, the observation of a clear D -process in 3P1Pal indicated that some form of supramolecular organization must exist even in the absence of strong conventional H-bonding.

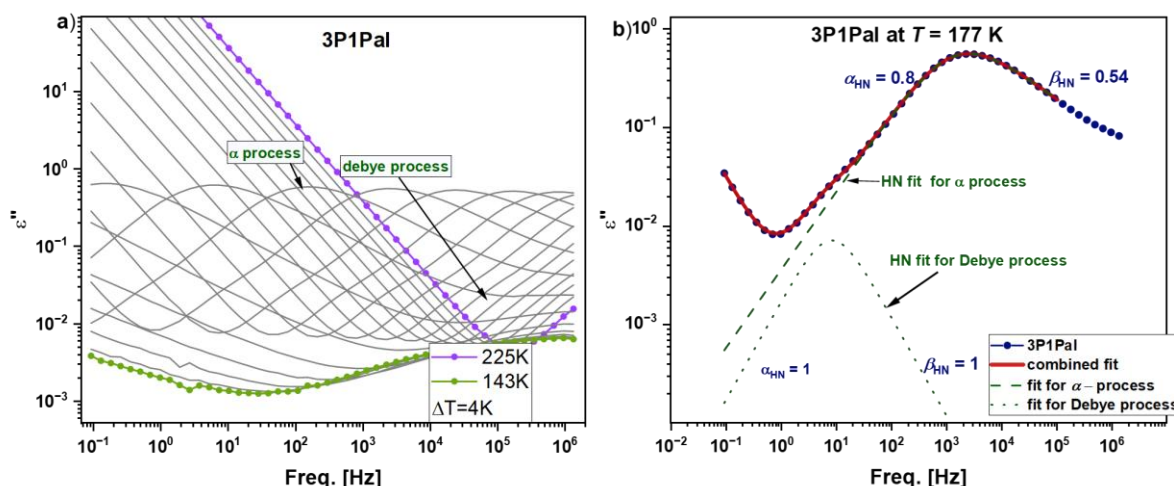


Figure 8. a) The representative dielectric loss spectrum of 3P1Pal, b) Fit functions used for the analysis of both relaxation processes (Debye and α) in 3P1Pal.

The analysis of the spectral shape revealed that the α -relaxation of 3P1Pal shows a high-frequency power-law behavior close to $\omega^{-0.5}$ near T_g , which is consistent with the so-called generic spectral shape expected for some simple supercooled liquids with weak dipolar cross-correlations [83,84]. In contrast, the slower process displayed nearly ideal D-like behavior, with shape parameters close to unity (**Fig. 8b**). This confirmed that the slow mode is not simply a broadened part of the structural relaxation, but a distinct dynamical process most likely connected with collective reorientation within supramolecular associates.

Further insight was obtained from the Kirkwood correlation factor (g_k)[85]. For 3P1Pol, the g_k factor was much larger than unity, which is typical for chain-like H-bonded structures with parallel dipole correlations. In contrast, for 3P1Pal, the g_k factor was below unity and slightly decreased upon cooling. This indicates a tendency toward antiparallel dipole arrangements, suggesting that the aldehyde molecules do not form alcohol-like linear chains, but rather smaller cyclic, dimeric, or antiparallel aggregates. This result is crucial because it

shows that the D-process in 3P1Pal might have a different molecular origin from the classical D-relaxation in the corresponding monohydroxy alcohol, 3P1Pol.

For further insight into the molecular ordering, XRD measurements were performed. Both liquids exhibited amorphous-like structure factors $S(Q)$, with a main broad maximum related to short-range intermolecular order. However, the main diffraction peak of 3P1Pal was broader and less intense than that of 3P1Pol, indicating a lower degree of nearest-neighbour ordering in the aldehyde. Upon cooling, an additional shoulder appeared near $Q \approx 1.9 \text{ \AA}^{-1}$ in the structure factor of 3P1Pal (**Fig. 3** in **A1**). This corresponds to a real-space distance of approximately 3.3 Å, which is characteristic of interactions between aromatic rings[86]. Therefore, the XRD data suggested an increasing contribution of π - π stacking interactions between phenyl groups at lower temperatures.

The vibrational spectroscopy results further confirmed the presence of weak but significant intermolecular interactions in 3P1Pal. Upon cooling, notable changes were observed in the C=O and aliphatic C-H stretching regions as shown in **Fig. 4** in **A1**. The carbonyl stretching band shifted and broadened, while changes in formyl and methylene C-H bands suggested interactions involving the carbonyl oxygen and neighbouring C-H groups. Dilution experiments in non-polar solvents helped distinguish aggregated from more isolated molecular states. In solution, the narrowing and shifting of the C=O bands indicated partial disruption of intermolecular aggregates. However, FTIR and Raman data alone could not unambiguously determine whether the observed spectral changes originated primarily from weak hydrogen bonds or from dipolar interactions.

This ambiguity was resolved using DFT and MD simulations. DFT calculations of the most stable 3P1Pal dimers revealed five main types of intermolecular interactions. These included formyl-formyl interactions, π -stacking between phenyl rings, formyl-phenyl interactions, C-H $\cdots$ O contacts between methylene groups adjacent to the formyl unit and carbonyl oxygen atoms, and interactions between methylene groups and aromatic rings (**Fig. 9**). Importantly, the calculations showed that formyl-formyl association is mainly governed by dipole-dipole interactions rather than classical H-bonding. The carbonyl groups tend to adopt orientations consistent with electrostatic attraction, while the methylene group neighbouring the formyl unit can behave as an unexpected weak H-bond donor toward the carbonyl oxygen.

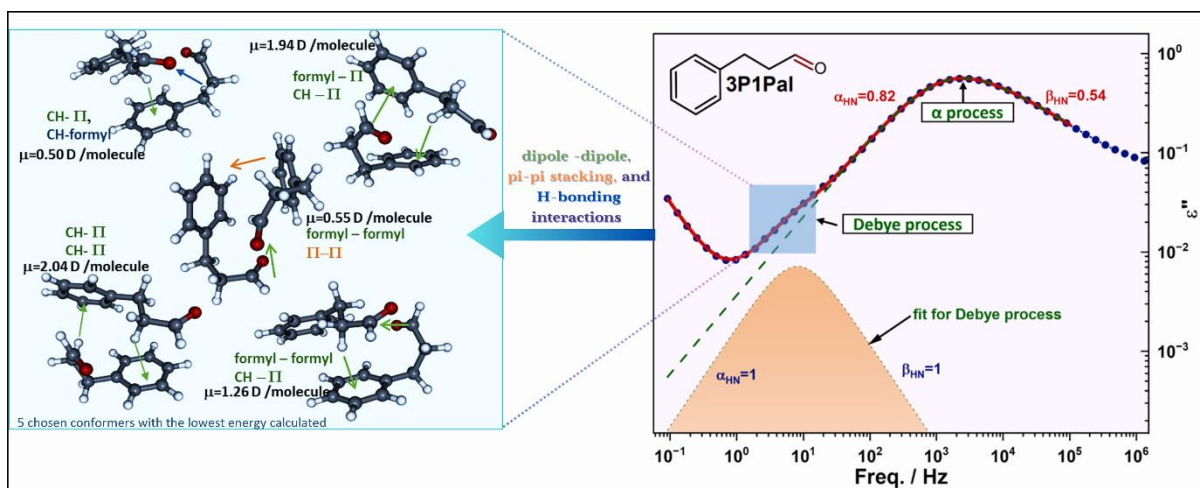


Figure 9. All the most stable dimers of aldehyde molecules and a variety of dominating interactions responsible for the origin of D-relaxation in 3P1Pal.

The MD simulations confirmed that these interactions are not isolated computational artefacts but are present in the bulk liquid. The simulations revealed that 3P1Pal mainly forms dimeric associates stabilized by several weak interactions acting cooperatively. The specific C–H $\cdots$ O contacts involving the methylene group and the carbonyl oxygen showed geometrical features consistent with weak H-bonds, while π -stacking and formyl-related dipolar contacts contributed to the stabilization and orientation of the aggregates. The combination of these interactions explains why 3P1Pal, despite lacking a classical strong H-bond donor such as O–H or N–H, still exhibits a Debye relaxation process.

The most important interpretation proposed here is that the D-process in 3P1Pal originates from the reorientational relaxation of formyl-based nano-associates. This mechanism differs from that observed in the alcohol reference system, where the D-process is associated with H-bonded clusters. Therefore, the work demonstrates that D-like relaxation should not be treated exclusively as a marker of classical H-bonded chain structures. Instead, it can also arise from weaker and more complex supramolecular organizations stabilized by dipolar interactions, π -stacking, and non-classical C–H $\cdots$ O H-bonds.

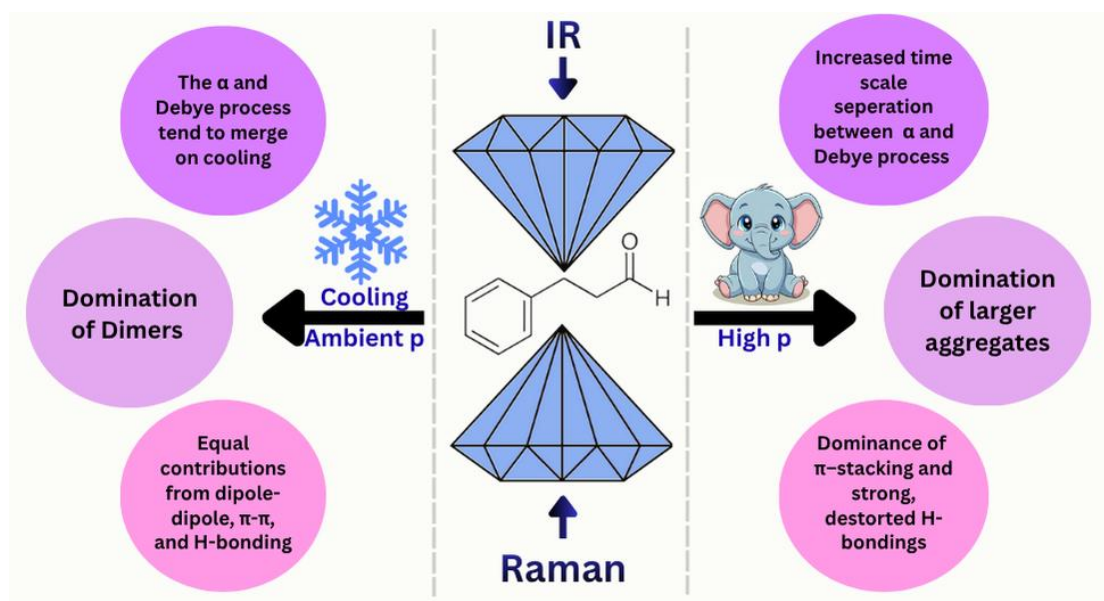
3.2. The impact of pressure on the molecular dynamics and intermolecular interactions in 3-Phenylpropanal

A2. Pressure-Induced Self-Assembly in 3-Phenylpropanal: Distinct Clustering via π -Stacking and Distorted Hydrogen Bonds

J. Phys. Chem. Lett. 17 (2026) 728–736.

<https://doi.org/10.1021/acs.jpcllett.5c03496>.

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Graphical abstract

The ambient-pressure study of 3P1Pal showed that this weakly associating aldehyde exhibits a Debye-like relaxation arising from formyl-rich supramolecular domains stabilized by dipole–dipole interactions, π -stacking, and weak nonclassical C–H $\cdots$ O contacts [87]. This raised a direct question: if such weak aldehyde-based associates are already present in the viscous liquid, how do they respond when intermolecular distances are reduced by compression? The aim of this study was therefore to determine how high pressure modifies the Debye-like process, the structural α -relaxation, and the underlying association pattern of 3P1Pal. This was particularly relevant because most high-pressure studies of associative molecular organization have focused on strongly H-bonded systems. In contrast, aldehydes governed by dipolar and aromatic interactions remain much less explored. HP BDS was

combined with FTIR, Raman spectroscopy, and MD simulations to link changes in dielectric dynamics to pressure-induced modifications in molecular packing and interaction geometry.

After interpreting the thermal and dielectric behaviour at ambient pressure as discussed in section 3.1, the next step was to follow the same relaxation modes under isothermal compression. The high-pressure spectra measured at 233 and 298 K are shown in **Fig. 1b** and **c** in **A2**. Increasing pressure shifted both α - and D-relaxations toward lower frequencies, as expected from reduced free volume and enhanced packing constraints. The nearly unchanged dielectric strength indicated that the liquid state was preserved during compression. The spectra were fitted using the HN function with a dc-conductivity term, and the obtained relaxation times are summarized in **Fig. S1** in **A2**.

The key dielectric result is shown in **Fig. 2** in **A2**, where spectra measured at different T , p conditions were compared at constant τ_α . Up to approximately 500 MPa, the α - and D-processes nearly superimposed, suggesting that cooling and compression initially lead to comparable dynamic states. Above this pressure, however, the behavior became anomalous: the Debye amplitude increased, and the time-scale separation between the D- and α -processes became larger (**Fig. 10**). This is opposite to the common trend observed in many monohydroxy alcohols, where compression often reduces the separation between Debye and structural relaxations [88]. The ratios plotted in **Fig. 2b, c** in **A2** show that the deviation begins above about 500–550 MPa and becomes most pronounced near 1.4 GPa. This finding resembles, to some extent, the behavior reported by Pawlus *et al.* for strongly associating 2-ethyl-1-hexanol under high compression, where the anomalous dynamic response was linked to pressure-induced changes in the supramolecular hydrogen-bonding architecture [48]. Thus, pressure not only slows the dynamics but also modifies the supramolecular organization responsible for the D-mode.

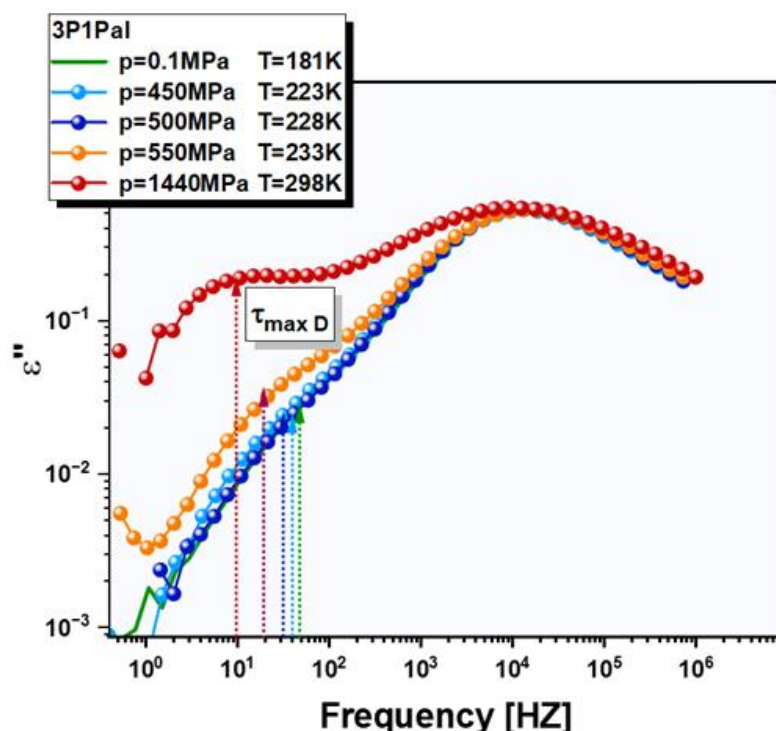


Figure 10. Comparison of the shapes of dielectric loss spectra obtained for 3P1Pal under varying T, p conditions. The arrows indicate the maximum of the D-relaxation process.

To identify how interactions are affected by compression, pressure-dependent FTIR and Raman spectra were collected and analyzed (**Fig. 3** in **A2**). From the data, it was evident that most vibrational bands shifted to higher wavenumbers under pressure, especially those associated with aliphatic and aromatic C–H vibrations, reflecting reduced intermolecular distances and bond stiffening. The carbonyl region behaved more subtly: the C=O overtone and Raman C=O stretching band changed only weakly. This was interpreted as a compensatory effect between pressure-induced C=O bond stiffening and strengthening of C–H $\cdots$ O interactions, which tend to shift the band in the opposite direction.

A direct comparison of spectra collected under low-temperature and high-pressure isochronal conditions is presented in **Fig. 4** in **A2**. Although both routes lead to a comparable slowing down of the structural dynamics, as inferred from BDS, the high-pressure state produces more pronounced shifts of selected vibrational bands, particularly those associated with aromatic C–H and ring modes. This indicates that compression modifies the local molecular environment and intermolecular contacts more strongly than cooling alone, confirming that pressure and temperature are not equivalent routes to slow dynamics. Compression enhances the contribution of π -stacking and reorganizes the aldehyde-specific interactions, rather than simply reproducing the low-temperature association pattern.

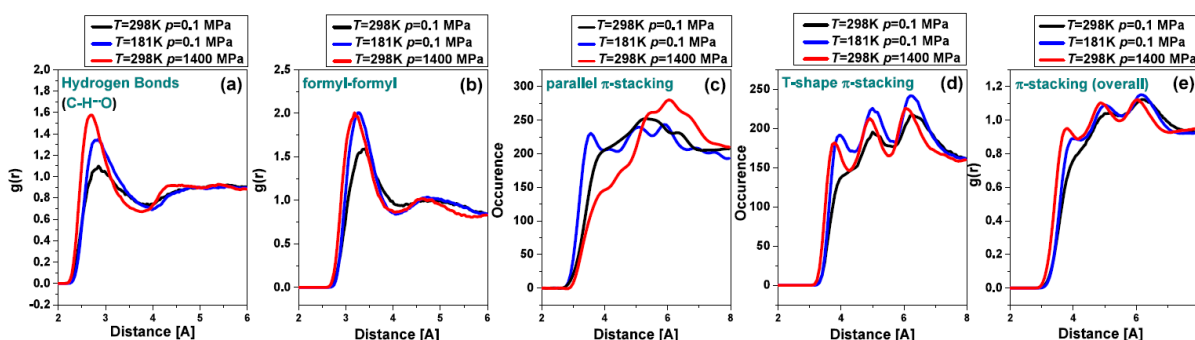


Figure 11. (a-c) The partial RDFs for formyl-formyl (C1-O1 pair), π -stacking (ring-ring), and H-bonds (H2-O1). In panels (d) and (e), the occurrence of T-shaped versus parallel π -stacking conformations was compared in all studied systems.

MD simulations provided the molecular interpretation of this behavior. Radial distribution functions (RDFs) and orientational analyses in **Fig. 11** (**Fig. 5** in A2, supported by **Fig. S5** in A2) showed that cooling and compression both strengthen association, but through different structural pathways. At low temperature, the dominant π -stacking motif is mainly T-shaped and the C–H $\cdots$ O contacts are closer to regular geometries. Under high pressure, mixed T-shaped and more parallel π -stacking motifs appear, while the C–H $\cdots$ O hydrogen bonds become stronger but more distorted. The simulations also showed that compression promotes larger aggregates: the fraction of higher-order clusters increased from 14.2% at 181 K and 0.1 MPa to 22.4% at 298 K and 1.4 GPa, while the monomer fraction decreased from 41.1% to 36.1%. The average C $\cdots$ O distance also shortened by about 0.1 Å, confirming the strengthening of weak hydrogen-bond-like contacts under compression.

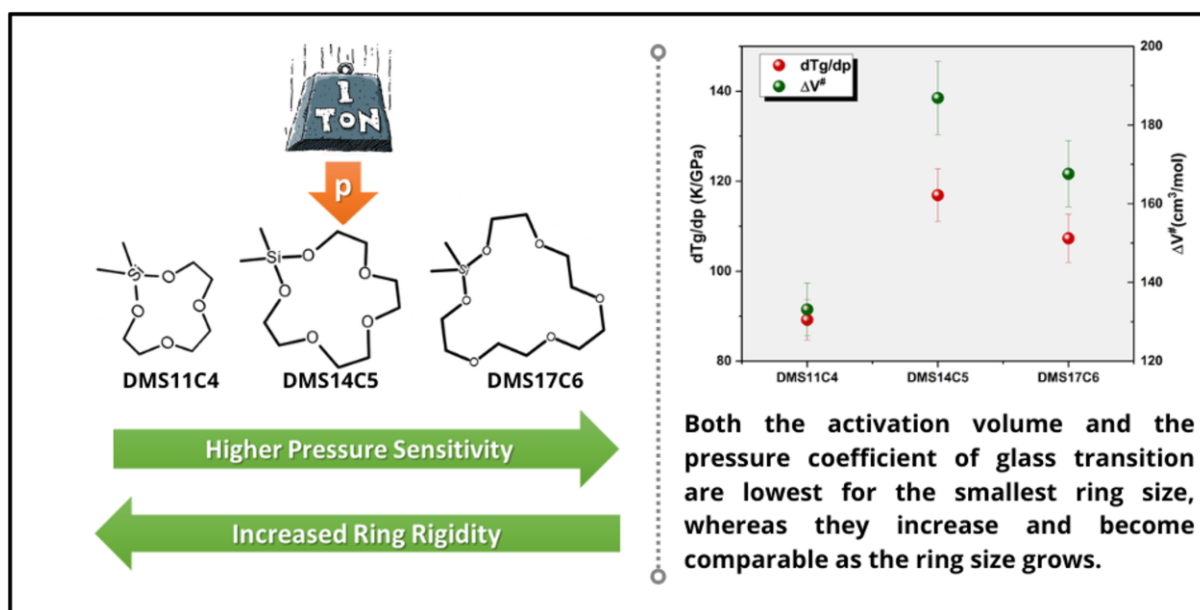
The central conclusion is that the high-pressure state of 3P1Pal is not a densified version of the low-temperature state. Cooling favors smaller aggregates dominated by T-shaped π -stacking and more regular C–H $\cdots$ O geometries, whereas compression promotes larger, more compact clusters stabilized by mixed π -stacking, formyl–formyl dipolar contacts, and distorted but stronger C–H $\cdots$ O interactions. This explains the unusual dielectric behavior above 500 MPa: the growing Debye-like amplitude and increasing separation between τ_D and τ_α reflect a pressure-induced change in the size, geometry, and dipolar character of the supramolecular domains.

3.3. The effect of high pressure on the molecular dynamics of cyclic dimethylsila crown ethers

A3. The Role of Ring Geometry and Rigidity in the Glassy Dynamics of Cyclic Dimethylsila Crowns under Elevated Pressure

Phys. Chem. Chem. Phys. 2026,

DOI: [10.1039/D6CP00287K](https://doi.org/10.1039/D6CP00287K)



Graphical abstract

Unlike the previous studies on 3P1Pal, where the main issue was weak supramolecular association and pressure-induced reorganization of a Debye-like process, this part of the dissertation addressed a different question: how does molecular topology and rigidity control the pressure sensitivity of glassy dynamics? Most high-pressure BDS studies have focused on linear, flexible, hydrogen-bonded, ionic, or pharmaceutical glass formers, whereas cyclic molecular liquids remain less explored. This gap is important because ring closure, rigidity, conformational constraints, and internal flexibility may determine how a molecule responds to densification. Therefore, this study examined whether ring size and rigidity in cyclic dimethylsila crown ethers affect the structural α -relaxation, secondary β -relaxation, activation volume, pressure coefficient of T_g , and cooperative length scale under elevated pressure. The investigated homologous series, DMS11C4, DMS14C5, and DMS17C6, are shown in **Fig. 1** in **A3**.

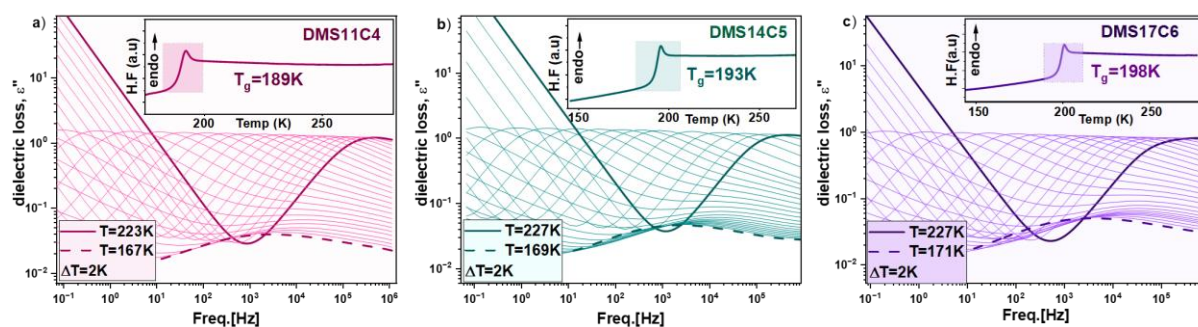


Figure 12. Ambient-pressure dielectric loss spectra of (a) DMS11C4, (b) DMS14C5, and (c) DMS17C6. Insets present the corresponding DSC thermograms obtained during the first heating run, with the endothermic step associated with the glass transition indicated.

The first stage established the thermal and ambient-pressure dielectric behavior of the three systems. DSC thermograms, shown as insets in **Fig. 12**, revealed a single glass-transition step without crystallization or melting, confirming the glass-forming character of all crowns. The calorimetric T_g increased with molecular size, from about 189 K for DMS11C4 to 193 K for DMS14C5 and 198 K for DMS17C6, indicating slower global dynamics in the larger rings. The dielectric spectra in **Fig. 12** showed three contributions: the structural α -relaxation, secondary β -relaxation, and low-frequency dc conductivity.

To compare structural dynamics within the series, the α -peaks were superimposed under isochronal conditions in **Fig. 3a** in **A3**. Their shapes were broadly similar, although DMS17C6 displayed the slightly broadest response, with $\beta_{KWW} \approx 0.48$, compared with approximately 0.50 for DMS14C5 and 0.51 for DMS11C4. This suggests a modest increase in dynamic heterogeneity with ring size, but the differences are small and should not be overinterpreted. The constant-temperature comparison in **Fig. 3b** in **A3** showed that the α -relaxation shifts to lower frequency with increasing molecular size, confirming that larger cyclic structures relax more slowly.

The temperature dependence of the relaxation times is summarized in **Fig. 4** in **A3**. The α -relaxation follows non-Arrhenius behavior, whereas the β -process follows Arrhenius behavior with similar activation energies, around 30 kJ/mol, for all three compounds. The CM analysis showed that the experimental τ_β values are close to the primitive relaxation times estimated from the α -process, supporting a JG-like assignment at ambient pressure. However, this agreement should be treated as supportive rather than definitive, because local intramolecular motions in cyclic or conformationally constrained molecules may appear close to the predicted primitive time scale.

This uncertainty motivated the high-pressure BDS measurements. In the previous study presented in **A2**, pressure revealed that a relaxation process well-defined at ambient pressure

could change its molecular meaning when the supramolecular structure was compressed. In the cyclic crowns, the question was whether the β -process remains coupled to the structural relaxation under compression, or whether pressure reveals a local, topology-sensitive contribution? Representative high-pressure spectra in **Fig. 5** in **A3** showed that increasing pressure shifts the relaxation processes to lower frequencies, as expected from densification and reduced free volume.

The key comparison is presented in **Fig. 6** in **A3**, where spectra measured at different T, p conditions were superimposed under isochronal conditions. The α -relaxation retained almost the same shape, indicating approximate TPS behavior for these cyclic van der Waals systems. The β -relaxation showed a more complex response: under pressure, its amplitude increased slightly, and the peak shifted modestly toward higher frequencies relative to the ambient-pressure response. After the subtraction of the α -contribution, the isolated β -peaks compared in **Fig. 13** did not overlap perfectly, but the deviation remained below about one decade in frequency. Thus, the pressure data do not reject the JG-like assignment, although they do not provide fully unambiguous confirmation. The β -process remains broadly compatible with JG behavior, while the slight pressure-induced shift suggests that cyclic topology and internal constraints may introduce a local contribution to secondary dynamics.

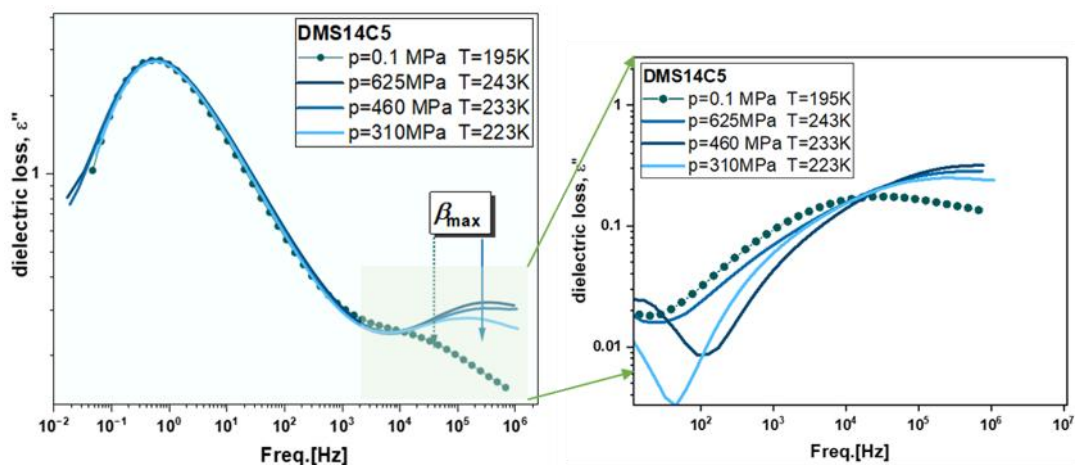


Figure 13. Superimposed dielectric loss spectra of the DMS14C5 measured at the indicated T, p conditions. The arrows represent the maximum of the β -relaxation peak obtained by the HN fit.

The pressure dependence of the structural relaxation was further analyzed using the modified Avramov approach. **Fig. 7** in **A3** shows the 3D $\tau_\alpha(T, p)$ surface fit for DMS14C5, while **Fig. 8** in **A3** presents the $T_g(p)$ dependences. The pressure coefficients were moderate: 89.2 K/GPa for DMS11C4, 116.9 K/GPa for DMS14C5, and 107.3 K/GPa for DMS17C6. These values are lower than typically expected for highly flexible van der Waals liquids, suggesting that the cyclic framework introduces additional rigidity and restricts compressibility [46]. The

smallest ring, therefore, exhibits the weakest pressure sensitivity, suggesting that its more rigid cyclic framework limits structural adaptation to compression.

The activation-volume analysis in **Fig. 9** in **A3** strengthened this interpretation. The values summarized in **Table 1** in **A3** are 0.19 nm³ for DMS11C4, 0.31 nm³ for DMS14C5, and 0.28 nm³ for DMS17C6, again showing the weakest pressure response for the smallest and most internally constrained ring. The cooperative length scales estimated from dielectric and calorimetric approaches fall in the nanometric range, approximately 1.9–2.7 nm, confirming that vitrification in these small cyclic liquids still involves spatially correlated dynamics. **Fig. 14** places these values within the literature trend between activation volume and cooperative length [89], while **Fig. 11** in **A3** shows a clear linear relation between ζ and $\Delta V^\ddagger$ within the cyclic series. The slope is markedly higher for DMS11C4, indicating that in the smallest and most rigid ring, changes in activation volume translate more efficiently into changes in cooperative length.

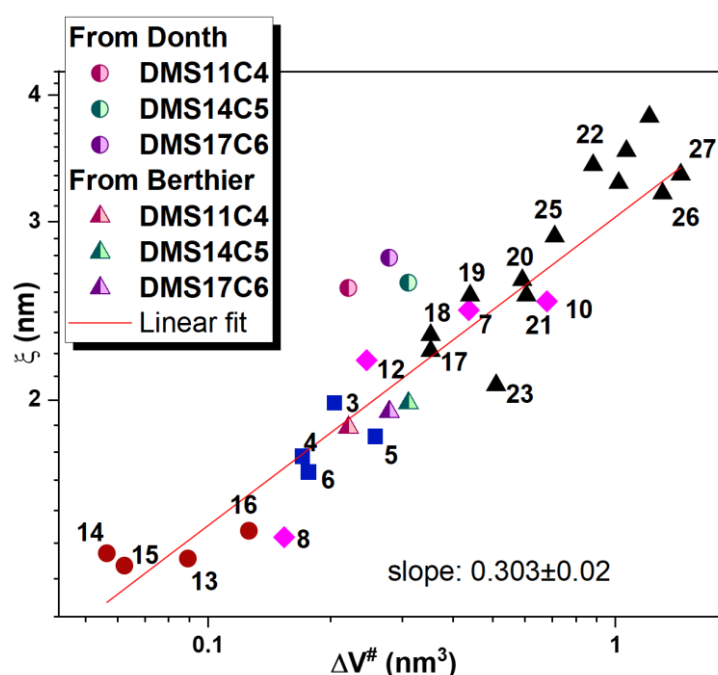


Figure 14. Correlation between the correlation length scale (ζ) and the activation volume ($\Delta V^\ddagger$) at T_g . The data reported by Hong *et al.* [89] were digitized and reused from Blazytko *et al.* [90], with added data for the compounds investigated herein (marked with partially filled triangles and circles, calculated using the Berthier and Donth equations, respectively). The presented numbers refer to different compounds taken from the table of data described in Ref. [89].

Overall, this study shows that cyclic topology is a key variable controlling pressure-sensitive glassy dynamics. In contrast to 3P1Pal, where pressure reorganized weak supramolecular clusters and modified a Debye-like process, dimethylsila crowns do not show pressure-induced self-assembly of the same type. Their response is instead governed by ring

size, rigidity, free-volume sensitivity, and the coupling between local and cooperative motions. The smallest crown, DMS11C4, is the most rigid and least pressure-sensitive, whereas the larger rings show somewhat stronger pressure sensitivity and slightly broader structural relaxation. The β -relaxation remains broadly consistent with JG-like behavior, but its modest pressure-induced shift prevents a fully definitive assignment and suggests a possible local ring-related contribution. This work therefore provides a bridge to the next dissertation stage: if cyclic topology already affects pressure sensitivity in the bulk, it becomes essential to ask how such molecules behave when their motion is restricted by mesoporous geometry and interfacial interactions.

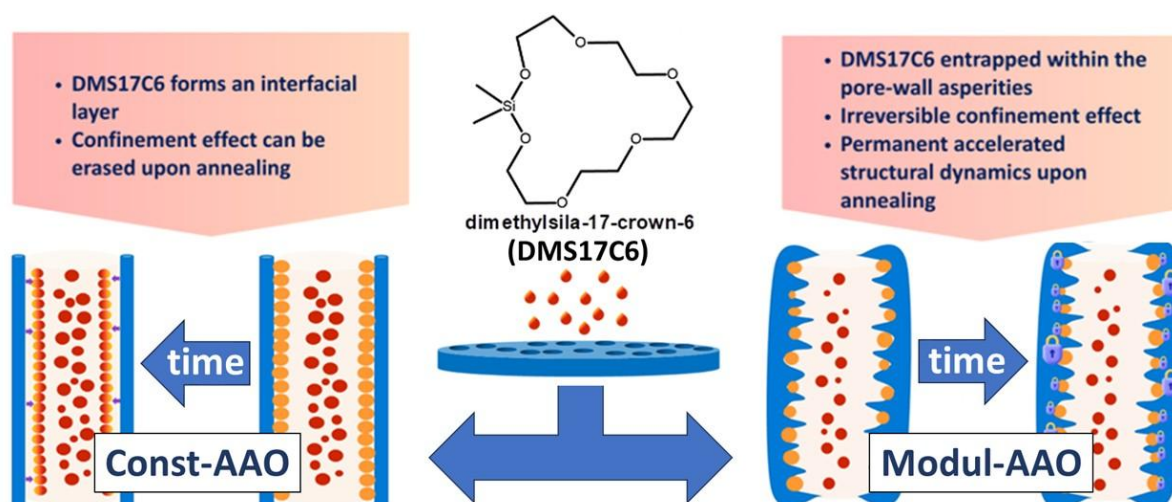
3.4. The effect of nanoconfinement and pore wall roughness on the dynamics of cyclic dimethylsila crown ether

A4. Nanoscale dewetting and unpredictable dynamics of cyclic liquid in curved and rough nanochannels

J. Colloid Interface Sci. 704 (2026) 139390.

<https://doi.org/10.1016/J.JCIS.2025.139390>.

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Graphical abstract

Following the ambient-pressure and high-pressure investigation of cyclic dimethylsila crowns in the bulk, the next step was to examine how cyclic topology responds to nanospatial restriction. This question is important because most confinement studies have focused on linear polymers, linear alcohols, or other flexible molecular systems, whereas cyclic molecular liquids remain far less explored. In such systems, ring closure, conformational constraints, and the absence of chain ends may lead to a confinement response that differs fundamentally from that of linear analogues. Therefore, this study focused on DMS17C6, the largest and most flexible crown in the investigated series, as a model cyclic liquid under mesoporous confinement. DMS17C6 was infiltrated into AAO membranes with constant pore diameters of 10 and 40 nm, as well as into modulated AAO pores with diameters varying between approximately 18 and 35 nm. The aim was to determine whether the confined dynamics are controlled mainly by pore diameter, or whether pore geometry, surface roughness, wettability, and local interfacial adhesion play an equally important role. The molecular structure and membrane morphology are shown in **Fig. 1** in **A4**.

The first important result came from DSC. While the bulk DMS17C6 exhibited a single glass-transition event near 198 K, all confined samples showed two distinct glass transitions (**Fig. 15**). The lower transition, assigned to $T_{g,core}$, appeared at 191, 190, and 189 K for const-AAO-10 nm, const-AAO-40 nm, and modul-AAO, respectively, while the higher transition, assigned to $T_{g,interfacial}$, appeared at 217, 218, and 223 K, respectively. This double glass-transition behavior indicates the coexistence of a more mobile core-like fraction and a slower interfacial fraction interacting with the pore walls. Importantly, the observation of two T_g values even in modulated pores challenges the assumption, suggested for some linear systems, that pore-wall roughness suppresses the formation or dynamic signature of an interfacial layer.

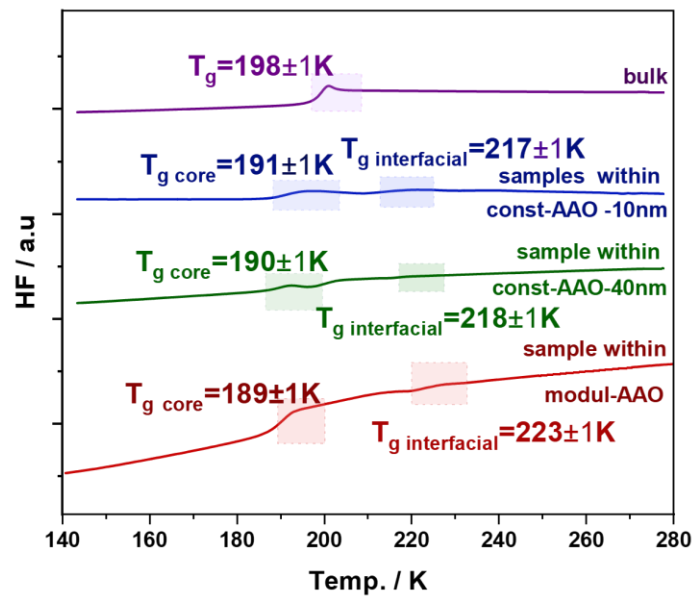


Figure 15. DSC thermograms of bulk and confined DMS17C6 systems.

To understand whether this behavior could be related to surface wetting, temperature-dependent contact-angle measurements were performed (**Fig. 2b** in **A4**). At room temperature, DMS17C6 showed good macroscopic wetting of alumina, with a contact angle of about 20°. Upon cooling, the contact angle increased to about 40°, indicating weaker but still favorable wetting and supporting the possible formation of an interfacial liquid layer.

Further, the dielectric spectra provided the dynamic counterpart of the calorimetric observations. As shown in **Fig. 3** in **A4**, bulk and confined DMS17C6 exhibit dc conductivity, a dominant structural α -relaxation, and a secondary β -process. Confinement strongly affected the α -relaxation, whereas the β -process remained almost unchanged. The isochronal comparison in **Fig. 4a** in **A4** showed that all confined samples have broader α -peaks than the bulk liquid, with β_{KWW} decreasing from about 0.48 in the bulk to lower values under confinement, reaching approximately 0.38 in modul-AAO. Such broadening is typical of

spatially restricted systems, where molecules experience a distribution of local environments

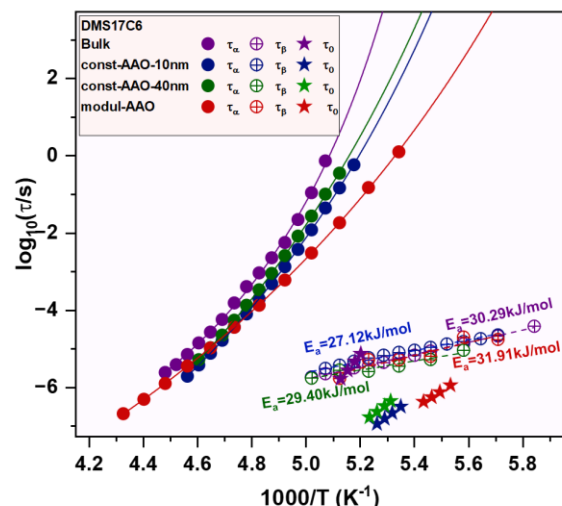


Figure 16. The temperature dependence of the relaxation times (τ_α and τ_β) obtained for all examined samples, with solid lines representing VFT fits and dashed lines for the Arrhenius fits. Colored stars indicate primitive relaxation times calculated from the CM formula (Eq. 13).

due to the coexistence of pore-wall, interfacial, and core regions [91].

The relaxation-time map in **Fig. 16** showed that the structural dynamics deviate from the bulk in the order modul-AAO > const-AAO-10 nm > const-AAO-40 nm. This means that the strongest confinement-induced acceleration of α -relaxation was not observed in the smallest constant pore, but in the rough and diameter-modulated membrane. This result is counterintuitive because previous studies on linear systems, such as poly (propylene glycol) or phenyl alcohols, showed more bulk-like behavior in modulated AAO compared with

constant pores [92,93]. Therefore, DMS17C6 behaves differently from previously studied linear liquids. The authors proposed that this difference arises from the cyclic molecular topology of DMS17C6. Its flexible crown-like ring structure may exploit roughness-induced free-volume regions and local voids more efficiently than linear molecules, leading to faster structural reorientation under confinement.

Further, the secondary relaxation gave an especially important result in relation to the previous bulk study. In bulk DMS17C6, the β -process was broadly compatible with the CM prediction and could be considered JG-like. Under confinement, however, the primitive relaxation frequency agreed with the experimental β -peak only for the bulk sample (**Fig. 3** in **A4**). For all confined systems, the predicted primitive frequency was shifted to much higher frequencies than the observed β -maximum, (**Fig. 4b** in **A4**). Since τ_β and activation energy, approximately 30 kJ/mol, remained almost unchanged regardless of confinement, the β -process is more likely related to local librational or intraring dipolar motions rather than a fully coupled JG relaxation.

Time-dependent annealing experiments were performed to test whether the confinement-induced changes are reversible. In const-AAO-40 nm, partial recovery toward bulk-like dynamics was observed, whereas const-AAO-10 nm and especially modul-AAO showed little or no recovery (**Fig. 5** in **A4**).

The microscopic origin of this behavior was clarified using AFM adhesion-force mapping (**Fig. 6 in A4**). The adhesion force associated with DMS17C6 was much higher in const-AAO-40 nm, about 38.45 nN, than in modul-AAO, about 17.60 nN. This difference indicates that nanoscale roughness and pore modulation reduce the effective liquid–surface contact, despite favorable macroscopic wetting. The proposed mechanism is summarized in **Fig. 17**: constant pores favor a more continuous Wenzel-like interfacial layer, whereas rough modulated pores may promote local dewetting or metastable Cassie–Baxter-like states, producing island-like filling and molecular trapping [91].

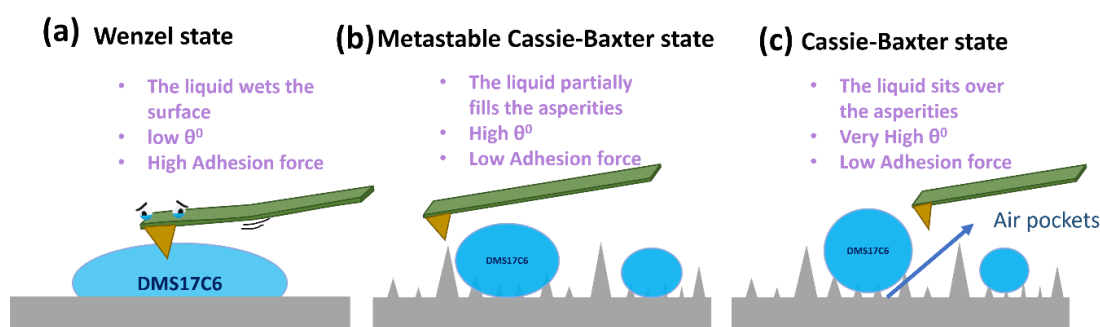


Figure 17. Schematic representation of (a) Wenzel state, (b) Metastable Cassie-Baxter state, and (c) Cassie-Baxter state.

Overall, this study shows that confined cyclic liquids cannot be treated as simple analogues of linear systems. In DMS17C6, nanoconfinement is controlled by the combined effects of cyclic topology, pore geometry, roughness, wettability, and interfacial adhesion. The work also extends the previous bulk study by showing that, although the β -relaxation in bulk DMS17C6 appeared broadly compatible with JG-like behavior, confinement introduced deviations from the expected CM correspondence. Does it suggest a possible local contribution to the secondary dynamics? This interpretation remains open and motivates further studies on other cyclic glass formers, including combined high-pressure and confinement experiments.

4. Contents of the articles constituting the basis of the doctoral thesis, together with the declarations of co-authors

4.1. Article 1 (A1) Specific interactions and mechanism of association in highly viscous aldehyde 3-phenylpropanal.

Specific interactions and mechanism of association in highly viscous aldehyde 3-phenylpropanal

Cite as: J. Chem. Phys. 163, 104505 (2025); doi: 10.1063/5.0283944

Submitted: 4 June 2025 • Accepted: 15 August 2025 •

Published Online: 9 September 2025



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ABSTRACT

In this paper, we investigated the thermal, dynamical, and structural properties, as well as association patterns, in 3-phenyl-1-propanol (3P1Pol) and 3-phenyl-1-propanal (3P1Pal), with special attention paid to the latter compound. Both systems turned out to be good glass formers, differing by 17 K in the glass transition temperature, which indicated a strong change in the self-assembly pattern. This supposition was further confirmed by the analysis of dielectric spectra, where, apart from the α -relaxation, also a unique Debye (D)-mode, being a fingerprint of the self-association, characterized by different dynamical properties (dielectric strength, timescale separation from the α -process), was detected in both samples. Further diffraction and infrared investigations, supported by density functional theory computations and molecular dynamics (MD) simulations, revealed that hydrogen (H)-bonds play a key role in the association in 3P1Pol, while in 3P1Pal, there are at least five different intermolecular interactions involving dipole-dipole forces and π -stacking, as well as extraordinary H-bonds formed between methylene groups neighboring with the formyl unit and carbonyl moiety. Finally, optimized dimeric structures, along with MD simulations, allowed us to propose a molecular mechanism responsible for the D-process in 3P1Pal. The presented data systematize previous understanding of molecular association as well as open new ways of exploring this phenomenon in aldehydes.

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I. INTRODUCTION

Systematic spectroscopy studies with the use of dynamical light scattering, mechanical, and broadband dielectric spectroscopy studies revealed that for the majority of the supercooled liquids approaching the glass transition temperature, the shape of the structural (α)-process, originating from the cooperative motions of the molecules and responsible for the vitrification phenomenon,

is clearly non-exponential.^{1–3} In fact, this experimental observation became an essential and universal feature of the low- and high-molecular-weight glass formers with varying translational or orientational degrees of freedom.^{1,4–6} Briefly, one can add that it is an emanation of the heterogeneous nature of the dynamics of the investigated system due to density fluctuations occurring across the sample. However, in some specific liquids, apart from the structural process, one can also observe an additional, slower relaxation mode,

which can be described by the exponential decay. This unique mode, called in the literature the Debye (D) relaxation, appears to show up only in liquids with a high tendency to self-assemble. In this context, one can mention water,⁷ secondary amides,⁸ *N*-mono-substituted amides,⁹ amines,^{10,11} carboxylic acids,¹² *m*-toluidine,¹³ monohydroxy alcohols (MAs),^{11,14–17} etc., all having the ability to form strong hydrogen (H)-bonds that bind molecules together into nanoclusters. Nevertheless, the existence of these specific interactions is not crucial for the appearance of the characteristic D-response function since it can also be detected in purely van der Waals compounds, such as dioxolanes,¹⁸ terconazole,¹⁹ or etoricoxib.²⁰ However, it must be stressed that in all these systems, some additional molecular organization via weak van der Waals forces was noted. Therefore, considering all the mentioned examples, one can try to link the presence of the D-process to some molecular motions occurring in the molecules organized spatially at the mesoscale. In the literature, there are many different theories or hypotheses trying to explain the nature of the Debye process.^{21–25} However, it seems that the transient chain model (TCM), assuming the attachment and detachment of the molecules at both ends of H-bonded chain-like structures, is one of the most common molecular explanations provided for this type of mode.¹⁶ Apart from this, there are some other well-established concepts behind the origin of the Debye process. Recently, Pabst *et al.* revealed a slow D-like process in polar van der Waals liquid tributyl phosphate (TBP) with no H-bonds and $g_K > 1$ at low temperature, which originates from the “dipole–dipole correlation” arising primarily from the breaking and reformation of anti-parallel dipole pairs.²⁴ Another model, “a H-bonding breakage facilitated sub-supramolecular reorientation,” analogous to the terminal relaxation in “living-polymers,” explained the Debye origin in 2-ethyl-1-hexanol (2E1H), where the aforementioned models failed.²⁵ At this point, it is limited to MAs but found analogous to the slow mode observed by Napolitano in non-equilibrated polymers.^{26,27} What is more, systematic studies on the dynamics of MAs also revealed that both relaxation times and the amplitude of the D-process allow insight into the pattern of the self-assembly phenomenon. For the systems with large (primary alcohols) or small amplitude (secondary and tertiary alcohols) of D-relaxation, the chain-like or ring-like structures are expected, respectively.^{17,21,28,29} This hint was used to understand the effect of solvent, temperature, chemical structure, or high pressure on the self-assembly in MAs and other systems.^{30–32} However, while there are numerous studies on the self-association in alcohols, amines, amides, and carboxylic acids at varying thermodynamic conditions, not much has been done for aldehydes, which are considered very weakly H-bonded systems, especially in the highly viscous regime close to the glass transition temperature (T_g).

As known, the formyl hydrogen (H) atoms are considered to be slightly hydridic compared to the analogous $C(sp^2)$ -H atoms in alkenes or the $C(sp^3)$ -H atoms in alkanes.^{33–35} Thus, a persistent question was whether or not a formyl group of aldehydes can donate its H atom to an oxygen atom acceptor and form a C-H $\cdots$ O H-bond. The presence of C-H $\cdots$ O H-bonds in the liquid and solid phases of methoxy-, ethoxy-, phenyl-, and fluorobenzaldehyde derivatives was confirmed by both vibrational and nuclear magnetic resonance (NMR) spectroscopic studies.^{36–40} The engagement of the carbonyl oxygen atom in the H-bond in these benzaldehydes was concluded from the splitting of the carbonyl

stretching mode and the ^{17}O NMR chemical shift. Particular attention was also paid to the spectroscopic effects related to the predicted shortening of the C-H bond engaged in the C-H $\cdots$ O contact. It should be noted that many spectroscopic and crystallographic investigations confirmed the existence of such an association in different phases of aldehydes based on the shifts observed in IR and NMR spectra.^{41–54} Generally, it was found that the acidity of formyl H-atoms depends on the substitution at the α -position and the supramolecular environment around the formyl group.⁴⁶ Parallel to these results, other studies based on crystallographic database mining have demonstrated that the close C-H $\cdots$ O contacts in the crystal structures of aldehydes can be directed by interactions between the formyl C=O and O-X dipolar interactions, e.g., the carbonyl–carbonyl interactions can be competitive with H-bonds.^{55–60} Thus, the association process of aldehydes revealed the significant role of dipolar interactions in maintaining the overall stability of the aggregate. On the other hand, although the formyl C-H $\cdots$ O H-bonds are weak, they contribute to the overall stability, of the clusters and their role seems to be underrated in small molecular complexes of aldehydes.⁴⁶

Herein, we explored the dynamics and association mechanism of 3-phenyl-1-propanal (3P1Pal) and 3-phenyl-1-propanol (3P1Pol) in a wide range of temperatures from room temperature to the glass transition temperature. To tackle this issue, we applied several spectroscopic methods along with x-ray diffraction (XRD) supported by molecular dynamics (MD) simulations and quantum mechanical computations.

II. MATERIALS AND METHODS

A. Material

3-phenylpropionaldehyde (3P1Pal, with a purity >95% and a molecular weight, $M \sim 134.18$ g/mol) and 3-phenyl-1-propanol (3P1Pol, with a purity >98% and $M \sim 136.19$ g/mol) were supplied by Sigma-Aldrich. Before each measurement, the samples were freeze-dried using liquid nitrogen to ensure the absence of water.

B. Differential scanning calorimetry (DSC)

Calorimetric measurements were carried out by a Mettler-Toledo DSC apparatus equipped with a liquid nitrogen cooling accessory and an HSS8 ceramic sensor (heat flux sensor with 120 thermocouples). Temperature and enthalpy calibrations were done by using indium and zinc standards. The sample was prepared in an open aluminum crucible (40 μ l) outside the DSC apparatus. Next, the aluminum-sealed crucible with the sample was cooled down to 120 K and measured on heating up to 298 K at a constant heating rate of 10 K/min.

C. Broadband dielectric spectroscopy (BDS)

Isobaric dielectric measurements were conducted on cooling in a wide range of temperatures ($T = 243$ –143 K) and frequencies ($f = 10^{-1}$ – 10^6 Hz) using a Novocontrol spectrometer, equipped with an Alpha Impedance Analyzer with an active sample cell. The temperature stability controlled by the Quatro Cryosystem using a nitrogen gas cryostat was greater than 0.1 K. The measurements were performed in a stainless steel parallel-plate cell (diameter: 15 mm and gap: 0.1 mm) immediately after the preparation of the sample.

D. X-ray diffraction (XRD)

The X-ray diffraction (XRD) experiments were carried out using a laboratory Rigaku-Denki D/MAX RAPID II-R diffractometer equipped with a rotating Ag anode, a (002) graphite monochromator in the incident beam path, and an image plate detector arranged in Debye-Scherrer geometry. The wavelength of the incident beam $\lambda_{K\alpha}$ was 0.5608 Å. Temperature control during measurements was ensured using an Oxford Cryostream 700 Series system. The samples were measured in glass capillaries with a diameter of 1.5 mm.

E. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were measured on the Nicolet iS50 spectrometer (Thermo Fisher Scientific, Massachusetts, USA) at a spectral resolution of 4 cm⁻¹, taking 16 scans. First, the spectrum of commercial 3P1Pal was recorded in the ATR mode at 293 K in the range of 4000–400 cm⁻¹. Next, FTIR data as a function of temperature were collected in the transmission mode in the 4000–1000 cm⁻¹ wavenumber region. The limited spectral range of these experiments was due to the absorption of CaF₂ windows, which were used to prepare a thin film (3.5 μm) of the 3P1Pal sample. The temperature was monitored with a Linkam heating/cooling stage (Linkam Scientific Instruments Ltd., Surrey, UK, model THMS600) with a stability of ±0.01 K. During the measurements, the FTIR spectrometer was purged with liquid nitrogen to remove water vapor and carbon dioxide from the instrument effectively. The temperature investigations of 3P1Pal were performed in two sequences: (i) upon cooling from 293 to 123 K and (ii) upon heating from 123 to 293 K, with a constant rate of 4 K/min. Moreover, FTIR spectra of aldehyde solutions (0.1M) in carbon tetrachloride (CCl₄) and cyclohexane (C₆H₁₂) were measured in the frequency range 4000–400 cm⁻¹ using a transmission solution cell with KBr windows (a path length of 1.03 mm) as well as a transmission solution cell with NaCl windows (a path length of 0.19 mm), respectively. A total of 16 scans with a spectral resolution of 4 cm⁻¹ were averaged for each sample.

F. Raman spectroscopy

Raman spectra were collected on a WITec alpha 300 R confocal Raman microscope (CRM) (WITec Wissenschaftliche Instrumente und Technologie GmbH, Ulm, Germany) equipped with an air-cooled solid-state laser ($\lambda = 532$ nm) and a spectrometer diffraction grating of 600 lines/mm (the 1.5–2 cm⁻¹ spectral resolution). Laser power was optimized to minimize heat-induced effects and was ~20 mW. Raman spectra were recorded from 50 to 3750 cm⁻¹ with an exposure time of 2 s and 30 accumulations. The THMS600 heating/cooling stage (Linkam Scientific Instruments Ltd., Surrey, UK) was used to control the temperature changes in the spectra in the same sequence as during FTIR measurements, i.e., upon cooling from 293 to 123 K and then heating from 123 to 293 K. The spectrometer monochromator was checked before the measurements using a silicon plate (520.7 cm⁻¹).

G. DFT calculations

Density functional theory (DFT) calculations were carried out in the ORCA quantum package 6.0.1, assisted with the XTB semiempirical package. The most stable aldehyde dimers were found by performing molecular dynamics on the random dimer geometry

with the use of XTB-ff, 350 K temperature, and then sampling the trajectory every 100 steps. Approximately 200 structures of dimers obtained from the MD module were then optimized at the BLYP/6-31G(d,p) level of theory. The ten most energetically stable dimers were subsequently optimized at the B97/D4/6-311+(2df,2pd) level of theory. Infrared spectra were calculated on the BLYP/6-311G(2df,2pd) level of theory. All the calculations were performed on an AMD Opteron 6380 4-processor cluster with 64 threads equipped with ECC RAM.

H. Molecular dynamics (MD) simulations

MD calculations were performed in Gromacs 2025.2 with the use of Amber FF and charges calculated in the bcc method. In all simulations, 1000 molecules were used in the box (both 3P1Pol and 3P1Pal). The equilibration dynamics was carried out in a NPT ensemble at a pressure of 1 bar (c-rescale barostat) and two different temperatures, i.e., 298 and 233 K. The equilibration simulation time of 80 ns was used for the system at 233 K and 20 ns at 298 K. This was sufficient to achieve equilibrium. The theoretical density for systems was calculated as 0.9809 ± 0.0002 g/cm³ at 298 K and 1.0473 ± 0.0002 g/cm³ at 233 K (for $p = 1$ bar). Afterward, 20 ns production runs in the NVT ensemble were done with sampling every 200 steps at 233 K and 5 ns at 298 K. For the analysis of trajectories, the TRAVIS package was applied (DOMA, DACC, and RDYN analyses were performed). In the production runs, the PME method was used for electrostatics. For van der Waals forces, we applied a treatment switch-cutoff scheme (cutoff from 0.9 to 1.2 Å). For the preparation of initial molecular boxes, the Packmol package was used. All the calculations were performed with single precision and using CUDA GPUs and Intel i7 processors.

III. RESULTS AND DISCUSSION

At first, we performed calorimetric measurements on both examined substances to determine whether they can be supercooled, avoiding crystallization. Representative thermograms measured at a 10 K/min heating rate are shown in the insets of Figs. 1(a) and 1(b). As can be seen, besides the single heat capacity jump, which is assigned as the glass transition temperature ($T_g = 165$ K for 3P1Pal and $T_g = 182$ K for 3P1Pol), there are no other thermal events that could be assigned to the crystallization, melting, or other phase transition. This simple experiment showed that both systems are good glass formers. Moreover, it was found that the T_g of the alcohol is much higher with respect to the aldehyde, which is not surprising since the former compound forms strong H-bonds, while in the latter one, these specific interactions are much weaker, if present at all.

Having these data at hand, we carried out dielectric measurements at a wide range of frequencies and temperatures on both samples. Representative dielectric loss spectra of 3P1Pol and 3P1Pal are presented in panels (b) and (a) of Fig. 1, respectively. As can be seen, in the former system, except for the dc-conductivity, a single dominant relaxation process shifting to the lower f with the temperature drop is noted. After fitting the detected loss peak to the Havriliak-Negami (HN) function,²

$$\epsilon(\omega)'' = \frac{\sigma_{dc}}{\epsilon_0 \omega} + \text{Im} \sum_{i=1}^2 \left(\epsilon_{\infty} + \frac{\Delta \epsilon_i}{[1 + (i\omega \tau_i)^{\alpha_i}]^{\beta_i}} \right), \quad (1)$$

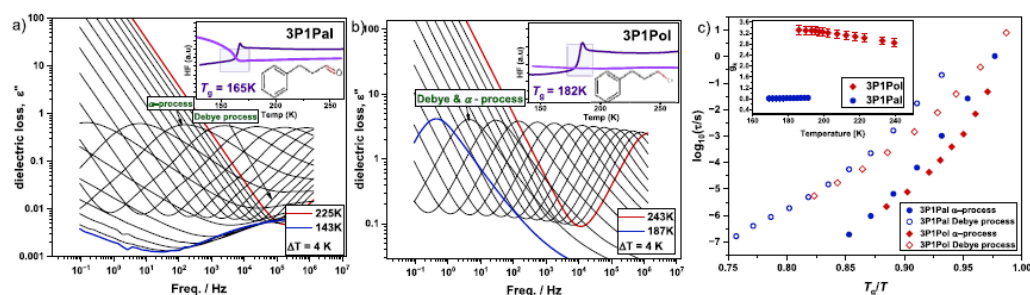


FIG. 1. Dielectric loss spectra of (a) 3P1Pal and (b) 3P1Pol. (c) Debye and structural (α)-relaxation times determined for the examined compounds, plotted as a function of T_g/T . The insets in panels (a) and (b) show the respective DSC thermograms with the indicated T_g , as well as chemical structures of 3P1Pol and 3P1Pal, and the inset in panel (c) presents the temperature dependences of g_k . The data for 3P1Pol [panel (c) and the inset] were taken from our recent paper.⁶¹

where σ_{dc} is the dc-conductivity, $\bar{\omega}$ is an angular frequency ($\bar{\omega} = 2\pi f$), ϵ_∞ is the permittivity at finite frequencies, ϵ_0 is the vacuum permittivity, $\Delta\epsilon$ is the dielectric relaxation strength, and τ is the HN relaxation times; we found that it can be described by α and β parameters (characterizing the shape of the peak) that are very close to unity; see Fig. 2(b). Hence, it can be labeled as a Debye relaxation. This is in line with what has been reported in the previous papers on phenyl derivatives of alcohols.^{61,62}

Nevertheless, it should also be pointed out that it was clearly demonstrated that the dominant process in these systems is composed of two contributions: a Debye (D) relaxation related to the mobility within nanoassociates and a structural process responsible for the vitrification phenomenon. However, due to the similar scale of both modes, they cannot be separated in the collected spectra.⁶¹ On the other hand, for the aldehyde, the situation looks different.

In this compound, we can detect two relaxation processes above the T_g , differing significantly in amplitude. In Fig. 2(a), we have shown HN fits to the loss spectra together with the parameters describing the shape of both modes. It is clearly visible that for the faster mode, the α parameter is close to unity, while β is around ~ 0.5 . Calculating the slope of the high-frequency part of the structural process near T_g obtains a value equal to $\omega^{-0.45}$ and is very close to $\omega^{-0.5}$. This requires special attention because recently much work has been done to shed new light on the concept of the “generic spectral shape” for supercooled liquids, particularly focusing on the value of high-frequency behavior “ $\omega^{-0.5}$ ” near their T_g . However, there are challenges to the notion of this universality in the α -relaxation spectra of supercooled liquids. Moch *et al.* reported that these are true for dynamic light scattering (DLS) studies, as almost every supercooled liquid exhibits the generic behavior of α -relaxation. However, the same systems

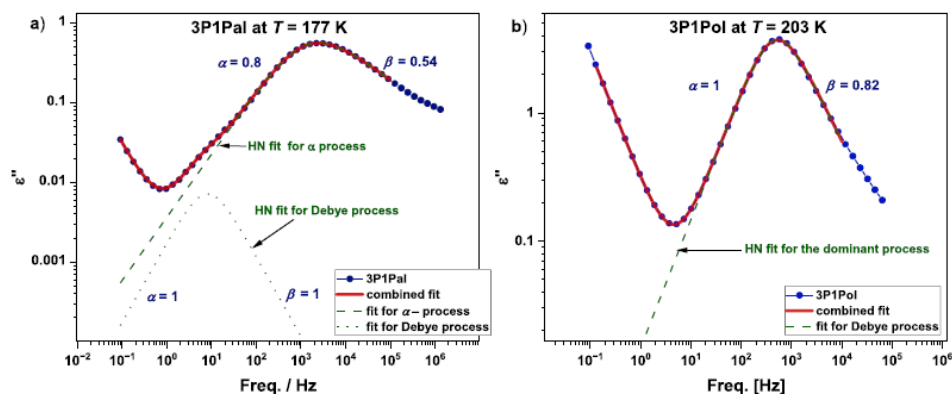


FIG. 2. Fit functions used for the analysis of both relaxation processes (Debye and α) in (a) 3P1Pal and (b) 3P1Pol.

in dielectric studies lack the evidence of universality in their relaxation behavior. They demonstrate this by investigating polar liquids such as propylene glycol, which exhibited a broader, more stretched dielectric response, reflecting system-specific dynamics rather than a universal pattern.⁶³ Their findings indicate that the spectral shape of the α -relaxation depends on molecular interactions, contradicting earlier assumptions of universality. Subsequently, a comprehensive review done by Böhmer *et al.* elucidates that the generic structural shape holds for simple supercooled liquids in the absence of strong dipolar cross correlations ($g_k \sim 1$).⁶⁴ Our data for aldehyde align with these observations, with a high-frequency power law exponent $\omega^{-0.5}$, preserving the conjecture of a generic spectral shape. At the same time, alcohol deviates from the generic shape due to contributions from the stronger orientational cross correlation of this highly polar liquid, as mentioned.

On the other hand, for the slower mode, α and β parameters are equal to 1. In fact, this simple fitting procedure shows that in the aldehyde, aside from the structural (α)-process (the faster mode), which is observed in each glass former, one can also identify a D-relaxation as being an inherent feature of the systems that tend to organize via H-bonds or van der Waals interactions. This result is quite surprising since aldehydes are regarded as weakly or non-associating compounds, where only very weak H-bonding, if present at all, is possible. To get additional insight into this issue, we have calculated a Kirkwood factor (g_k) from dielectric data for alcohol and aldehyde from the following equation:⁶⁵

$$g_k = \frac{9k_B\epsilon_0MT}{\rho N_A\mu^2} \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2}, \quad (2)$$

where k_B is Boltzmann's constant; ϵ_s and ϵ_∞ are the static and infinite permittivity, respectively; M is the molar mass of the substance; ρ is the density; N_A is Avogadro's number; and μ is the molecular dipole moment determined from DFT computations. Herein, one can add that ϵ_s was obtained from the plateau regime at lower frequencies of $\epsilon''(f)$ dependency, while ϵ_∞ has been calculated from the refractive index using the following relationship: $n^2 \approx \epsilon_\infty$.

It should also be mentioned that the Kirkwood factor provides information about a long-distance correlation between dipoles and, eventually, the architecture of the associates. In the inset of Fig. 1(c), we plotted a temperature dependency of the g_k in both samples. As expected, it is much higher than the unity for the alcohol, which means that there are H-bonded chain-like structures. A completely different situation is noted for the aldehyde, where g_k is smaller than unity and slightly decreases (within uncertainty) with lowering temperature. That means that in this system, dipoles tend to arrange antiparallelly to each other. Alternatively, one can suppose that cyclic structures can probably be formed in the supercooled aldehyde. This issue will be discussed in the latter part of this paper. It is also worth noting that the correlation between g_k and the high-frequency power law exponent, describing the high-frequency part of the structural process of both samples. Aligns with the observation by Blochowicz *et al.* for different supercooled liquids.⁶⁶

Aside from the mentioned analysis, we fitted all the dielectric spectra collected at a wide range of temperatures to the superposition of the two HN functions [Eq. (1)] to determine Debye and α -relaxation times in aldehyde. It should be noted that the data for alcohol were taken from Ref. 61, where the authors analyzed the

derivative of $\epsilon''(f)$ to extract both dynamic variables. Then, characteristic relaxation times (τ_D , τ_α) were plotted vs $1/T$, and subsequently, the glass transition temperature (T_g) for both systems was calculated. The obtained values ($T_g = 161$ K for aldehyde and $T_g = 180$ K for alcohol) are given in Table I. One can add that the T_g was defined as a temperature at which $\tau_\alpha = 100$ s. As can be seen, there is a very good agreement between T_g s obtained from calorimetric and dielectric data.

Hence, having T_g determined, we replotted τ_D and τ_α vs T_g/T [Fig. 1(c)]. What is more, in Fig. S1 of the supplementary material, we added the temperature evolution of the relaxation times of the Debye mode and α -process in ibuprofen (IBU) along with the τ_α/τ_D vs T_g/T (inset) dependency obtained for the considered samples. Herein, one can mention that the D-relaxation in IBU was assigned to the motions within dimers or alternatively to the synperiplanar to antiperiplanar conformational changes.¹² In this way, one can easily find that there is a quite notable timescale difference between the Debye and α -process in alcohol, IBU, and aldehyde. This is probably due to a different association scheme and, eventually, the size of the nanoclusters formed in these samples.

For further insight into the molecular ordering, we performed XRD measurements at a series of temperatures, from room temperature down to T_g . The recorded two-dimensional diffraction patterns were subsequently converted into a one-dimensional intensity functions $I(Q)$, where $Q = 4\pi \sin \theta / \lambda_{K\alpha}$ is the scattering vector, and 2θ is the scattering angle. The maximal Q reached in the experiment was $20 \text{ \AA}^{-1}$. The recorded scattering data were corrected for background, polarization, sample absorption, and incoherent Compton scattering and, subsequently, normalized using a data processing procedure developed for high-energy X-ray measurements.⁶⁷ In the following step, the data were converted into the structure factor $S(Q)$ representation. This was calculated by considering the contributions of all atomic species present in 3P1Pol and 3P1Pal. In particular, $S(Q)$ was derived from the corrected and normalized intensity $I_{CN}(Q)$, using the following equation:

$$S(Q) = \frac{I_{CN}(Q) - (\langle f^2 \rangle - \langle f \rangle^2)}{\langle f \rangle^2}, \quad (3)$$

where $\langle f^2 \rangle = \sum_n c_i f_i^2$ and $\langle f \rangle = \sum_n c_i f_i$, with c_i representing the concentration, f_i representing the atomic scattering factor of the i th atomic species, and n numbering the atomic species. The structure factor $S(Q)$ reflects only the spatial distribution of atoms and, thus, describes the sample's internal structure independently of the atomic scattering strength. Moreover, it can also be easily obtained from a structural model in the form of the coordinates of atoms. Therefore, $S(Q)$ functions were calculated using the Debye equation from the

TABLE I. Molecular weights and glass transition temperatures obtained from DSC and BDS measurements of the investigated compounds, together with the values of g_k (at $T_g + 10$ K) and dipole moment (μ).

Sample	M (g/mol)	T_g DSC (K)	T_g BDS (K) at $\tau = 100$ s	g_k at $T_g + 10$ K	μ (D)
3P1Pal	134.18	165	161	0.82	2.3
3P1Pol	136.19	182	180	3.3	1.725

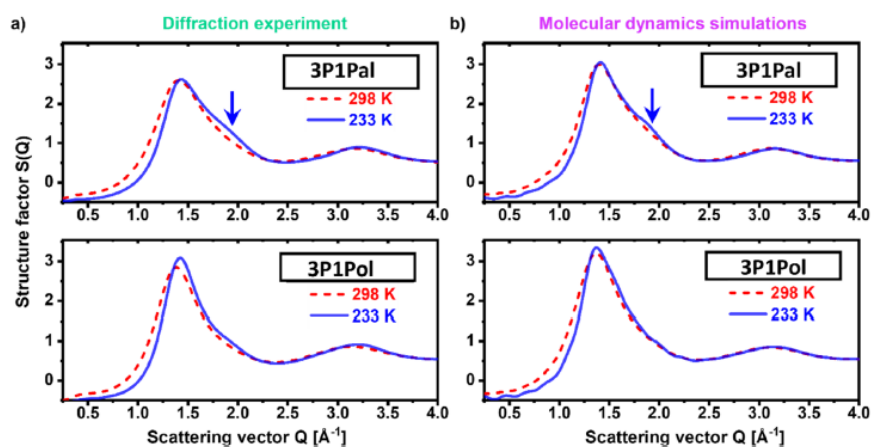


FIG. 3. Comparison of the results of experimental x-ray diffraction data (a) and molecular dynamics simulations (b) in the form of structure factors for 3P1Pal (upper panels) and 3P1Pol (lower panels) at 298 (red) and 233 K (blue). The blue arrow indicates an additional peak that arises at the right shoulder of the main diffraction peak for 3P1Pal at lower T .

structural models derived from the MD simulations and supported the interpretation of the experimental data.

The X-ray diffraction patterns of both compounds, 3P1Pol and 3P1Pal, collected at 298 and 233 K, normalized to the form of the structure factors $S(Q)$, are presented in Fig. 3(a). They look like typical structure factors for amorphous-like molecular liquids with one main broad maximum located around $1.41 \text{ \AA}^{-1}$, which arises from the short-range intermolecular correlations. The peaks appearing for Q values greater than $2.5 \text{ \AA}^{-1}$ are primarily due to intramolecular correlations, and they do not differ between 298 and 233 K for both systems; therefore, only a limited range of $S(Q)$, up to $4 \text{ \AA}^{-1}$, is presented. One can see that the main diffraction peak is broader and less intense for 3P1Pal than for 3P1Pol. This indicates that the alcohol is characterized by a higher degree of the nearest-neighbor structural order than the aldehyde. This is in agreement with the fact that the alcohol may form supramolecular clusters via H-bonds, while the molecules of the aldehyde do not interact to such an extent and do not organize themselves through strong H-bonds.

It is worth mentioning that common and well-documented features of x-ray and neutron diffraction/scattering data for alcohols, related to the organization of molecules by H-bonds, are the so-called pre-peaks appearing in the low Q range, before the main diffraction peak.^{68,69} These features generally arise from medium-range order structural correlations due to the formation of self-assembly of molecules in H-bonded clusters.⁷⁰ In the diffraction patterns presented in Fig. 3 for 3P1Pol, no clear pre-peak is observed. However, the absence of such a feature for phenyl alcohol is consistent with previous reports,⁷¹ which showed that through a balance of the positive atom–atom correlations (for like species atoms) and negative correlations (for cross species) in phenyl alcohols, they compensate, despite the fact that there are medium-range order correlations due to H-bond clustering. A similar behavior of enhancing

or diminishing the pre-peak feature due to positive and negative atom–atom correlations was also observed for aqueous mixtures of alcohols.⁷²

With lowering temperature, the main diffraction peaks for both compounds shift toward higher Q values and get sharper because of the increase in density. However, there is an additional change with the temperature drop, which cannot be explained based on a simple thermal effect, namely, an additional peak arises on the right shoulder of the main diffraction peak (indicated by the blue arrow), at around $1.9 \text{ \AA}^{-1}$, and this component is more intense at 233 K for 3P1Pal than for 3P1Pol. The position $Q \approx 1.9 \text{ \AA}^{-1}$ gives the real space distance $d = 2\pi/Q \approx 3.3 \text{ \AA}$, while the position $Q \approx 1.42 \text{ \AA}^{-1}$ gives $d = 2\pi/Q \approx 4.4 \text{ \AA}$. That greater d value is the average repeating distance between molecules in these systems. That shorter one indicates an additional periodic organization of molecules with such a separation distance between them, and it is known from the literature that it is about the average distance between the planes of the aromatic rings in π – π stacking interactions between phenyl rings.⁷³ Therefore, one can expect a rise in such interactions with lowering temperature in the liquid aldehyde system. Moreover, Fig. 3(b) shows the $S(Q)$ functions calculated based on the optimized MD models. The model-based $S(Q)$ behavior with lowering temperature mimics the changes observed in the experimental data for both compounds. Therefore, these models were used to obtain information on the temperature-activated transformation of the structure of the studied compounds. These data will be discussed in the section dedicated to the outcomes of MD simulations.

Subsequently, we decided to perform further infrared and Raman measurements over a wide range of temperatures. An assignment of vibrational bands of the FTIR and Raman spectra recorded at room temperature (293 K) to the molecular motions of the aldehyde was shown in the [supplementary material](#) (Fig. S2).

Temperature-dependent FTIR and Raman measurements were carried out during the cooling cycle (293–123 K) at a rate of 4 K/min to gain deeper insights into the mechanism of aldehyde association through the analysis of the changes in the peak parameters occurring with temperature variation. Representative spectra are provided in Figs. S3 and S5 of the [supplementary material](#), whereas the temperature evolution of the integrated intensities (areas) of selected IR and Raman bands is shown in Figs. S4 and S6 of the [supplementary material](#). Comparative spectra recorded at selected temperatures of 293 and 157 K (T_g determined from vibrational measurements) are illustrated in Fig. S7 of the [supplementary material](#). The comparison of the spectra obtained at temperatures of 293 and 157 K, along with those of 3P1Pal in carbon tetrachloride and cyclohexane solutions, is presented in Fig. 4.

As shown in Fig. 4, the IR spectrum of 3P1Pal at 293 K shows the bands in the high-wavenumber region assigned to the first overtone C=O (~ 3415 cm^{-1}), aromatic C–H (3050–3000 cm^{-1}), and aliphatic C–H (3000–2700 cm^{-1}) stretching vibrations. A strong band at 1725 cm^{-1} corresponds to the C=O stretching, while the bands below 1650 cm^{-1} correspond to the C–H bending, C–O stretching, C=C stretching, and C–C stretching and bending vibrations (for more detailed information, please see the [supplementary material](#)). It can be noted that the collected absorption signals are relatively broad and blurred, which is a characteristic feature of the liquid sample. When cooled to 157 K, some bands assigned to the aromatic ring vibrations essentially remain unchanged, with only a minor shift to lower wavenumbers ($\Delta\nu = -1$ cm^{-1}), likely due to thermal contraction and the associated increase in material density. Notable spectral changes appear in the $\nu_{\text{C=O}}$ and $\nu_{\text{C-H}}$ regions, sensitive to the formation of the C–H $\cdots$ O intermolecular interactions.⁴⁰ As highlighted in Fig. S7, red shift effects were seen for the C=O stretching ($\Delta\nu = -5$ cm^{-1}) and its first overtone ($\Delta\nu = -9$ cm^{-1}), while blue and red shifts were observed for the C–H bands

(the formyl C–H stretching: $\Delta\nu = 6$ cm^{-1} , 2725 vs 2731 cm^{-1} and 2825 vs 2831 cm^{-1} ; the methylene C–H stretching: $\Delta\nu = -3$ cm^{-1} , 2893 vs 2890 cm^{-1}). Moreover, the intensities of the $\nu_{\text{C=O}}$ and aliphatic $\nu_{\text{C-H}}$ bands increased, indicating an increase in the number of interactions involving these groups at lower temperatures. In addition, the $\nu_{\text{C=O}}$ band broadened at low temperatures, suggesting the formation of various H-bonded aggregates (more inhomogeneous distribution of the H-bonding network). It should be mentioned that similar spectral effects upon cooling were detected in Raman spectra, but the main variations in peak parameters were visible for the methylene C–H stretching (2950–2850 cm^{-1}), the C–H wagging (850–720 cm^{-1}), and in-plane C–H rocking (1420–1350 cm^{-1}) (Fig. S7). Noteworthy, based on the integrated intensity values of the selected bands in IR and Raman spectra measured as a function of T , the T_g value was determined (~ 157 K, Figs. S4 and S6), which was close to that determined from the DSC experiment (165 K).

For deeper study on the nature of weak C–H $\cdots$ O interactions, 3P1Pal was diluted in CCl_4 and cyclohexane, and IR spectra of the solutions (0.1M) were measured (Fig. 4). The dilution of 3P1Pal in CCl_4 caused the shifts of the $\nu_{\text{C=O}}$ ($\Delta\nu = 5$ cm^{-1}), formyl $\nu_{\text{C-H}}$ ($\Delta\nu \sim -8$ cm^{-1}), and methylene $\nu_{\text{C-H}}$ ($\Delta\nu = -1$ cm^{-1}) bands, indicating the reduction of the existing intermolecular interactions. On the other hand, dilution of aldehyde with the solvent (as CCl_4) might yield the opposite effect, namely, the formation of H-bonds involving the C–H groups and the electronegative chlorine atoms. To eliminate additional interactions, cyclohexane was used as a solvent. In this case, the $\nu_{\text{C=O}}$ and the first overtone of the $\nu_{\text{C=O}}$ bands blue-shifted by 9 and 22 cm^{-1} compared to the pure 3P1Pal, respectively, indicating the destruction of the aggregates and monomer formation (Fig. 4). Compared to 3P1Pal diluted in cyclohexane, the formyl $\nu_{\text{C-H}}$ bands in pure 3P1Pal were blue-shifted by ~ 14 cm^{-1} (2711 $\text{cm}^{-1} \rightarrow 2725$ cm^{-1} and 2811 $\text{cm}^{-1} \rightarrow 2825$ cm^{-1}). This trend was also

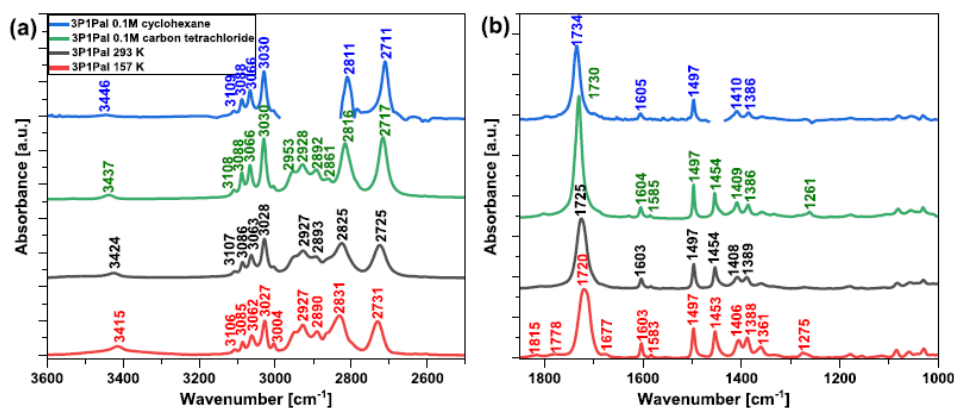


FIG. 4. FTIR spectra of 3P1Pal in bulk at (black) 293 K and (red) T_g as well as dissolved in non-polar solvents [(green) carbon tetrachloride and (blue) cyclohexane], in the ranges of (a) 3600–2500 cm^{-1} and (b) 1850–1000 cm^{-1} . The regions in the spectrum of 3P1Pal diluted in cyclohexane that were disturbed by the bands of the C–H stretching (2927 and 2852 cm^{-1}) and the C–H bending (1450 cm^{-1}) vibrations of cyclohexane were removed for clarity.

seen in other aldehydes, such as benzaldehyde derivatives or caffeine hydrate.^{36,38,39,74} Prior studies by Thakur *et al.* reported even larger average blue shifts (50 cm^{-1}) of the formyl $\text{C}_{\text{sp}^2}\text{-H}$ bonds in the $\text{C}_{\text{sp}^2}\text{-H}\cdots\text{O}$ contacts for various possible dimer geometries of aldehydes,⁴⁶ using Bader's atom in molecule (AIM) analysis. Moreover, the effect of the electron-withdrawing group and substitution at the α -position enhanced the electropositive character of the formyl H-atoms. The smaller blue shift values were calculated for other (than formyl) C-H groups of aldehydes participating in C-H $\cdots$ O interactions (from the aliphatic skeleton or aromatic ring).⁴⁶ It can be added that for the methylene $\nu_{\text{C-H}}$ bands of diluted 3P1Pal in CCl_4 , only minor shifts ($\sim 1\text{ cm}^{-1}$) were observed, while the aromatic $\nu_{\text{C-H}}$ and $\delta_{\text{C-H}}$ bands showed slight red shifts ($\Delta\nu = -2\text{ cm}^{-1}$), suggesting the existence of possible additional weak π - π stacking interactions between phenyl rings in pure aldehyde. Moreover, in both solvents, the $\nu_{\text{C=O}}$ bands were narrower than in pure 3P1Pal, suggesting the presence of isolated molecules. It is also worth noting that the detected shifts of the C-H signals corresponding to the formyl and methylene groups of the aldehyde in the liquid phase, relative to those observed in the solvents, provide direct evidence for the presence of intermolecular interactions. Nevertheless, the nature of these interactions remains ambiguous, based solely on the spectroscopic measurements, i.e., it is unclear whether they predominantly arise from the H-bonding or are primarily the result of dipolar interactions. Thus, to address this question and explore the supramolecular organization of aldehyde molecules better, the next step of our study will involve theoretical investigations of 3P1Pal using DFT calculations and MD simulations.

Nevertheless, to end this part, it is worth adding that our previous experimental studies of intermolecular interactions in 3P1Pal shed light on the supramolecular self-assembly, structural order, and H-bond patterns in this aromatic system.^{75,76} It was shown that the $\nu_{\text{O-H}}$ band of H-bonded hydroxyl groups located at 3331 cm^{-1} (293 K) was red-shifted to 3280 cm^{-1} (182 K , T_g), which indicated the weakening of the O-H bonds due to the formation of strong HBs. Moreover, on cooling, the $\nu_{\text{O-H}}$ band of non-H-bonded (free) hydroxyl groups ($\sim 3559\text{ cm}^{-1}$) disappeared, confirming nearly total association of 3P1Pal molecules at low T . It can be noticed that the $\nu_{\text{O-H}}$ band of 3P1Pal was broader than that in 3-cyclohexyl-1-propanol, which suggested the existence of additional interactions involving aromatic rings (O-H $\cdots\pi$) (also proposed by DFT calculations) apart from the O-H $\cdots$ O contacts. Based on the investigation of 3P1Pal diluted in CCl_4 , the average number of H-bonded associates (n) was calculated ($n \sim 3$), so the trimers dominated in 3P1Pal at 293 K . It can be added that the aromatic $\nu_{\text{C-H}}$ band positions remained constant under cooling, while those of the methylene $\nu_{\text{C-H}}$ band showed a slight red shift ($\Delta\nu = -1\text{--}2\text{ cm}^{-1}$). Therefore, the association of 3P1Pal molecules was governed by the typical O-H $\cdots$ O H-bonds and competitive O-H $\cdots\pi$ interactions.

Herein, theoretical methods (DFT and MD) were used to understand the molecular clustering effects in aldehyde. We focused on the interactions in the dimeric structures of 3P1Pal. To check the interaction schematics in the dimer, molecular dynamics with a semi-empirical XTb forcefield was performed for dimers at 350 K during a 100-ps simulation time. From the two subsequent runs, 150 dimeric conformations were saved as geometries. After this step, every conformation was optimized on the BLYP/6-311G** level of theory, and 50 more stable conformers were once again optimized

at the B97-d4/6-311+G(2df,2pd). The use of additional diffuse (+) and polarization functions (2df,2pd) in the basis set allowed for the proper modeling of weak interactions in the system, such as π -stacking. In Fig. 5(a), the five most stable dimeric conformers are shown. In these structures, five major interactions have been identified. The first one is an attraction between two formyl groups. As was already stated, it is widely accepted that the formyl groups interact with each other, and aldehydes are able to form clusters due to the formyl groups' attraction forces. As mentioned in the Introduction and the description of infrared data, in many papers, one can read about weak H-bonds between formyl groups. However, our studies within the framework of DFT calculations indicate that the nature of this force is different. The formation of the H-bond between two formyl groups is not possible because of other stronger interactions between these groups. In fact, there are two potential polarities of the C=O bond and the more subtle effect of oxygen lone pair donation to the antibonding Π^* orbital ($n\text{-}\Pi^*$). In the dimeric structures presented in Fig. 5, two carbonyl groups tend to obtain perpendicular orientation, which means that the dipole-dipole attraction dominates. In the case of the $n\text{-}\Pi^*$ interaction, both formyl groups should be oriented parallel to each other because the lone electron pair on the oxygen atom is on the π -type orbital, perpendicular to the plane of the formyl group. The second observed interaction, which occurs naturally in the low-molecular-weight systems with phenyl rings, is π -stacking between rings. In the obtained conformations, π -stacking contact is present, i.e., the rings tend to orient parallel or perpendicular to each other, creating a parallel displaced or T-shaped π -stacking formation. The third interaction is a mixed one, namely, between the formyl group and phenyl ring, which is a purely electrostatic dipole-dipole attracting force between the highly polarized C=O group and phenyl ring. As shown in Fig. 5, the formyl group is in a T-shaped configuration with a phenyl ring. The last two interactions that were found in the system are surprising. In these interactions, the major role belongs to the CH_2 (methylene) group, which is neighboring the formyl group. Due to the high polarization of the C=O group, the CH_2 groups behave like H-bond donors. Since the carbonyl oxygen is a great H-bond acceptor, there is a possibility of a true H-bond formation between the CH_2 and C=O groups (these interactions are labeled in Fig. 5 as CH-formyl). The last type of interaction is even more striking, i.e., DFT calculations indicate that the CH_2 group can be electrostatically attracted by the π -ring.

In the next step, we calculated IR spectra for the five most stable aldehyde dimers. The average spectrum was obtained by applying Boltzmann weights to each dimer calculated for $T = 293\text{ K}$, and it was compared with that of a reference dimer lacking strong interactions between the formyl and methylene groups (Fig. S8). The formyl-formyl and CH_2 interactions lead to the band shifts occurring in the $1750\text{--}1700$ and $3000\text{--}2700\text{ cm}^{-1}$ wavenumber regions. The rise of dominating interactions noted in the DFT system can be compared to the effect caused by the temperature decrease in the IR experiment. Two major band shifts observed in FT-IR spectra, i.e., the red shift in the $1750\text{--}1700\text{ cm}^{-1}$ region and the blue shift in the $2850\text{--}2700\text{ cm}^{-1}$ region, which are characteristic of formyl group vibrations, were confirmed by DFT calculations. What is more interesting, the calculations have shown that in the $2850\text{--}2700\text{ cm}^{-1}$ region, where the formyl C-H vibration is observed, higher shifts are noted for the dipolar interaction than for the $n\text{-}\Pi^*$ one, where

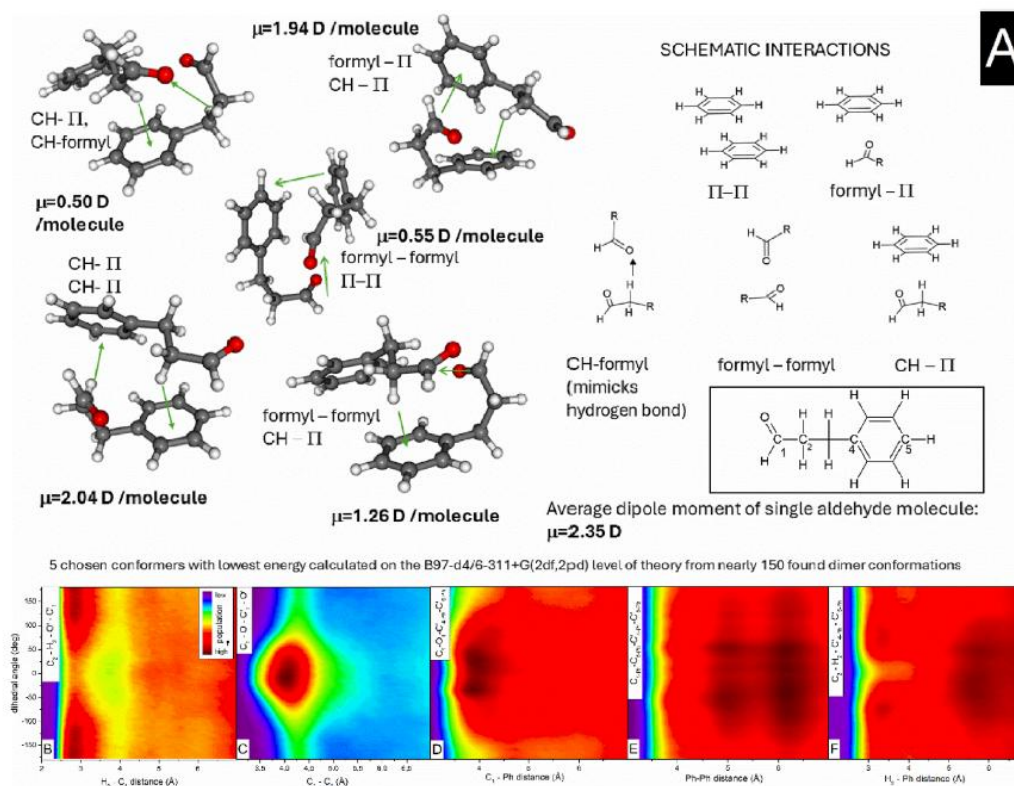


FIG. 5. Results of quantum and MD calculations for 3P1Pal. In panel (a), all the most stable dimers of aldehyde molecules and a variety of dominating interactions are shown. At the bottom of the figure, in panels (b)–(f), all the main interactions between aldehyde molecules are depicted on the RDF/DDF maps. For each type of interaction, the angles and average distances are shown: (b) CH₂-O, (c) formyl-formyl, (d) formyl-phenyl ring, (e) phenyl-phenyl π -stacking, and (f) CH₂-phenyl.

formyl groups need to be oriented parallel to each other. Hence, these computations indicated that the shifts of bands related to the vibrations of the formyl moiety are connected to the dipolar interactions rather than the formation of H-bonds.

As the studied system is very complex, all the mentioned interactions were tested in the bulk system of 1000 molecules at the two temperatures (298 and 233 K) and a pressure of 1 bar. From the analysis of molecule trajectories, structure factors, partial structure factors, and distribution functions (radial and dihedral) were constructed and plotted. Distribution function maps were plotted as RDF (radial distribution function) vs DDF (dihedral distribution function), which were defined for each type of interaction separately. In panels (b)–(f) of Fig. 5, all five interactions identified earlier in DFT studies were visualized in the MD trajectory. In Fig. 5(b), H-bonds between the CH₂ and C=O groups are present. As one can

see, the dihedral angle is close to -180° and 180° , which means that these bonds behave like typical H-bonds, where the C-H...O angles are close to linear but with a certain distribution ($\pm 30^\circ$). The average distance between H and O atoms is ~ 2.8 Å, and the average total H-bond distance from C to O equals 3.8 Å. The second major interaction in the system is attraction between the formyl groups [Fig. 5(c)]. MD simulations indicate that in the bulk system, the orientation of planar C=O groups is close to the parallel one, which suggests that the n- Π^* attraction mechanism is dominant. The next observed interaction between 3P1Pal molecules is π -stacking. As shown in Fig. 5(e), the maxima in the map for the phenyl-phenyl distance of 5 Å correspond to the dihedral angles in the range from -60 to $+60$, which means that there is a portion of parallel and T-shaped orientations, but with the angles between rings close to 50° – 60° . Mixed interactions between the carbonyl

C=O group and phenyl rings are presented in Fig. 5(d), where the studied groups tend to achieve parallel orientation (close to 0°). The most exotic interaction between the CH₂ and phenyl ring has been shown in Fig. 5(f). As can be observed, there are very weak maxima at a distance of H-phenyl equal to 3.5 Å and perpendicular orientation (90°). Although such interactions can be found in a molecular dynamics run, they are very weak.

In addition, MD simulations carried out at $T = 233$ K allowed us to verify the origin of the additional shoulder [denoted as a blue arrow in Figs. 3(a) and 3(b)] detected on the structure factor diagram constructed for aldehyde at this T . It turned out that both experimental and theoretical data are in almost perfect agreement. One can also add that the experimentally determined density agrees well with the one obtained from MD simulations [within a few percent; $d_{\text{exp}} = 1010.39$ g/cm³ (298 K) and $d_{\text{exp}} = 1067.25$ g/cm³ (233 K) vs $d_{\text{MD}} = 0.9809 \pm 0.0002$ g/cm³ (298 K) and $d_{\text{MD}} = 1.0473 \pm 0.0002$ g/cm³ (233 K) (both for $p = 1$ bar)]. What is more, the change in this parameter measured at both temperatures ($T = 298$ K and $T = 233$ K) is very similar to that derived from the experiment.

It was earlier stated that the new peak originates from the interacting groups at a distance equal to 4.4 Å. Based on the literature data obtained for some alcohols, it was proposed earlier in this paper that it may originate from the repeating phenyl π - π units in the aldehyde. However, if one takes a closer look at the RDF-DDF maps in Fig. 3, the average distance between phenyl rings is much higher than 3.3 Å, i.e., ~ 5 Å. Only two mapped interactions fit this distance criterion. The first one is the formyl-formyl interaction, and the second one is the formyl-phenyl ring interaction. The formyl-formyl attraction is dominant in the system. Thus, in both temperatures, 298 and 233 K, it is similar in terms of the strength. The formyl- π -ring interaction is much weaker, and in consequence, it is more temperature-dependent. Therefore, the formyl- π -ring attraction is probably responsible for the additional shoulder on the structure factor at lower temperature. In Fig. S9 of the supplementary material, a direct comparison of partial radial distribution functions was presented as 2D diagrams. In panel (a), it can be seen that there is a visible excess wing in the vicinity of a distance equal to ca. 3.5 Å at a temperature equal to 233 K. In panel (b), different partial RDFs were compared to give insight into which interactions are mostly associated with this additional peak. It was confirmed that it is related mostly to the formyl-formyl interactions (the highest peak). It was also noted that the appearance of the excess wing on the RDF for 3P1Pal after lowering the temperature to 233 K may be related to the increasing role of the CH₂...O=CH-bonds.

MD simulations enabled us to find that the dominating forces causing the formation of dimers in the studied system are (i) the attraction between formyl groups and (ii) the CH₂...O=CH-bonds. Moreover, such interactions can be found in every aldehyde, as they are universal. In addition to π - π stacking, the formyl- π and CH₂- π interactions can stabilize dimers and may elongate dimer lifetime but are not deciding forces about the geometry of the cluster.

Having the association pattern in aldehyde well addressed, in the next part of this paper, we would like to focus our attention on the molecular origin of the Debye process observed in dielectric loss spectra of this compound. To start the discussion, one can hypothesize that the Debye mode is the orientational relaxation of the molecular dimers or even higher domains. There is strong evidence, both theoretical and experimental, suggesting that such a scenario

is probable. In the aldehyde, there is a compensation of dipole moments in dimeric complexes (2.35 D in a single molecule due to a highly polarized C=O group vs 1.10–2.00 D in dimers bonded via the formyl group), which is confirmed experimentally for this system by the calculated Kirkwood factor of $g_k < 1$. On the other hand, the situation is quite the opposite with alcohol. The average dipole moment of 3P1Pol (1.45 D) is smaller than the dipole moment of higher mers (2.35 D for the dimer), which stays in agreement with the Kirkwood factor of $g_k > 1$. This can explain the difference in dielectric strength of the Debye mode in both systems. To test this hypothesis, we performed additional calculations and analyses of long 20 ns molecular dynamics trajectories at 233 K. Reorientational dynamics were studied by utilizing the vector between the carbon and oxygen atoms of the formyl (aldehyde) and hydroxyl (alcohol) groups, representing the direction of the molecular dipole moment. Time-resolved reorientation was detected by calculating the autocorrelation function of the second Legendre polynomial $P_2(\cos \theta)$. This function is commonly utilized in dielectric relaxation studies, as it exclusively relies on the angle between the initial and current dipole orientation and does not respond to the dipole vector inversion. The analysis yielded a reorientational time of 6.4 ns for the aldehyde and 3.6 ns for the alcohol. These values are counterintuitive at first sight, as the H-bonds are stronger than the weak formyl-formyl interactions. Having this in mind, one can suppose that such a long reorientational time indicates the existence of larger domains in the case of aldehyde molecules. To further study this phenomenon, dimer autocorrelation function (DCAF) and Voronoi tessellation-based domain analysis (DOMA) were additionally performed. From the DCAF analysis, we obtained the lifetime of domain-level dimers. In aldehyde dimers, it was found to be equal to 1.6 ns, while for the H-bonded dimers of alcohol, it was equal to 832 ps (0.8 ns). However, the more sophisticated is DOMA analysis, which gives insight into the domain distributions, topology of domains, and their dynamics. Additional computations within the framework of this model enabled us to find that aldehyde domains reach volumes up to ~ 5000 Å³, while alcohol domains are significantly smaller, limited to ~ 2000 Å³. The DOMA analysis indicated that the dominating domain unit in alcohol is a dimer, while in aldehyde, it is a tetramer or even a pentamer (40 vs >100 Voronoi cells). Despite the fact that formyl interactions are weaker than H-bonds in alcohol, formyl interactions are not limited to the linear geometry. The dipole-dipole and n - π^* interactions between formyl groups can occur at different geometries, and they are not linear like H-bonds. The angles between C=O vectors in two neighboring molecules can vary up to $\pm 60^\circ$. This geometric flexibility is the reason for the possible formation of larger domains in aldehyde despite the weaker attraction forces between formyl groups. The next parameter we have calculated is the isoperimetric quotient (IQ), which tells about the topology of the entire domain. The IQ parameter close to 1.0 means that the domain is compact, highly ordered, and spherical. In aldehyde, IQ values achieve 0.82, while in alcohol, this parameter rarely exceeds 0.77. Although these parameters are similar for both compounds, the domains in the aldehyde are slightly more compact.

These results indicate that, unintuitively, aldehyde molecules form larger, longer-lived, and spatially coherent domains in contrast to smaller, transient H-bonded clusters in alcohol. This observation, derived from the MD simulations, may help us to understand the

molecular origin of the D-process observed in loss spectra of aldehyde and alcohol. If we assume that the reorientational dynamics of the domain is responsible for this unique polarization decay in both systems studied herein, one can easily find that at a given temperature, this relaxation should be slower in alcohol, which is not the case. However, when we renormalize τ_D vs τ_α (which accounts for the reorientational time of the single molecules), it can be easily determined that in such a representation, there is much greater timescale separation of both processes in aldehyde than in alcohol. Consequently, at isochronal (isoviscosity) conditions, the Debye process is slower in the aldehyde (Fig. S1 of the [supplementary material](#)). Having this in mind, one can postulate that the exponential polarization decay in the former compound arises from the sparse but stable dipolar domains, while in the latter one, faster dipolar fluctuations dominate due to dynamic H-bonding and a smaller domain size. Nevertheless, one should point out that differences in the relaxation times of the domains in both studied systems do not mimic the ones observed in the experiment at a given temperature. This is probably due to different timescales of the MD simulations and the experiment.

Finally, one should also comment that DFT computations enabled us to explain the value of the Kirkwood factor for aldehyde, which is smaller than unity. It turned out that dimers present in the investigated systems have lower dipole moments than monomer units. Consequently, the measured static permittivity is smaller with respect to the value that can be calculated based on a dipole moment of the isolated molecule. A completely different situation is noted in alcohol, where an increasing number of monomeric units increases the overall dipole moment of the self-assemblies, contributing to the high static permittivity and g_k .

IV. CONCLUSIONS

In this paper, we have investigated dielectric, structural, and thermal properties as well as association patterns of molecules in the two glass formers, namely, 3-phenyl-1-propanol and 3-phenyl-1-propanal. Importantly, in the dielectric loss spectra of alcohol and aldehyde, we detected a Debye (D)-process, which is a fingerprint of self-assembly. It was found that the dynamical properties of this mode, such as dielectric strength and time scale separation from the structural relaxation, are much different between these compounds, indicating a strong variation in their association pattern. Further diffraction and infrared experimental investigations enabled us to conclude that, as expected, H-bonds play a key role in the association in the alcohol, while a much more complicated and less clear picture was found in the aldehyde. To gain deeper insight into this issue, DFT computations complemented by the MD simulations were carried out at two different temperatures for 3P1Pal. Collected data revealed that there are mainly dimeric associates in 3P1Pal, where molecules are connected via different kinds of weak intermolecular dipole-dipole interactions as well as π -stacking contacts (most likely the formyl- π - π ring attraction), which are reflected as an additional shoulder in the structure factor appearing for scattering vector around $1.9 \text{ \AA}^{-1}$ at lower temperatures. Moreover, these calculations indicated the formation of very specific H-bonds between methylene groups neighboring the formyl moiety and the carbonyl units that have not been reported or considered before. Moreover, the

collected data enabled us to claim that various dynamical properties of the D-process in alcohol and aldehyde might be related to the different sizes and the lifetime of the associates in both systems. Finally, based on the computations of the dipole moment of the single molecule and nanoassociates, we were able to explain the low and high values of g_k in aldehyde and alcohol, respectively, as well as to propose a molecular mechanism responsible for the presence of D-relaxation in the loss spectra. It was postulated that it can be assigned to the reorientational relaxation of formyl (aldehyde) and H-bonded (alcohol) clusters. We believe that the data presented in this paper will help to better understand intermolecular interactions and association schemes in aldehydes in a wide range of temperatures in the highly viscous regime.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) contains experimental details and additional figures, including the relaxation times of 3P1Pal and 3P1Pol compared to that of IBU, ATR-FTIR and Raman spectra of 3P1Pal measured at room temperature, temperature-dependent FTIR and Raman spectra of 3P1Pal measured under cooling, temperature dependence of the integrated intensities of selected FTIR and Raman bands of 3P1Pal measured under cooling, comparison of FTIR and Raman spectra of 3P1Pal measured at 293 and 157 K, calculated DFT spectra for the lowest energy dimers and the reference dimer of aldehyde, and comparison of radial distribution functions for 3P1Pal. Additional [supplementary material](#) files: Specific interactions and mechanisms of association in highly viscous aldehyde 3-phenylpropanal.

ACKNOWLEDGMENTS

This research was funded in whole by the National Science Center (Poland), Grant Number: Opus 24 No. 2022/47/B/ST4/00236. For the purpose of Open Access, the author has applied a CC BY 4.0 public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

A. Krishna Sudhakaran Nair Valsala Kumari: Data curation (equal); Formal analysis (lead); Investigation (equal); Writing – original draft (lead). **B. Hachula:** Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **M. Tarnacka:** Investigation (equal). **E. Kamińska:** Investigation (equal); Writing – original draft (equal). **J. Grelska:** Investigation (equal). **T. Lamrani:** Investigation (equal). **K. Jurkiewicz:** Formal analysis (equal); Investigation (equal). **P. Włodarczyk:** Formal analysis (equal); Investigation (equal); Writing – original draft (equal). **K. Grzybowska:** Investigation (equal). **K. Kamiński:** Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supplementary Material

**Specific interactions and mechanism of association in highly
viscous aldehyde 3-phenylpropanal**

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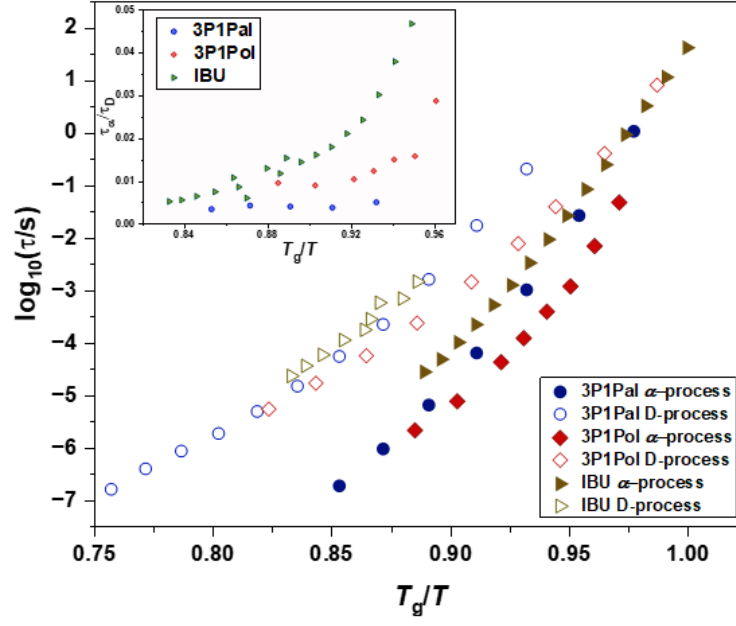


Fig. S1. (a) The relaxation times of α - and D-process in 3P1Pal compared with those of ibuprofen (IBU)¹ and 3P1Pol². The inset shows the time scale separation of α - and D-process in the examined systems.

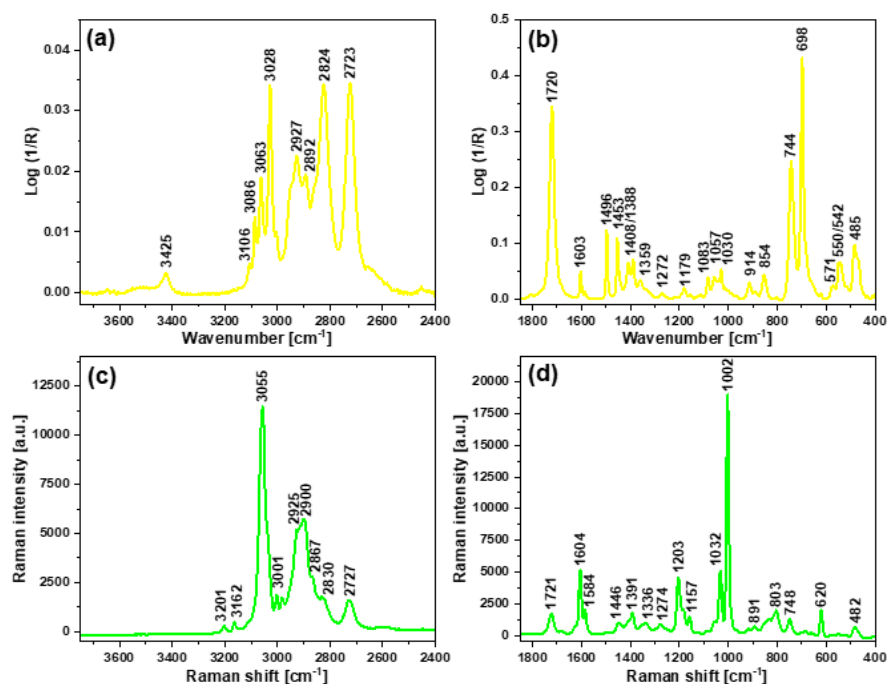


Fig. S2. ATR-FTIR (a,b) and Raman (c,d) spectra of 3P1Pal measured at room temperature in the spectral ranges of (a,c) 3750-2400 cm^{-1} and (b,d) 1850-400 cm^{-1} .

As shown in Fig. S2, FTIR and Raman spectra of 3P1Pal exhibit the group of intense peaks in the 3200-3000 cm^{-1} region corresponding to the asymmetric and symmetric aromatic C-H stretching vibrations of the phenyl ring (FTIR: 3106, 3086, 3063, and 3028 cm^{-1} ; Raman: 3201, 3162, 3055 and 3001 cm^{-1}), as well as the series of the bands in the 3000-2850 cm^{-1} range assigned to the CH_2 (methylene) stretching vibrations (FTIR: 2927, and 2892 cm^{-1} ; Raman: 2925, 2900, and 2867 cm^{-1}). Moreover, there are two peaks (FTIR: 2824 and 2723 cm^{-1} , Raman: 2830 and 2727 cm^{-1}) in the aldehydic C-H stretching range. These two bands are induced by the interaction between the fundamental vibration and the overtone vibration. Such interaction is known as Fermi resonance, i.e., the coupling of aldehyde C-H fundamental stretching vibration (near 2790 cm^{-1}) and the first overtone bending vibration (near 2780 cm^{-1}), which appears at 1380 cm^{-1} , produces two new modes of vibration with frequencies higher and lower than that observed when interaction is absent³. A band located at 1720 cm^{-1} (FTIR) and 1721 cm^{-1} (Raman) is assigned to the stretching vibration of the carbonyl group

(C=O). As reported in the literature⁴⁻⁶, the signals located at 1603 cm⁻¹ (FTIR) as well as at 1604 and 1584 cm⁻¹ (Raman) are associated with the ring C=C stretching vibrations, whereas the C-H bending vibrations of the propyl and aldehyde groups are observed in the 1500–1325 cm⁻¹ range. Thus, the 1496 and 1453 cm⁻¹ peaks (FTIR) are associated with the CH₂ scissoring and wagging vibrations. The bands at 1408, 1388, and 1359 cm⁻¹ originate from the in-plane C-H rocking vibrations⁶. A signal at 1203 cm⁻¹ in the Raman spectrum is related to the mixed C-H bending and aromatic in-plane C-H deformation vibrations⁶. The bands located at 1083 and 1057 cm⁻¹ (FTIR) are due to the C-C and C-O stretching vibrations. The doublet of bands at 1057 and 1030 cm⁻¹ originates from the mixed vibrations, i.e., the CO stretching, CH₂ asymmetric deformation, CH₂ rocking, ring bending deformation (1057 cm⁻¹), and CH₂ rocking, ring bending deformation, ring breathing (1030 cm⁻¹). A very intense signal at 1002 cm⁻¹ in the Raman spectrum corresponds to the ring breathing and ring bending deformation. A medium intensity band observed at 914 cm⁻¹ in the FTIR spectrum is due to the ring C-H wagging vibrations. A signal at 854 cm⁻¹ (FTIR) corresponds to the C-H deformation vibrations of the formyl group. The 744 cm⁻¹ and 698 cm⁻¹ bands (FTIR) and a peak at 620 cm⁻¹ (Raman) are assigned to the ring bending deformations⁴⁻⁶. A doublet observed at 550 and 542 cm⁻¹ in the FTIR spectrum is associated with the ring and C-C deformation. The signals at 485 cm⁻¹ (FTIR) and 482 cm⁻¹ (Raman) are connected with the C-C-O bending and the ring deformation.

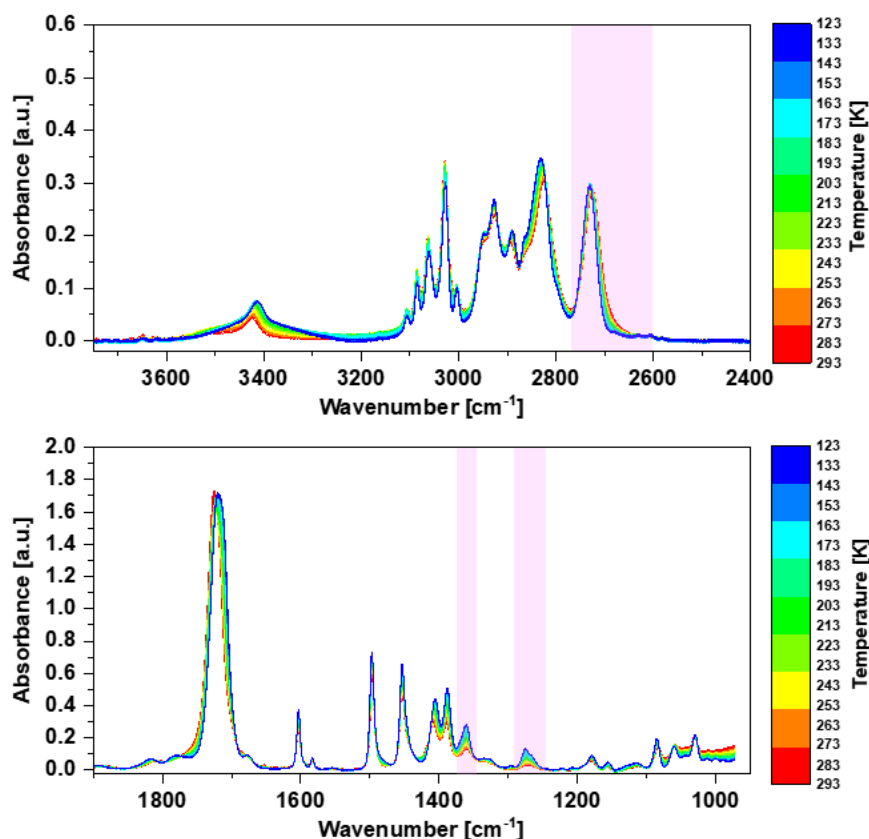


Fig. S3. Temperature-dependent FTIR spectra of 3P1Pal measured under cooling at a rate of 4 °C min⁻¹ in two wavenumber regions of (upper) 3750–2400 cm⁻¹ and (bottom) 1900–950 cm⁻¹. The spectral ranges analyzed in the plots have been highlighted.

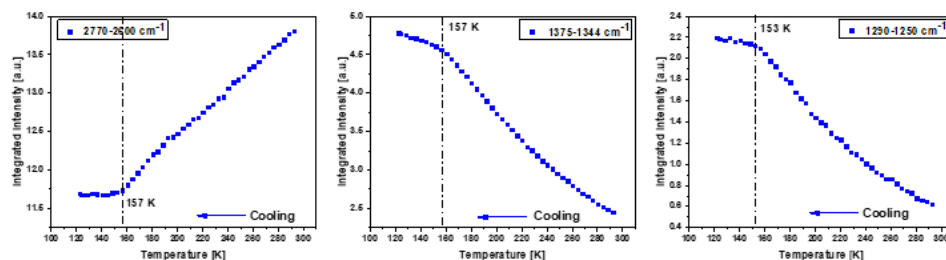


Fig. S4. Temperature dependence of the integrated intensity of selected FTIR bands occurring in the regions: 2770–2600 cm⁻¹, 1375–1344 cm⁻¹, and 1290–1250 cm⁻¹, measured for 3P1Pal under cooling.

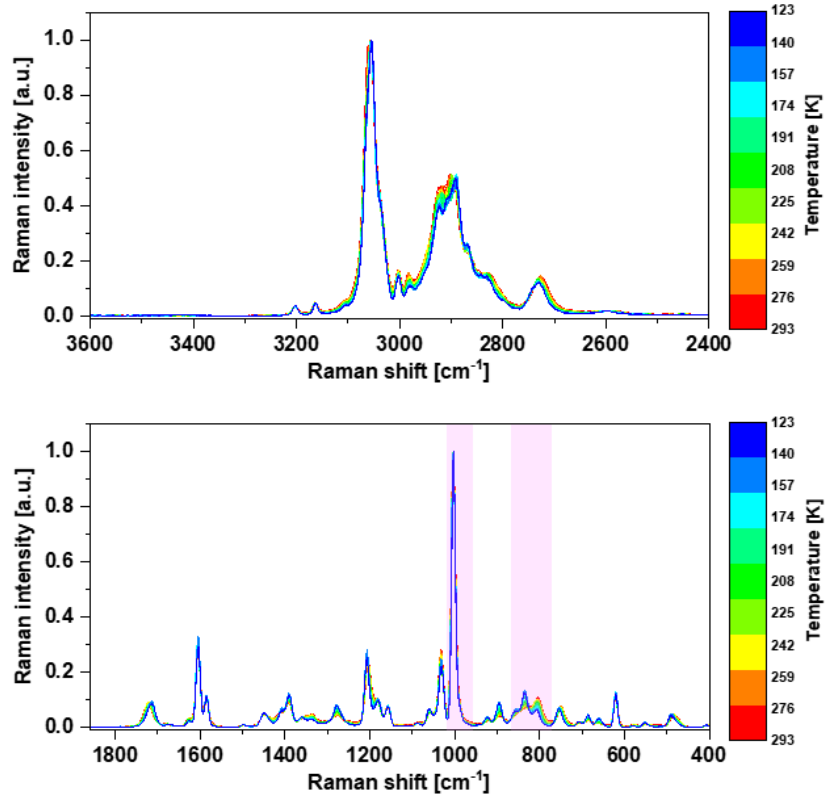


Fig. S5. Raman spectra of 3P1Pal measured under cooling, as indicated by the color-coded legend, at a rate of $4\text{ }^{\circ}\text{C min}^{-1}$, in two spectral regions of (upper) $3600\text{--}2400\text{ cm}^{-1}$ and (bottom) $1850\text{--}400\text{ cm}^{-1}$. The spectral ranges analyzed in the plots have been highlighted.

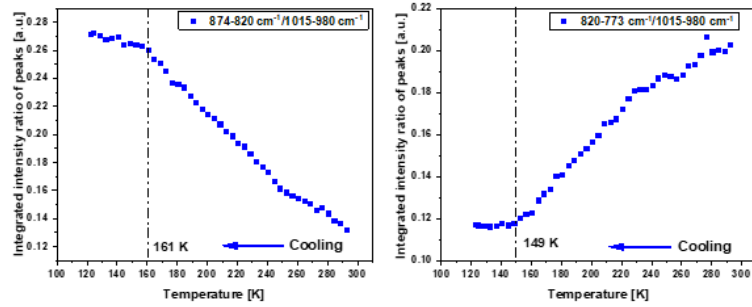


Fig. S6. The integrated intensity (I) ratio of Raman peaks of 3P1Pal occurring in the regions: (left) $874\text{--}820\text{ cm}^{-1}$ and $1015\text{--}980\text{ cm}^{-1}$ as well as (right) $820\text{--}773\text{ cm}^{-1}$ and $1015\text{--}980\text{ cm}^{-1}$, as a function of temperature.

S6

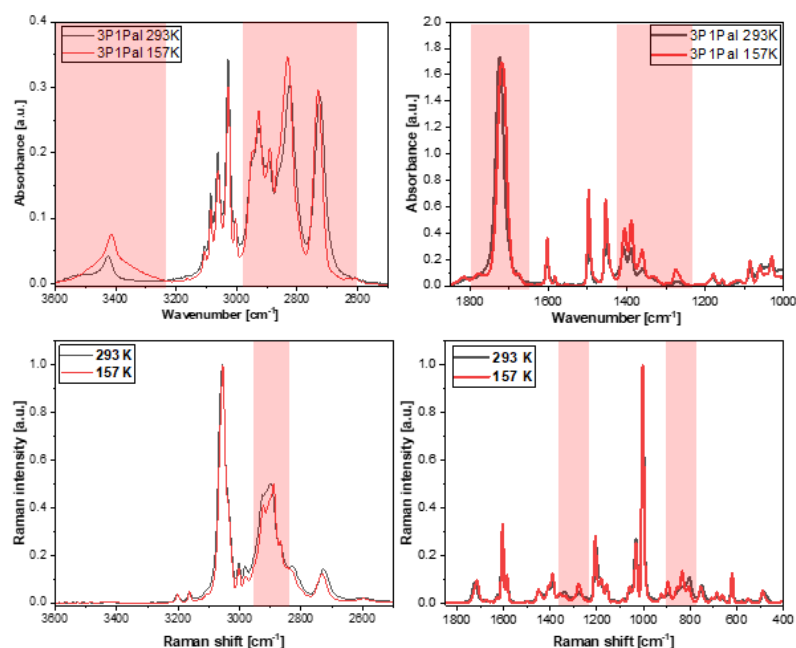


Fig. S7. Comparison of FTIR and Raman spectra of 3P1Pal measured at (black) 293 K and (red) 157 K in the spectral ranges of (left) 3600-2500 cm^{-1} and (right) 1850-1000 cm^{-1} (FTIR) as well as (left) 3600-2500 cm^{-1} and (right) 1850-400 cm^{-1} (Raman). The regions in which the most significant changes in the peaks' parameters occurred during cooling were highlighted.

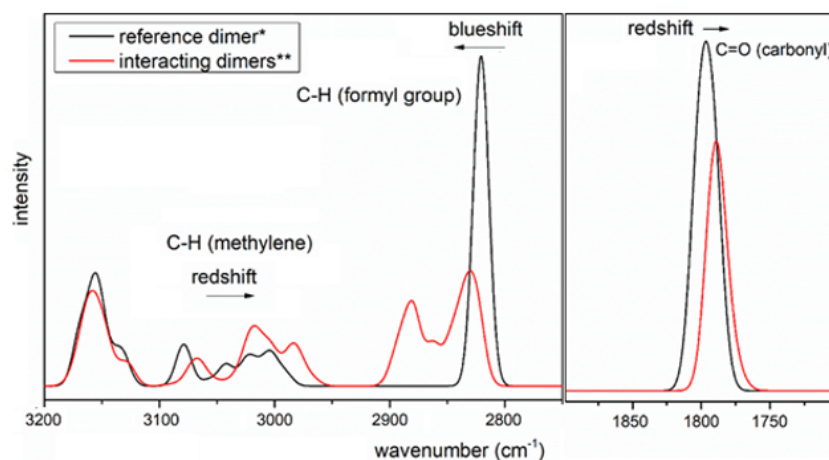


Fig. S8. Calculated DFT spectra for the lowest energy dimers (interacting dimers) and the reference dimer (without strong interactions). **The interacting dimer is an average spectrum of the 5 lowest energy dimers found by DFT calculations. *A reference dimer is a dimer without strong interactions in the formyl and CH_2 group region.

S7

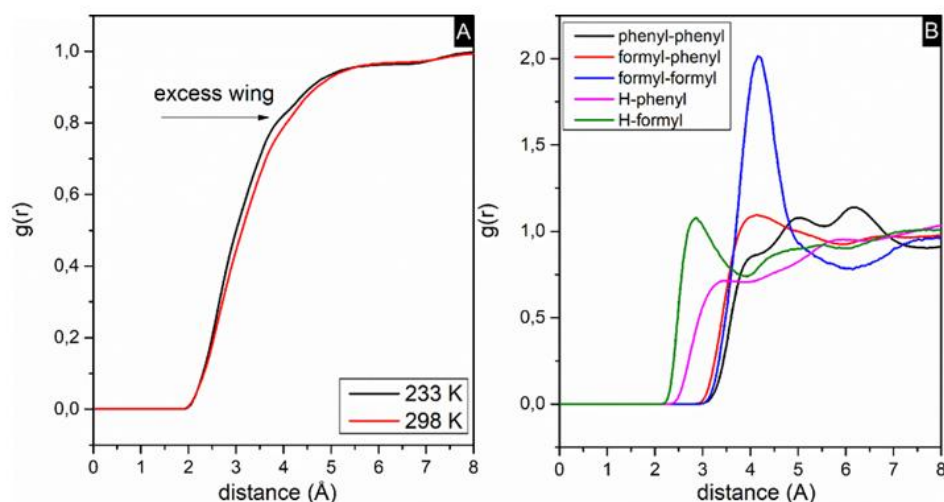


Fig. S9. Comparison of radial distribution functions for 3P1Pal. In panel A, a global RDF for two temperatures, i.e., 233 K and 298 K, has been shown. In panel B, partial RDFs for 3P1Pal have been compared.

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4.2. Article 2 (A2) Pressure-induced self-assembly in 3-Phenylpropanal: Distinct clustering via π -stacking and distorted Hydrogen bonds

Pressure-Induced Self-Assembly in 3-Phenylpropanal: Distinct Clustering via π -Stacking and Distorted Hydrogen Bonds

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Cite This: *J. Phys. Chem. Lett.* 2026, 17, 728–736

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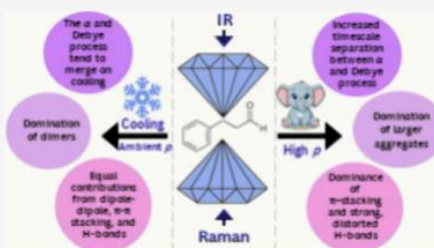
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ABSTRACT: This paper investigates the effect of high pressure on the dynamics, intermolecular interactions, and association mechanisms of 3-phenylpropanal (3P1 Pal). Dielectric investigations have revealed an unusual behavior of the Debye process at high compression, indicating a distinct clustering mechanism. Complementary Fourier Transform Infrared and Raman spectroscopy studies, supported by molecular dynamics simulations, have shown that, at high pressure, molecular clustering is dominated by π -stacking and strong, distorted hydrogen bonds, with larger and more compact aggregates, compared to those formed at low temperatures. Overall, high compression effectively tunes both dynamics and association patterns in 3P1 Pal, revealing key aspects of self-assembly in viscous molecular liquids.



All life on Earth can be viewed as an application of supramolecular chemistry, where noncovalent interactions, such as hydrogen bonding (H-bonding), ionic forces, hydrophobic effects, and van der Waals contacts, govern molecular self-assembly (the static self-assembly).^{1–3} These interactions determine the structure, function, and dynamics of biological molecules and various molecular systems such as supramolecular assemblies, micelles, vesicles, molecular machines, and nanomaterials.^{4,5} While most of the self-assembly occurs spontaneously, it can also be directed by external factors such as temperature (T), pressure (p), light, electric and magnetic fields, the nature of the solvent, or confinement in nanostructured/porous environments, influencing the material's structure and behavior (the dynamic self-assembly).^{6,7} Such directed self-assembly provides a promising path for the formation of advanced materials with novel optical, mechanical, and electrical properties.^{6,8,9}

High hydrostatic pressure (p) is a particularly powerful tool for controlling molecular association. Unlike temperature, which alters both thermal energy and volume of a system, p affects only the latter parameter, inducing precise changes in intermolecular distances.¹⁰ This can trigger/promote phase transitions and bond rearrangements, leading to changes in electronic structure, optical behavior, and thermal or electrical conductivity.^{11–13} Pressure can promote aggregation in various systems, including liquids, gases, and micelles. The studies on H-bonded hexane derivatives (2-ethyl-1-hexanol, 2-ethyl-1-hexylamine) and monohydroxy alcohols revealed that high compression enhances molecular aggregation and H-bond cooperativity, forming denser, more-ordered networks.^{14,15} In amines, such as 4-aminobenzonitrile and n -hexylamine,

moderate p induces H-bond rearrangements and stronger intermolecular interactions, facilitating p -driven self-assembly processes.^{16,17} In contrast, in proteins and other biomolecular assemblies, p often weakens hydrophobic contacts and promotes dissociation or unfolding by allowing water molecules to penetrate hydrophobic cores.¹⁸ However, the effect of p may be different when a tightly bound structure (e.g., disulfide bonds covalently stabilizing interdomain interactions) with few readily exposed nonpolar residues occurs. In such a case, p will cause a general compression of the structure, and unless the protein is otherwise perturbed (either thermally or through the addition of a chemical chaotropic reagent), it will maintain its compact conformation.^{19,20} In surfactant micelles in water, p up to about 150 MPa causes the dehydration of surfactant head groups and a collapse of the hydrophilic micelle shell (as observed in $C_{8}E_5$ micelles).²¹

Generally, high- p can drive both association and dissociation processes, which are particularly relevant for designing advanced materials and understanding the stability of biological macromolecules under extreme conditions. To date, most high- p studies have predominantly focused on systems stabilized by H-bonding, such as water, alcohols, amines,

Received: November 6, 2025
Revised: December 11, 2025
Accepted: December 30, 2025
Published: January 8, 2026



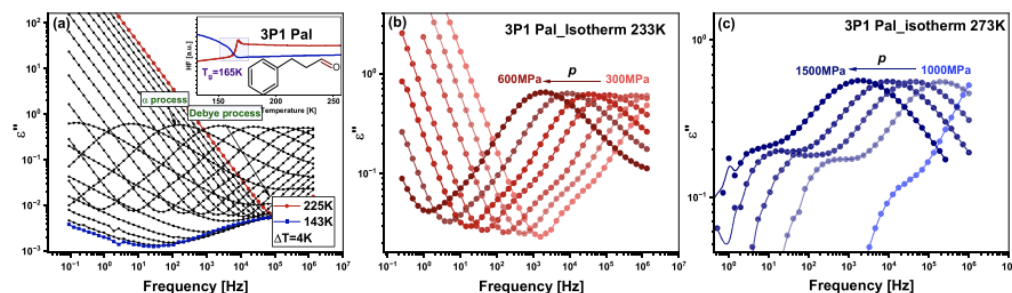


Figure 1. Representative dielectric loss spectra collected for 3P1 Pal (a) at ambient p and a T -range of 225–143 K, and (b, c) under isothermal conditions ($T = 233$ K and $T = 273$ K, respectively) under varying p . The inset in panel (a) shows the DSC thermogram obtained during both cooling and heating, as well as the chemical structure of 3P1 Pal.

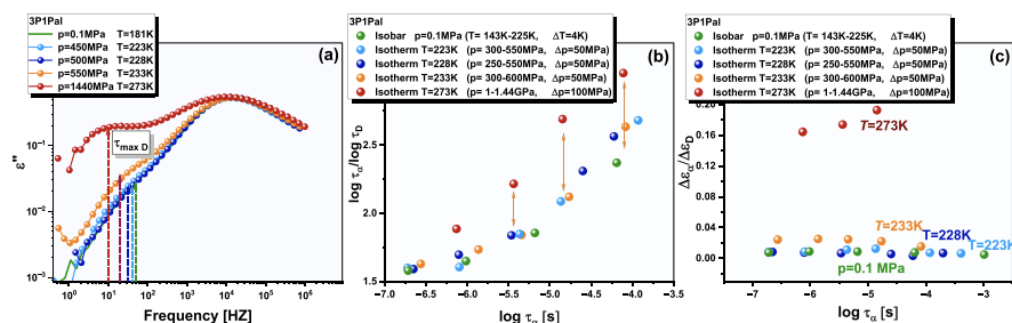


Figure 2. (a) Comparison of the shape of dielectric loss spectra obtained for 3P1 Pal under varying T , p conditions. The arrows indicate the maximum of the Debye (D) relaxation process. Panels (b) and (c) show the ratio of relaxation times of α - and D-process as well as the ratio of dielectric strengths, $\Delta\epsilon_D$ and $\Delta\epsilon_\alpha$, against the $\log \tau_\alpha$, respectively. The double-headed arrows in panel (b) is used to highlight the difference in the shift.

proteins, or nucleic acids,^{14,15,22–25} whereas there is a noticeable lack of experimental investigations on the effect of compression in systems dominated by dipole–dipole or π – π stacking interactions, like aldehydes. Previous papers have mainly addressed the polymerization of simple aliphatic aldehydes (*n*-butyraldehyde, isobutyraldehyde, crotonaldehyde, and propionaldehyde) under high- p ; however, no experimental studies have explored how compression affects the structure, intermolecular interactions, electronic, optical, and transport properties of aliphatic or aromatic aldehydes.^{26–28} Here, we examine the molecular dynamics and intermolecular associations of 3-phenylpropanal (3P1 Pal) under high- p conditions using Fourier Transform Infrared (FTIR), Raman, and Broadband Dielectric Spectroscopy (BDS), supported by Molecular Dynamics (MD) simulations, to gain deeper insight into p -induced structural changes, molecular organization, and aggregation behavior of the studied aromatic aldehyde.

At first, Differential Scanning Calorimetry (DSC) measurements were performed to investigate the thermal behavior of 3P1 Pal. We found that the sample can be easily supercooled without crystallization, indicating good glass-forming properties. The DSC trace exhibits only a single step-like change in heat capacity, corresponding to the glass-transition temperature (T_g), with no additional exothermic or endothermic events associated with crystallization or melting, as shown in

the inset of Figure 1a. Having established the glass-forming ability of the examined system, we measured the dielectric loss spectra (i.e., frequency (f) dependences of ϵ'') at ambient p over a wide T range upon cooling using BDS. The representative spectra are presented in Figure 1a. As seen in the figure, the $\epsilon''(f)$ dependences display three distinct processes: a structural α -relaxation, a unique and slower Debye-type relaxation, and a low-frequency dc-conductivity contribution. Upon cooling, both the α and Debye (D) relaxation peaks systematically shift toward lower frequencies (f), reflecting the pronounced slowing of molecular mobility as the glass transition is approached. The most intriguing aspect of these spectra lies in the presence of the D-process, a characteristic feature typically observed in associating liquids such as water, monohydroxy alcohols, amines, etc., which is attributed to their H-bonding ability.²⁹ Herein, one can add that aldehydes are considered weakly interacting systems, and their ability to form effective H-bonds is questioned. Nevertheless, recent investigations combining BDS, FTIR, and computational analysis suggest that the D-relaxation in these systems arises from supramolecular structures formed through various intermolecular interactions, including dipole–dipole coupling, π – π stacking, and weak H-bonding interactions between methylene groups adjacent to the formyl unit and the carbonyl moiety. Among these, the latter

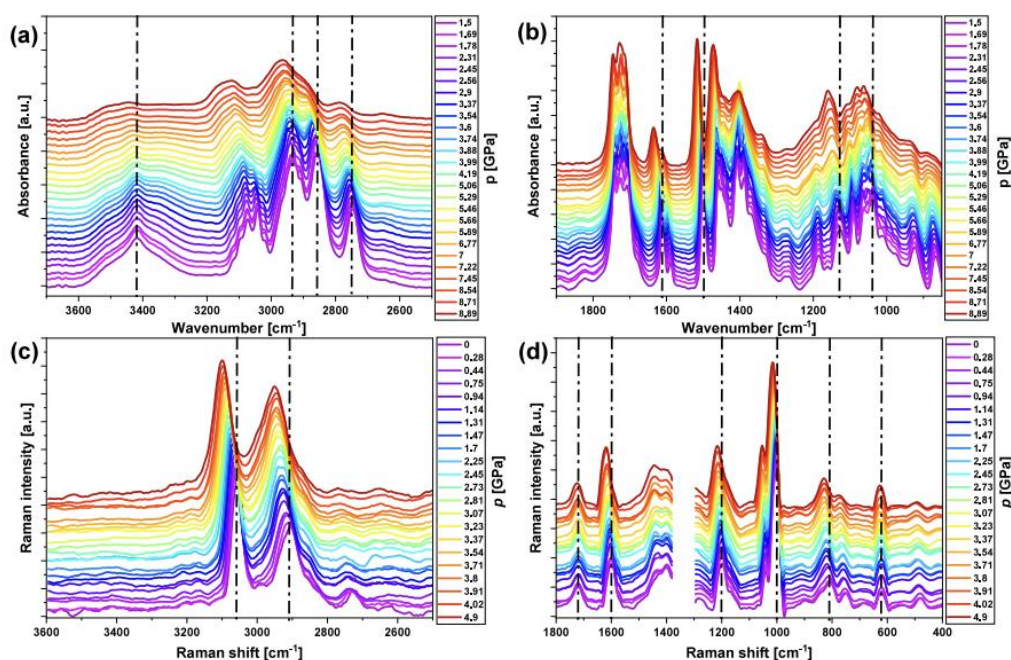


Figure 3. Pressure-dependent (a, b) FTIR and (c, d) Raman spectra of 3P1 Pal measured at room temperature (RT) in the wavenumber regions of (a) 3750–2500 cm^{-1} , (b) 1900–850 cm^{-1} , (c) 3600–2500 cm^{-1} , (d) 1800–400 cm^{-1} . The region in the Raman spectrum of 3P1 Pal that was disturbed by the bands of the diamond (1380–1300 cm^{-1}) was removed for clarity.

interaction is particularly noteworthy, as it represents a unique and unexpected mode of association in such systems.³⁰

Having in hand the dielectric data at ambient p , it was interesting to observe how the dynamics of both α - and D -processes evolve with pressure and what we can learn about the change in the interaction pattern in this compound. Hence, we performed the dielectric studies under high p under different isothermal conditions. Figures 1b and 1c display the isothermal dielectric loss spectra recorded under varying compressions at 233 and 273 K, respectively. In both cases, increasing p causes a systematic shift of the α - and D -relaxation toward lower f , signifying a slowdown in molecular mobility due to reduced free volume and strengthened intermolecular interactions. The relaxation strength ($\Delta\epsilon$) remains nearly constant with p , implying a lack of crystallization upon compression.

To get more detailed information about the relaxation properties of the system studied, the data presented in Figure 1 were fitted using the Havriliak–Negami (HN) function with the dc-conductivity term:

$$\epsilon(\omega)'' = \frac{\sigma_{\text{dc}}}{\epsilon_0\omega} + \text{Im} \sum_{i=1}^2 \left(\epsilon_{\infty} + \frac{\Delta\epsilon_i}{[1 + (i\omega\tau_i)^{\alpha_i}]^{\beta_i}} \right)$$

where $\sigma_{\text{dc}}/\epsilon_0\omega$ defines the dc-conductivity contribution, ϵ_{∞} is the high- f permittivity limit, $\Delta\epsilon$ is the dielectric strength, ω is the angular frequency, τ corresponds to the HN relaxation time, and the exponents α and β are the shape parameters.³¹ The relaxation times (τ_{α} and τ_{D}) obtained from the fitting,

plotted versus temperature, are shown in Figure S1(a) in the Supporting Information (SI). In turn, pressure dependences of τ_{α} and τ_{D} for all isotherms are presented in Figure S1(b). Figure 2a illustrates the comparative analysis of the $\epsilon''(f)$ measured at various combinations of T and p , superimposed at equivalent isochronal conditions ($\tau_{\alpha} = \text{constant}$). Here, we have an intriguing result that, up to 500 MPa, there is almost a perfect superposition of the D - and α -processes, in terms of both relaxation times and dielectric strengths. However, surprisingly, above 500 MPa, we observe a systematic and significant increase in the amplitude of the D -process, as well as a separation in the time scale of both relaxation modes. These changes are prominent at very high p (~1400 MPa). To quantify the observed effect, we analyzed and plotted the ratio of relaxation times of α and D -processes, as well as the ratio of their $\Delta\epsilon$ against the $\log \tau_{\alpha}$ (for the data obtained under varying thermodynamic conditions, see Figures 2b and 2c, respectively). The results clearly highlight the emergence of an unexpected behavior above 500 MPa. Up to this p value, the liquid exhibits nearly identical trends, indicating comparable dynamic responses. However, beginning at $p = 550$ MPa, a systematic increase in the ratio becomes evident, which intensifies dramatically at the highest investigated p value (1400 MPa). This finding mimics, in some way, the behavior of strongly associating 2-ethyl-1-hexanol at high compression. As shown by Pawlus et al., density scaling was found to hold up to approximately 500 MPa but failed at higher p values in this compound.³² They attributed this breakdown to a p -induced change in the H-bonding pattern of the alcohol at very high

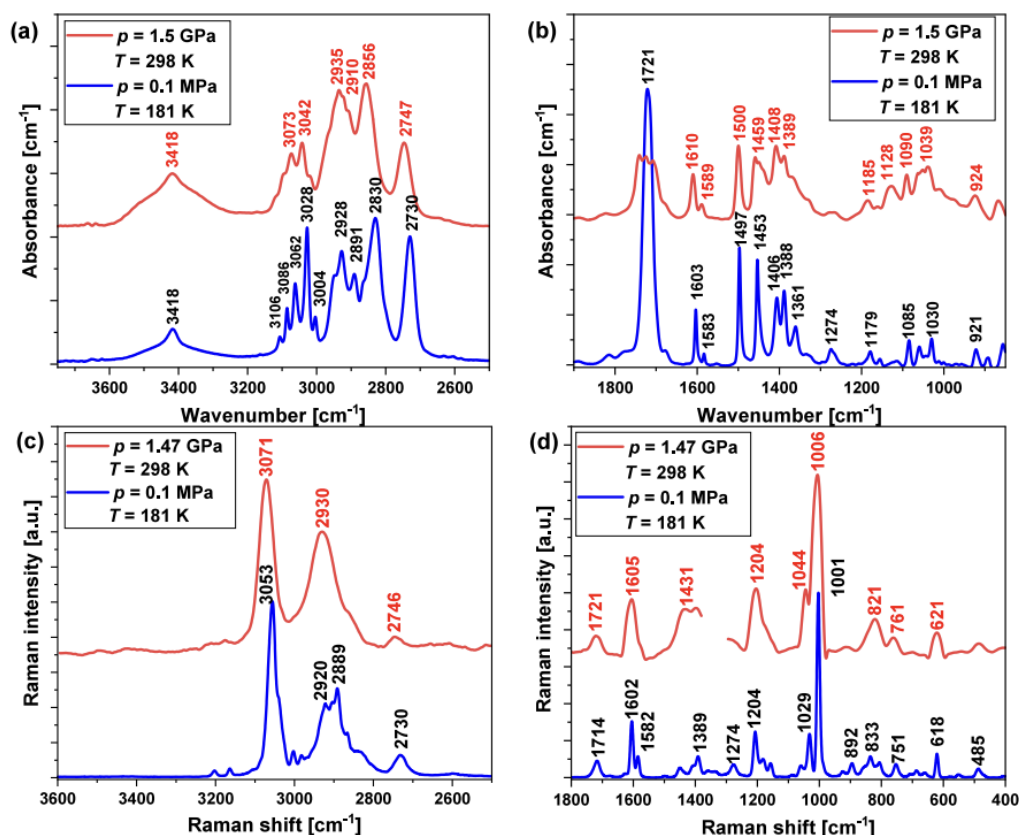


Figure 4. Comparison of (a, b) FTIR and (c, d) Raman spectra of 3P1 Pal measured at (blue) 181 K and (red) 1.5 GPa in the spectral ranges of (a) 3600–2500 cm⁻¹, (b) 1850–1000 cm⁻¹ (FTIR), and (c) 3600–2500 cm⁻¹ and (d) 1850–400 cm⁻¹ (Raman).

compression. It is also worth noting that, to date, various studies have demonstrated that, in the case of associating liquids like monohydroxy alcohols (MA), the amplitude of the D-relaxation either remains constant, increases, or decreases with increasing p .³³ This behavior depends on the position of the OH units in the molecular skeleton and the type of architecture of the associates. It is explained that compression influences the balance between ring (preferred in secondary and tertiary alcohols) and linear (characteristic of the first-order MA) aggregates, which manifests in dielectric spectra as a change in the amplitude of the D-mode. Furthermore, the time scale separation between the structural (α) and D-processes is generally found to diminish under compression, leading to their convergence at very high pressures, especially in alcohols containing a terminal –OH group.^{34,35} Thus, overall, elevated p leads to a merging of relaxation time scales and variation in the amplitude of the Debye peak, signifying the fluctuation in the long-range dipolar correlations and a change in the architecture of the formed nanoassociates.^{33,36} The unexpected increase in the amplitude of the D-process and the growing separation of relaxation times of this mode, with respect to the α -process, are a unique behavior not previously

reported in the literature for associating liquids. That is why, to understand the molecular origin of such atypical behavior, complementary FTIR measurements supported by MD simulations were employed.

However, before presenting the results, the assignment of vibrational bands in the FTIR and Raman spectra of 3P1 Pal, recorded at room temperature (RT = 293 K), relative to the corresponding molecular motions, is provided in the SI (Figure S2). Briefly, as can be seen, the IR spectrum of 3P1 Pal at 293 K exhibits characteristic bands related to the stretching and bending vibrations of C–H and C=O groups, including the first overtone of the C=O vibration (~ 3415 cm⁻¹), aromatic C–H stretching (3050–3000 cm⁻¹), aliphatic C–H stretching (3000–2700 cm⁻¹), the C=O stretching (1725 cm⁻¹) and the ring C=C stretching vibrations (1603 cm⁻¹). Multiple bands occurring below 1500 cm⁻¹ are connected with the mixed C–H and H–C=O bending, as well as the C–C stretching and bending modes (for more-detailed assignments, see the SI). Having the assignment procedure done, we presented representative T - and p -dependent IR and Raman spectra measured during the cooling cycle (293–123 K) at ambient p

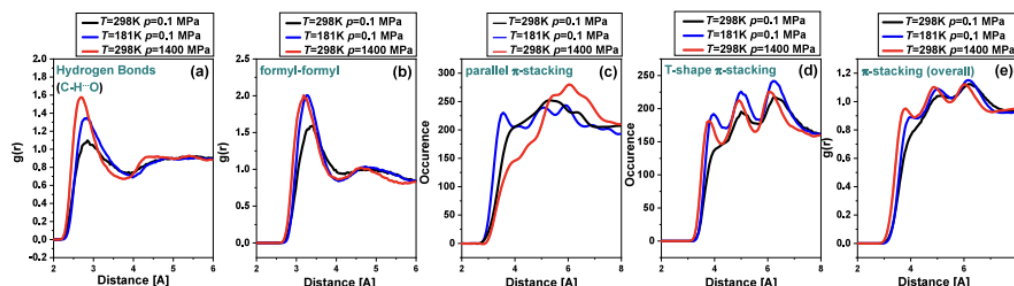


Figure 5. (a, b, e) Partial RDFs for H-bonds (H2–O1), formyl–formyl (C1–O1 pair), and π -stacking (ring–ring). In panels (c) and (d), the occurrence of parallel π -stacking versus T-shape π -stacking conformations was compared in all studied systems.

and at $T = 298$ K up to ~ 9 GPa (IR) and ~ 5 GPa (Raman) in Figures S3 and S4 in the SI, as well as in Figure 3, respectively.

Upon cooling to 123 K at $p = 0.1$ MPa, the aromatic C–H stretching and the skeletal C–C vibration bands in both IR and Raman spectra of 3P1 Pal remain nearly unchanged, showing only a minor shift due to thermal contraction and the associated increase in material density (Figures S3 and S4 in the SI). More pronounced changes occur in the C=O (1780 – 1680 cm^{-1}) and the aliphatic C–H (3000 – 2800 cm^{-1}) stretching vibration regions, where the shifts in band positions and increased intensities indicate the strengthening of C–H $\cdots$ O interactions and the formation of H-bonded aggregates at low T . Moreover, the $\nu_{\text{C=O}}$ band broadens as the T decreases, reflecting a more heterogeneous distribution of the H-bonding network. Herein, one can be briefly reminded that previous MD simulations have revealed the existence of at least three different intermolecular interactions between molecules of 3P1 Pal under these conditions, involving dipole–dipole forces and π -stacking, as well as extraordinary H-bonds formed between methylene groups neighboring the formyl unit and the carbonyl moiety.³⁰

The application of p causes distinct shifts of nearly all vibrational bands in the IR and Raman spectra toward higher wavenumbers (blue shifts). This effect arises from the compression of the liquid, which causes a reduction in the average interatomic distances and consequently an increase in the vibrational frequencies (Figure 3). Thus, the bands related to the aliphatic and aromatic C–H vibrations exhibit a noticeable blue shift and also broaden as p increases, due to different local environments (nonuniform packing). Surprisingly, the first overtone of the C=O vibration (~ 3415 cm^{-1}) exhibits no frequency shift under compression, instead showing only band broadening. Unfortunately, the carbonyl stretching band in the IR spectra (1780 – 1650 cm^{-1}) could not be analyzed due to saturation; however, it can be examined in the Raman spectra. Interestingly, the C=O vibration peak in Raman spectra, located at ca. 1720 cm^{-1} , seems to remain nearly unchanged in position during compression. This “rigidity” of the carbonyl moiety can suggest a compensatory effect: p -induced shortening and stiffening of the C=O bond (which would tend to blue-shift the vibrational frequency) is compensated by enhanced intermolecular H-bonding interactions upon compression (which tend to red-shift the frequency).

Since the dielectric data presented in Figure 2a revealed peculiar behavior of the D-process, suggesting changes in the

association pattern at high p , we decided to compare the IR and Raman spectra recorded under the same isochronal (isoviscosity) conditions, i.e., at 181 K ($p = 0.1$ MPa) and at 1.5 GPa ($T = 298$ K) (Figure 4). It can be observed that p has a much stronger influence on the spectroscopic properties—and, consequently, on the molecular structure and intermolecular interactions—than T . Indeed, the bands associated with the aliphatic C–H group vibrations of the aldehyde measured at 1.5 GPa are blue-shifted, relative to those recorded at 181 K (the formyl C–H stretching: $\Delta\nu = 17$ cm^{-1} , 2747 vs 2730 cm^{-1} ; $\Delta\nu = 26$ cm^{-1} , 2856 vs 2830 cm^{-1} ; the methylene C–H stretching: $\Delta\nu = 19$ cm^{-1} , 2910 vs 2891 cm^{-1}). Even larger shifts toward higher wavenumbers are observed for the bands assigned to the aromatic C–H vibrations when comparing the spectra measured at 1.5 GPa and 181 K ($\Delta\nu = 14$ cm^{-1} , 3042 vs 3028 cm^{-1} ; $\Delta\nu = 11$ cm^{-1} , 3073 vs 3062 cm^{-1} ; $\Delta\nu = 7$ cm^{-1} , 1610 vs 1603 cm^{-1} ; $\Delta\nu = 6$ cm^{-1} , 1589 vs 1583 cm^{-1}). This fact clearly suggests that, under high- p conditions, the contribution of intermolecular π – π interactions involving aromatic C–H groups becomes more significant. Importantly, no frequency shift of the C=O overtone band is observed in the IR spectra, and only a slight change in the C=O stretching peak position ($\Delta\nu = 7$ cm^{-1}) is detected in the Raman spectra when comparing the spectra measured at 181 K and 1.5 GPa. Thus, the blue shift of the C=O band measured at 1.5 GPa, relative to that at 181 K, suggests that high p significantly shortens the C=O bond length, which, in turn, affects the strength of the C–H $\cdots$ O H-bonds and consequently influences/changes molecular organization and the way of association of 3P1 Pal, compared to that observed at low T . To further investigate this hypothesis and gain a deeper understanding of the supramolecular organization of aldehyde molecules at high compression, we conducted MD simulations of 3P1 Pal under similar thermodynamic conditions.

MD simulations were carried out at elevated p ($T = 298$ K, $p = 1400$ MPa) and at atmospheric p and reduced temperature ($T = 181$ K, $p = 0.1$ MPa). Subsequently, the obtained data were compared. The system under ambient conditions ($T = 298$ K, $p = 0.1$ MPa) served as a reference. It should be mentioned that, in the previous studies of 3P1 Pal performed at ambient T and p , three major types of molecular interactions were identified.³⁰ The most dominant was the dipole–dipole interaction between two formyl groups, and two additional clustering forces were also recognized: (i) π – π stacking between phenyl rings and (ii) weak H-bonds formed between the H atom of the α -methylene group and the O atom of the

formyl group. Although, by applying high- p or by lowering T , the system density substantially increases, a much different situation is observed in the association pattern of the considered aldehyde. This can be clearly seen in Figure 5 by comparing the RDFs corresponding to all three interaction types.

At low temperature (181 K, 0.1 MPa), a pronounced enhancement of both π -stacking and H-bonding interactions is observed. The strongest π -stacking interaction, characterized by an inter-ring distance of about 4 Å, corresponds to a 90° orientation, indicating a T-shaped π -stacking motif. The parallel π -stacking pattern is suppressed, even in comparison to the sample measured at RT at $p = 0.1$ MPa. When comparing this result with that obtained at high p ($p = 1400$ MPa, $T = 298$ K), a different π -stacking pattern emerges. In this case, maxima appear at both 180° and 90° orientations. For the shortest ring-to-ring distance (~ 3.8 Å), both T-shaped and parallel π -stacking arrangements are present. Although H-bonds are enhanced in both systems (high- p and low- T), only in the low-temperature system, they adopt nearly linear, classical geometries. At high compression, H-bond angles vary broadly from 0° to 90°, indicating more distorted, nonclassical configurations (see RDF/ADF map in Figure S5 for details). RDF analysis for H-bonds in Figure 5a reveals that increasing p has a more significant effect on H-bond stability than decreasing T . Moreover, in all systems, strong dipole interactions exist between formyl groups. At ambient conditions, formyl–formyl dipole interactions primarily drive the clustering and determine the cluster geometry. At a low T (181 K), clustering is mainly governed by strong T-shaped π -stacking and H-bonds, whereas at high p (1400 MPa), it is controlled by mixed π -stacking patterns and strong H-bonds. In both cases, formyl–formyl dipole interactions act as a stabilizing factor, reinforcing the rigidity of the clusters. The formyl groups in all systems tend to align either parallel or antiparallel to each other.

Furthermore, MD simulations enabled us to compare H-bond clusters at different thermodynamic conditions. At low T ($T = 181$ K), the average distance between the carbon donor atom of the CH_2 group and the oxygen acceptor of the formyl group is 3.54 Å. At elevated p ($p = 1.4$ GPa, $T = 298$ K), this distance decreases by approximately 0.1 Å to 3.44 Å. Using cutoff distances of 3.54 Å for $T = 181$ K and 3.44 Å for $p = 1.4$ GPa, we analyzed the distribution of cluster sizes. At $T = 181$ K and $p = 0.1$ MPa, the system consists of 41.1% monomers, 22.2% dimers, 14.3% trimers, 8.2% tetramers, and 14.2% larger clusters. In contrast, at $T = 298$ K and $p = 1.4$ GPa, we observe 36.1% monomers, 20.1% dimers, 12.8% trimers, 8.6% tetramers, and 22.4% higher-order aggregates. These results indicate that elevated p promotes the formation of larger clusters, although the overall effect remains moderate.

Having discussed all the collected data, one can clearly state that the association mechanism of the studied aldehyde changes at high p conditions, compared to that at low T . Compression of the studied liquid leads to an increased contribution of π - π interactions in the association process, which might be evidenced by a pronounced blue shift of the bands assigned to the stretching and bending vibrations of aromatic C–H groups. This effect was not observed under cooling, where these bands exhibited only negligible shifts of ca. 1 cm^{-1} . Moreover, H-bonds of the C–H $\cdots$ O=C type seem not to respond to high- p , as the C=O stretching bands show nearly no response to pressure increase, which can be

attributed to a compensatory effect (the interplay between blue-shift due to the compression and the red-shift connected with the strengthening of H-bonding interactions).

Hence, one can conclude that elevated pressure promotes the formation of larger molecular aggregates, whereas at low temperature, slightly smaller clusters prevail. Furthermore, upon compression, the geometry of the resulting associates becomes increasingly governed by a combination of mixed π - π stacking, formyl–formyl dipole interactions, and distorted yet stronger H-bonds. Notably, analogously to the behavior observed for 2-ethylhexanol, the change in the association pattern of 3P1 Pal becomes more pronounced above $p = 500$ MPa, where fluctuations in the amplitude of the Debye process and an increasing disparity between τ_α and τ_D emerge (see Figures 2a and 2c). Both phenomena can be attributed to the growing number of molecules participating in cluster formation and to the pressure-induced variation between T-shaped and parallel π - π stacking motifs³⁷. Consequently, it is plausible that the growing amplitude of Debye relaxation includes an additional contribution arising from pressure-dependent changes in the molecular dipole moment associated with these evolving interaction geometries. One may further emphasize that the shift in the π - π stacking scheme — toward more parallel molecular orientations under high compression — may offer additional insight into the observed changes in the association pattern of the aldehyde above $p = 500$ MPa. It appears that the increased density and more efficient molecular packing reinforce modifications in the geometry of the associates, ultimately leading to fluctuations in the dynamical properties of the Debye process in the aldehyde.

Moreover, MD simulations revealed that the average C $\cdots$ O distance decreases by approximately 0.1 Å at 1.4 GPa, compared to that at 181 K, indicating a strengthening of H-bonds under compression. When analyzing the C=O band in the Raman spectrum, this effect is not directly observed due to the compensatory effect as was mentioned above; however, it becomes evident when examining the positions of the formyl C–H bands, which exhibit pronounced blue shifts of about 17 cm^{-1} and 26 cm^{-1} , respectively. Such a pronounced shift most likely results from the superposition of the two effects (two blue-shifts): one associated with compression, which shortens chemical bonds at high pressure, and the other related to the formation of H-bonds involving C–H groups, as a similar although much smaller blue shift of a few cm^{-1} was also observed upon cooling. Thus, our findings provide valuable insight into the association mechanisms under different T and p conditions in formerly unexplored molecular systems such as aldehydes.

EXPERIMENTAL SECTION

Materials

3-Phenylpropionaldehyde (3P1 Pal, with a purity >95% and a molecular weight, $M \approx 134.18\text{ g/mol}$) was provided by Sigma–Aldrich. Before each measurement, the sample was freeze-dried using liquid nitrogen to ensure the absence of water.

Methods

Differential Scanning Calorimetry (DSC). Calorimetric measurements were carried out by a Mettler-Toledo DSC apparatus equipped with a liquid nitrogen cooling accessory and an HSS8 ceramic sensor (heat flux sensor with 120 thermocouples). Temperature and enthalpy calibrations were done by using indium and zinc standards. The sample was prepared in an open aluminum crucible (40 μL) outside the DSC apparatus. Next, the aluminum-sealed

crucible with the sample was cooled down to 120 K and measured on heating up to 298 K at a constant heating rate of 10 K/min.

Broadband Dielectric Spectroscopy (BDS). Isobaric dielectric measurements were conducted on cooling in a wide range of temperatures ($T = 230\text{--}140\text{ K}$) and frequencies ($f = 10^{-1}\text{--}10^6\text{ Hz}$) using a Novocontrol spectrometer, equipped with an Alpha Impedance Analyzer with an active sample cell. The temperature stability, which was controlled by a Quatro Cryosystem using a nitrogen gas cryostat, was greater than 0.1 K. The measurements were performed in a stainless steel parallel-plate cell (diameter: 15 mm, gap: 0.1 mm) immediately after the preparation of the sample.

The dielectric measurement at elevated p was conducted using a hydraulic press, which generated the hydrostatic p in the measuring chamber. The sample was enclosed in a Teflon capsule containing a parallel-plate capacitor assembly. Teflon O-rings were positioned at both ends of the capsule to secure the thin Teflon spacers placed between the capacitor plates, ensuring proper alignment and electrical insulation. The entire assembly was then mounted inside the high- p chamber. High- p measurements were performed under isothermal conditions at room temperature, with a step of 100 MPa, ranging from 1.0 to 1.5 GPa.

Fourier Transform Infrared (FTIR) and Raman Spectroscopy. FTIR spectra were measured on the Nicolet iS50 spectrometer (Thermo Fisher Scientific, Massachusetts, USA) at a spectral resolution of 4 cm^{-1} , taking 16 scans. The spectrum of commercial 3P1 Pal was recorded in the ATR mode at 293 K in the range of $4000\text{--}400\text{ cm}^{-1}$. FTIR data as a function of temperature were collected in the transmission mode in the $4000\text{--}1000\text{ cm}^{-1}$ wavenumber region. The limited spectral range of these experiments was due to the absorption of CaF_2 windows, which were used to prepare a thin film ($3.5\text{ }\mu\text{m}$) of the 3P1 Pal sample. The temperature was monitored using a Linkam heating/cooling stage (Linkam Scientific Instruments Ltd., Surrey, U.K., model THMS600) with a stability of $\pm 0.01\text{ K}$. During the measurements, the FTIR spectrometer was purged with liquid nitrogen to remove water vapor and carbon dioxide from the instrument effectively. The temperature investigations of 3P1 Pal were performed upon cooling from 293 K to 123 K with a constant rate of 4 K/min .

Raman spectra were collected on a WITec alpha 300 R confocal Raman microscope (CRM) (WITec Wissenschaftliche Instrumente und Technologie GmbH, Ulm, Germany) equipped with an air-cooled solid-state laser ($\lambda = 532\text{ nm}$) and a spectrometer diffraction grating of 600 lines/mm (the $1.5\text{--}2\text{ cm}^{-1}$ spectral resolution). Laser power was optimized to minimize heat-induced effects and was ca. 20 mW. Raman spectra were recorded from 50 to 3750 cm^{-1} with an exposure time of 2 s and 30 accumulations. The THMS600 heating/cooling stage (Linkam Scientific Instruments, Ltd., Surrey, U.K.) was used to control the temperature changes in the spectra upon cooling from 293 K to 123 K. The spectrometer monochromator was checked before the measurements using a silicon plate (520.7 cm^{-1}).

High-Pressure Fourier Transform Infrared (FTIR) and Raman Spectroscopy. FTIR spectra were measured in the transmission mode on a Hyperion II FTIR microscope coupled to an INVENIO spectrometer (Bruker Optik GmbH, Ettlingen, Germany). The microscope was equipped with a liquid nitrogen-cooled mercury–cadmium telluride ($\text{LN}_2\text{-MCT}$) detector, and the spectra were recorded in the mid-infrared region ($4000\text{--}850\text{ cm}^{-1}$) with the spectral resolution of 4 cm^{-1} and 32 coadded scans per spectrum. The absorption of the diamond anvils without any sample was used as the reference spectrum, which was subtracted as background from the spectrum of each sample. Measurements were collected using the OPUS 8.8.4 software (Bruker Optik GmbH, Ettlingen, Germany).

Raman spectra were measured on an alpha300R confocal Raman microscope (CRM) (WITec Wissenschaftliche Instrumente und Technologie GmbH, Ulm, Germany) equipped with an air-cooled solid-state laser ($\lambda = 532\text{ nm}$) and a spectrometer diffraction grating of 600 lines/mm (the $1.5\text{--}2\text{ cm}^{-1}$ spectral resolution). Laser power was optimized to minimize heat-induced effects and was ca. 15 mW at

the sample. Data were recorded from 50 to 3750 cm^{-1} with an exposure time of 1 s and 120 accumulations.

For both high- p -FTIR and high- p -Raman measurements, a typical Merrill-Bassett diamond anvil cell (DAC; High Pressure Diamond Optics, Inc., Tucson, AZ, USA), with type IIa diamonds (a culet size of 0.65 mm in diameter) embedded in stainless-steel anvil rings, was used. The sample was placed in a $90\text{-}\mu\text{m}$ -diameter hole in a 0.25-mm-thick BeCu gasket that was firmly seated on one of the diamond anvils. No pressure-transmitting fluid was used as the studied compound was liquid. Thus, the pressure was transferred from the anvil piston to the sample using the studied substance as the medium and a BeCu gasket. Ruby crystals were used to determine the value of the pressure applied.

Molecular Dynamics (MD) Simulations. Molecular dynamics simulations under various thermodynamic conditions were performed using the GROMACS 2025.3 software package.^{38–42, 43} The simulation box contained 1000 molecules of 3P1 Pal. For each condition, a 150 ns NPT equilibration run was conducted with a 1 fs time step, using the V-rescale thermostat and C-rescale barostat to maintain T and p , respectively. After equilibration, 40 ns NVT production runs were carried out with a 0.5 fs time step. Structural and orientational analyses were performed using the TRAVIS program.^{44,45} In particular, radial distribution functions (RDFs), RDF–ADF correlation maps (distance–angle distributions), and cluster size distributions were evaluated to characterize the spatial organization and orientational preferences of molecular aggregates under different thermodynamic conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.5c03496>.

Additional figures, including the relaxation times of α - and Debye relaxations of 3P1 Pal plotted against T ($p = 0.1\text{ MPa}$) and p for different isotherms; ATR-FTIR and Raman spectra of 3P1 Pal measured at room temperature; T -dependent FTIR and Raman spectra of 3P1 Pal measured under cooling; two-dimensional RDF–CDF maps for the examined system under different thermodynamic conditions (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded in whole by the National Science Centre (Poland), Grant No. Opus 24 No. 2022/47/B/ST4/00236. For the purpose of open access, the author has applied a CC BY 4.0 public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

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Pressure-Induced Self-Assembly in 3-Phenylpropanal: Distinct Clustering via π -Stacking and Distorted Hydrogen Bonds

Supporting Information

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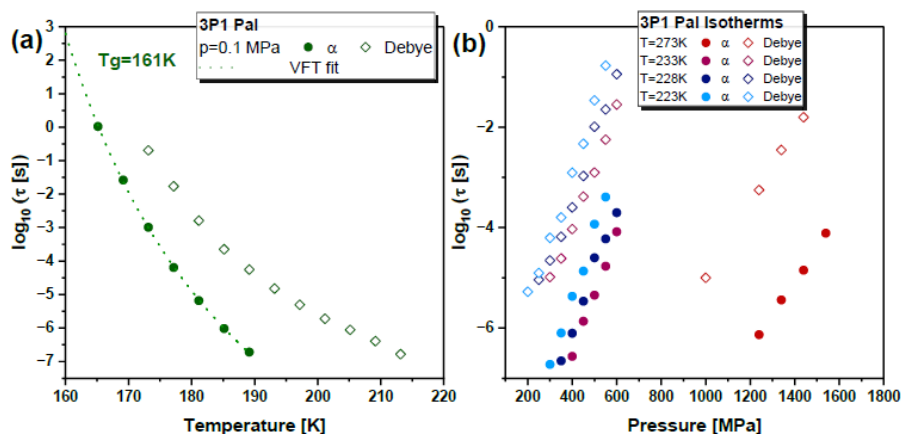


Figure S1. The relaxation times of α - and Debye (D)-relaxations of 3P1 Pal plotted against (a) temperature at ambient pressure conditions and (b) pressure for different isotherms. The dashed line in panel (a) is the representative VFT fit for the α -process.

S1

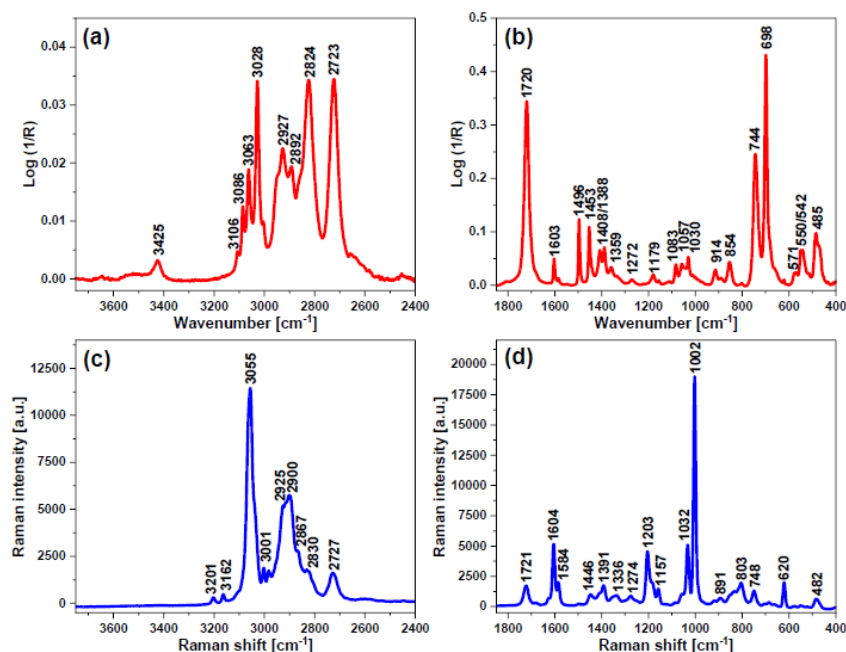


Figure S2. ATR-FTIR (a,b) and Raman (c,d) spectra of 3P1 Pal recorded at room temperature in the spectral ranges of (a,c) 3750–2400 cm^{-1} , and (b,d) 1850–400 cm^{-1} .

As illustrated in **Figure S1**, FTIR and Raman spectra of 3P1 Pal show the intense bands in the high-wavenumber range (3200–2850 cm^{-1}) assigned to the asymmetric and symmetric aromatic C-H stretching vibrations of the phenyl ring (FTIR: 3106, 3086, 3063, and 3028 cm^{-1} ; Raman: 3201, 3162, 3055 and 3001 cm^{-1}), and the CH_2 (methylene) stretching vibrations (FTIR: 2927, and 2892 cm^{-1} ; Raman: 2925, 2900, and 2867 cm^{-1}). Moreover, the two peaks located at 2824 and 2723 cm^{-1} (FTIR), and 2830 and 2727 cm^{-1} (Raman) correspond to the aldehydic C-H stretching vibrations. It can be noted that these two bands arise from the coupling between the aldehyde C–H fundamental stretching vibration (near 2790 cm^{-1}) and its first overtone bending vibration (near 2780 cm^{-1}), which appears at 1380 cm^{-1} . As a result, two new modes of vibration, with frequencies higher and lower than those observed when interaction is absent, are detected (Fermi resonance).¹

In the low-wavenumber region, a peak assigned to the stretching vibration of the carbonyl (C=O) group is detected (1720 cm^{-1} (FTIR) and 1721 cm^{-1} (Raman)). Based on the literature, the ring C=C stretching vibrations are observed at 1603 cm^{-1} (FTIR) and at 1604 and 1584 cm^{-1} (Raman).²⁴ Moreover, the C–H bending vibrations of the propyl and aldehyde groups are visible in the 1500–1325 cm^{-1} range. The CH_2 scissoring and wagging vibrations occur at 1496 and 1453 cm^{-1} (FTIR). The peaks located at 1408, 1388, and 1359 cm^{-1} are associated with the in-plane C-H rocking vibrations.⁴ A signal at 1203 cm^{-1} observed in the Raman spectrum originates from the mixed C-H bending and aromatic in-

plane C-H deformation vibrations.⁴ The bands at 1083 and 1057 cm^{-1} (FTIR) are related to the C-C and C-O stretching vibrations. The doublet of bands located at 1057 and 1030 cm^{-1} is due to mixed vibrations, i.e., the CH_2 asymmetric deformation, CH_2 rocking, ring bending deformation (1057 cm^{-1}), and CH_2 rocking, ring bending deformation, ring breathing (1030 cm^{-1}). The ring breathing and ring bending deformation are observed at 1002 cm^{-1} (Raman). A medium intensity signal at 914 cm^{-1} (FTIR) corresponds to the ring C-H wagging vibrations, whereas a peak at 854 cm^{-1} (FTIR) is due to the C-H deformation vibrations of the formyl group. The bands at 744 cm^{-1} and 698 cm^{-1} (FTIR) and a peak at 620 cm^{-1} (Raman) are assigned to ring bending deformations.²⁻⁴ A doublet occurring at 550 and 542 cm^{-1} (FTIR) is associated with the ring and C-C deformation. The peaks at 485 cm^{-1} (FTIR) and 482 cm^{-1} (Raman) are attributed to C-C-O bending and ring deformation.

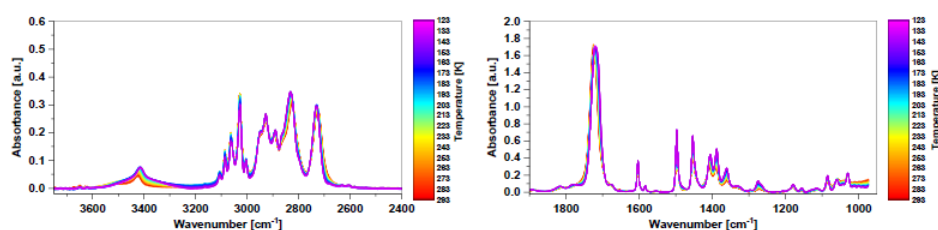


Figure S3. Temperature-dependent FTIR spectra of 3P1 Pal measured under cooling at a rate of 4 $^{\circ}\text{C min}^{-1}$ in two wavenumber regions of (upper) 3750–2400 cm^{-1} and (bottom) 1900–950 cm^{-1} .

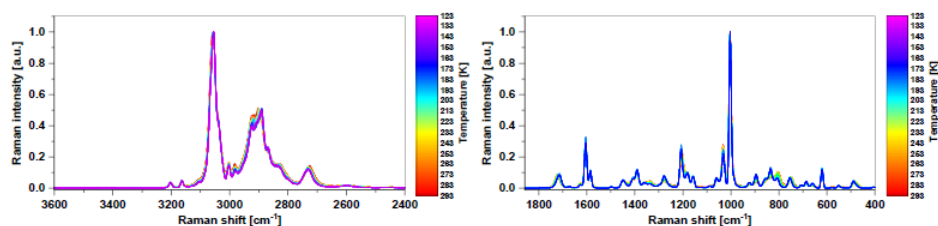


Figure S4. Raman spectra of 3P1 Pal recorded under cooling, as indicated by the color-coded legend, at a rate of 4 $^{\circ}\text{C min}^{-1}$, in two spectral regions of (upper) 3600–2400 cm^{-1} and (bottom) 1850–400 cm^{-1} .

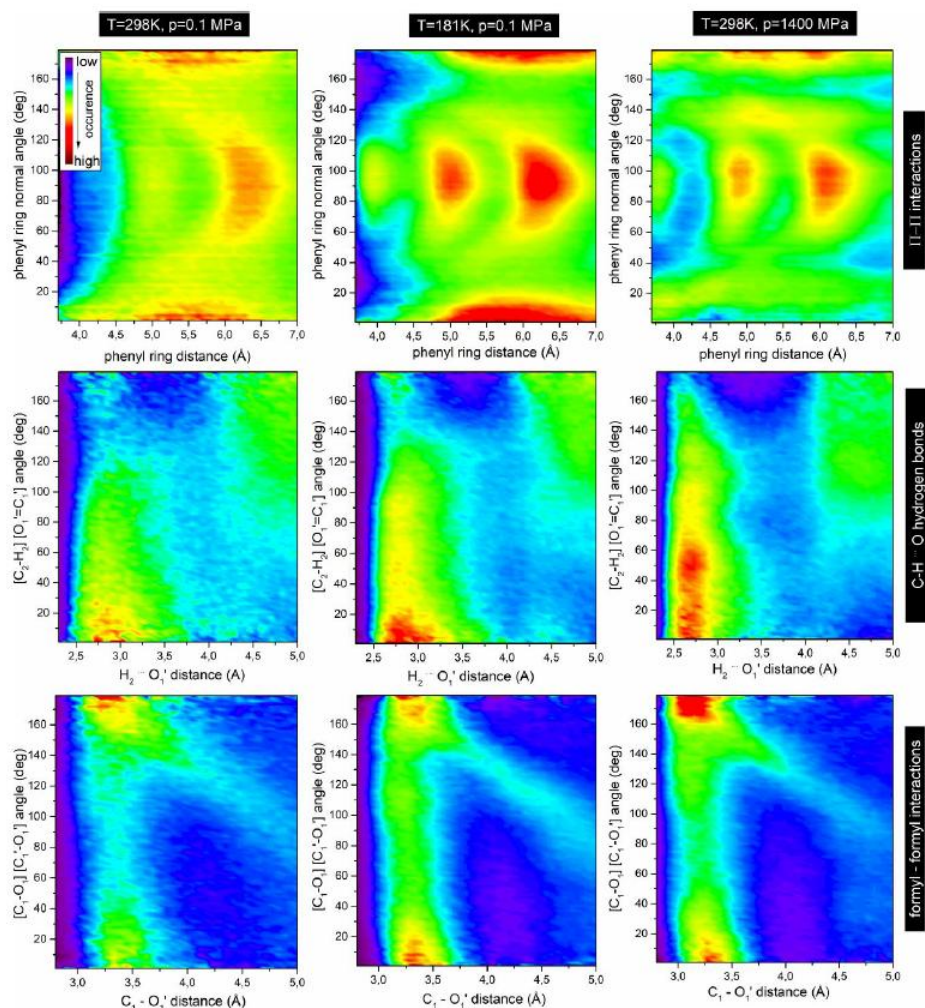


Figure S5. Two-dimensional RDF-CDF maps for 3P1 Pal under different thermodynamic conditions. Each column corresponds to a distinct combination of temperature and pressure, illustrating the structural changes upon cooling or compression. Rows represent various types of dominant intermolecular interactions: (a) π - π interactions between phenyl rings (first row), (b) CH_2 -O hydrogen bonds involving the methylene donor and formyl oxygen acceptor (second row), and (c) formyl-formyl interactions (third row).

The RDF-CDF maps display the probability density as a function of the intermolecular distance (r) and the cumulative distribution function (CDF) value, reflecting both spatial and orientational correlations between interacting groups. The comparison across thermodynamic conditions highlights the evolution of molecular organization and clustering motifs in 3P1 Pal.

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4.3. Article 3 (A3) The role of ring geometry and rigidity in the glassy dynamics of cyclic dimethylsila crowns under elevated pressure



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The Role of Ring Geometry and Rigidity in the Glassy Dynamics of Cyclic Dimethylsila Crowns under Elevated Pressure

View Article Online
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Abstract

The interplay between molecular topology, rigidity, and cooperative relaxation remains central to understanding glassy dynamics in complex liquids. Here, broadband dielectric spectroscopy and differential scanning calorimetry were employed to investigate the relaxation behavior of cyclic dimethylsila crown ethers (DMS11C4, DMS14C5, and DMS17C6) under ambient and high-pressure conditions. The systems exhibit distinct α and β -relaxations, where the secondary (β) process displays typical Johari–Goldstein features at ambient pressure and follows nearly the same trend upon compression, showing only slight shift with respect to the structural process within the studied range of thermodynamic conditions. The pressure coefficients of the glass transition temperature (90–120 K/GPa) and activation volumes (0.2–0.3 nm³) reveal moderate compressibility and enhanced structural rigidity arising from the cyclic molecular framework. Notably, the smallest crown ether exhibits the lowest sensitivity of global dynamics to applied pressure, which can be attributed to its increased rigidity arising from the reduced ring size. Furthermore, calorimetric and dielectric analyses consistently yield nanometric cooperative length scales ($\xi \approx 1.9$ –2.7 nm), reflecting the spatial extent of cooperative rearrangements in the supercooled state, which are in agreement with those obtained from purely thermodynamic estimates. Additionally, a clear linear correlation between activation volume and cooperative length is observed for the data obtained at ambient pressure. Overall, the results demonstrate that molecular ring geometry and internal constraints play a decisive role in governing dynamic heterogeneity and pressure sensitivity in van der Waals glass formers. This work provides a molecular-level framework for tuning glassy dynamics through targeted structural design.

Keywords: *dimethylsila crowns, dielectric spectroscopy, high pressure, correlation length, activation volume*

1. Introduction

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DOI: 10.1039/D6CP00287K

The glass transition remains one of the most intriguing phenomena in condensed matter physics and materials science [1,2]. When a liquid is cooled below its melting point without crystallizing, it enters the supercooled state, where its molecular dynamics changes dramatically [3,4]. The most prominent feature of this regime is the steep slowdown of structural relaxation, referred to as α -relaxation, which controls viscous flow. As the glass transition temperature (T_g) is approached, both the relaxation time (τ_α) and viscosity increase by many orders of magnitude, exhibiting a pronounced non-Arrhenius behavior, i.e., an exponential temperature dependence [5,6].

Several theoretical frameworks have been proposed to interpret the vitrification phenomenon, among which the Adam–Gibbs theory and the free volume model are the most widely discussed. While the Adam–Gibbs theory links the significant slowdown in dynamics to a decrease in configurational entropy, which requires larger cooperative rearrangements, the free volume concept describes the kinetic arrest as resulting from the shrinking space available for collective molecular motion [7,8]. Importantly, in the literature, one can find numerous experimental studies complemented by additional computer simulations that support these concepts [9,10].

The reliability and spatial implications of both the above-mentioned theories, especially the latter (free volume concept), can be critically assessed through high-pressure (HP) experiments, which provide an independent thermodynamic pathway to the glassy state. Although cooling is the conventional route to inducing the glass transition, applying pressure is a powerful and complementary method [11,12]. Compression reduces the free volume, enhances packing efficiency, affects the potential well describing intermolecular interactions, and finally slows down the dynamics in a manner reminiscent of cooling. Nevertheless, in contrast to the temperature effect, which influences the kinetic energy of molecules and the population of various conformations, pressure allows for probing different aspects of soft matter properties and offers deeper insight into a better understanding of the factors governing molecular dynamics in the vicinity of the T_g .

Despite the different impacts of temperature and pressure on the properties of molecules, the systematic dielectric studies have indicated that the shape of the structural (α) process, that is responsible for the viscous flow, remains constant at various thermodynamic conditions when $\tau_\alpha = \text{const}$. This intriguing finding, called the Temperature-Pressure Superposition (TPS) rule, is satisfied in the majority of van der Waals and ionic liquids as well

as polymers [13–16]. The exceptions to the TPS are hydrogen (H)-bonding systems and some other systems, where temperature and pressure have a strong impact on the population and distribution of these specific intermolecular forces, and thus molecular dynamics [17–23]. Recently, the theory of isomorphs developed by the Dyre group has indicated that the TPS rule is satisfied because, in fact, under various thermodynamic conditions, the internal structure of the studied systems is not affected at isochronal conditions (so-called isomorph state) [24,25].

HP dielectric experiments also allow for assessing the molecular origin of relaxation processes observed in the loss spectra recorded for various systems. To do so, one can determine the activation volume ($\Delta V^\ddagger$), which provides some insight into the volume required for reorientational motion [26,27]. This knowledge, together with the activation energy (E_a) and additional computations, may reveal the real molecular mechanism of dielectric processes active in the experimental window above and below the T_g . The second approach relies on the application of the Coupling Model (CM), which enables us to discriminate between the natures of secondary relaxation processes detected in the close vicinity and below the T_g . This is a crucial aspect for a better understanding of the vitrification phenomenon and the physical stability of the glasses. In this context, it is worth emphasizing that some special local movements known as Johari-Goldstein (JG) relaxations are precursors of collective structural mobility and govern the dynamics below the T_g .

In fact, in many cases, the CM predictions are used to verify whether a given secondary mode is a JG relaxation (i.e., involves non-cooperative motions of the whole molecule) or a non-JG process (originates from the reorientation of some polar fragments of the molecule) under ambient conditions [23,28,29]. Nevertheless, the final conclusion and proof regarding the nature of the secondary relaxation come from HP dielectric investigations. In fact, if there is a superposition of the structural and the secondary process at various T and p conditions at constant τ_α , we can be sure that the latter mode is a JG relaxation [30]. If this requirement is not satisfied, then the detected process is a non-JG relaxation. In the literature, numerous examples indicate that the predictions of the CM are positively evaluated at high pressure in simple van der Waals, ionic, or H-bonding liquids, low- and high-molecular-weight systems, single, and two-component mixtures, etc [31]. However, there are some reports demonstrating that high compression negatively verifies the CM predictions made for the data collected at $p=0.1$ MPa. For example, Molecular Dynamics (MD) simulations of elastomers showed that while the TPS rule works for large-scale segmental motions (α -relaxations), it fails for smaller reorientations (secondary relaxations) [21,32]. Modes that appear JG-like at ambient conditions

are revealed under pressure to arise from purely intramolecular motions, as demonstrated by nuclear magnetic resonance (NMR) and broadband dielectric spectroscopy (BDS) in rigid cyclohexane derivatives [33]. Sometimes they even show signatures of intramolecular motions, such as aromatic ring flipping[34]. A similar breakdown is observed in aqueous glass formers, where the α -relaxation can be matched at constant τ_α by varying p and T , but the secondary β -relaxation, found to be a JG-mode that aligned with the CM predictions at ambient pressure, breaks down at isochronal conditions [21,35]. Yet under pressure, the β -process often becomes more clearly decoupled from the α -relaxation, unmasking its underlying character. To cite some of the evidence found in the literature, one can recall the studies carried out in probucol [19], loratadine [21], propylene glycol [36], etc. Hence, based on the above, one can state that compression provides an experimental filter that can disentangle cooperative dynamics from localized molecular motions. Such observations underscore how pressure not only slows the dynamics but also clarifies the fundamental distinction between local and collective relaxation mechanisms.

As aforementioned in the previous section, one of the key parameters with a fundamental basis that can be determined from the high-pressure data is $\Delta V^\ddagger$. According to transition state theory, it defines the difference between the volumes of the transition and ground states [37]. In fact, this quantity allows one not only to get insight into the molecular origin of the relaxation processes but also provides a direct measure of the impact of densification on the dynamics of the observed relaxation process. The higher $\Delta V^\ddagger$, the more significant the role of density in controlling the dynamics of structural/ segmental, or local motions. Moreover, recent investigations have indicated that the activation volume provides a direct link to the cooperative length scale (ξ) of the α -relaxation [38–40]. Systems with large $\Delta V^\ddagger$ exhibit broad cooperative regions spanning multiple nanometers, whereas those with $\Delta V^\ddagger$ comparable to the molecular volume behave more like independent entities [26,41]. Studies across van der Waals liquids, rigid elongated molecules, and hydrogen-bonded systems have confirmed a near-linear correlation between $\Delta V^\ddagger$ and ξ at T_g , establishing $\Delta V^\ddagger$ as a practical proxy for cooperative size[26,40].

In this work, we investigate the dielectric response of dimethylsila crowns (DMSCs) of varying molecular size and molecular weight under both ambient and elevated pressures (up to ~600 MPa). Dimethylsila crowns, the silicon-based analogs of crown ethers, are highly valued in experimental chemistry due to their distinctive structural flexibility and ability to act as ionophores [42,43]. Consequently, they are valuable compounds for applications in ion

sensing, separation science, and catalysis [44]. Moreover, they hold an advantage over the rigid oxygen-based crowns as they are reported to have lower toxicity; specifically, when studied as therapeutic agents, they exhibit no acute oral toxicity [45]. The incorporation of silicon further allows for targeted chemical modification, facilitating the creation of hydrophobic derivatives [46]. Ultimately, the functional efficacy of these macrocycles is governed by their molecular-scale dynamics, including dipole reorientation and charge transport. Therefore, understanding these dynamic processes is essential for leveraging their full potential in material design [47–50]. By quantifying the pressure dependence of relaxation times and activation volumes, and correlating these with cooperative length scales, we aim to elucidate how molecular architecture, particularly ring size and rigidity, governs glassy dynamics. The pressure response of different systems was quantified as the activation volume; subsequently, the analysis was extended to include its correlation with the number of cooperative molecules (N_c), as well as the correlation volume. Finally, the article concludes by examining how the molecular rigidity influences the behavior under high pressure and how the ring size affects this rigidity.

2. Materials and Methods

2.1. Materials

Dimethylsila-17-crown-6 (DMS17C6), dimethylsila-14-crown-5 (DMS14C5), and dimethylsila-11-crown-6 (DMS11C4) with a purity of ~90%, and with molecular weights (M_w) of 294.42 g/mol, 250.37 g/mol, and 206.31 g/mol, respectively, were supplied by Gelest, Inc. Their chemical structures are shown in **Figure 1**. Prior to all measurements, the samples were freeze-dried to remove any residual moisture and ensure sample purity.

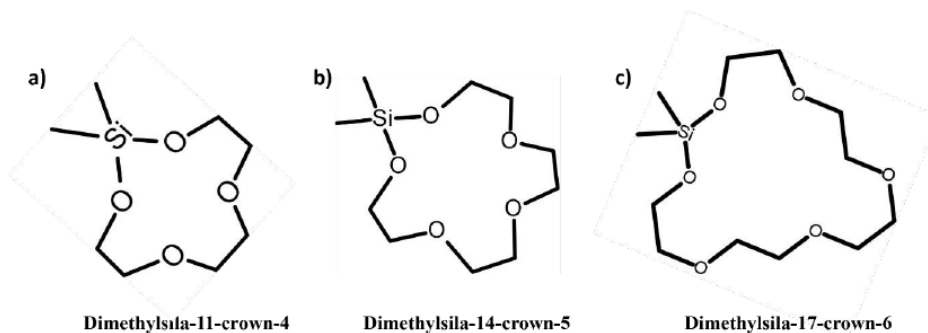


Figure 1. Chemical structure of the molecules.

2.2. Differential Scanning Calorimetry (DSC)

Calorimetric measurements were performed using a Mettler-Toledo heat-flux DSC equipped with a liquid nitrogen cooling accessory and an HSS8 ceramic sensor (120 thermocouples). The DSC was calibrated for temperature and enthalpy using certified indium and zinc standards (Mettler Toledo). The calibration was carried out under the same conditions as the sample measurements (same crucibles, purge gas and flow rate, and a heating/cooling rate of 10 K/min). An empty-pan baseline was recorded for baseline correction. Temperature calibration was based on the melting onset of indium and zinc, and enthalpy calibration was performed by integrating the melting peaks. The accuracy of calibration was checked at the beginning of each measurement series. The sample was placed in a 40 μ L open aluminum crucible and prepared outside the DSC chamber. After sealing, the crucible was inserted into the measurement cell, and the sample was cooled to 130 K with a rate of 10 K/min. Subsequent heating was performed up to 298 K at the same constant rate. All measurements were repeated to ensure the reproducibility and accuracy of the obtained data.

2.3. Temperature-modulated differential scanning calorimetry (TMDSC)

Using the stochastic temperature-modulated differential scanning calorimetry (TMDSC) technique implemented by Mettler-Toledo TOPEM®, the dynamics of the dimethylsilacrowns were examined across a frequency range of 4–30 mHz in a single measurement at a heating rate of 0.5 K/min. The experiment employed a temperature pulse amplitude of 0.5 K, with switching times ranging between 15 and 30 s. Structural relaxation times, $\tau_\alpha = 1/2\pi f$, were calculated from the temperature dependence of the real part of the complex heat capacity, $C_p'(T)$, measured at different frequencies within the glass transition region of the crowns. The glass transition temperature (T_g) was determined for each frequency as the temperature corresponding to the half-step height of $C_p'(T)$.

2.4. Broadband Dielectric Spectroscopy (BDS)

Isobaric dielectric measurements were carried out upon cooling using a Novocontrol spectrometer system comprising an Alpha Impedance Analyzer with an active sample cell and Quatro Cryosystem, over a temperature range of 230–170 K and a frequency range of 10^{-1} – 10^6 Hz. All samples were measured using a parallel-plate capacitor (15 mm diameter, 0.1 mm gap), as described in Ref. [51].

The HP dielectric measurements were conducted using a high-pressure Unipress setup (Warsaw, Poland). The sample was enclosed in a Teflon capsule containing a parallel-plate capacitor assembly. Teflon O-rings were positioned at both ends of the capsule to secure the thin Teflon spacers placed between the capacitor plates, ensuring proper alignment and

electrical insulation. The entire assembly was then mounted inside the high-pressure chamber. Compression measurements were performed under isothermal conditions at various temperatures (243 K, 233 K, and 223 K for each sample), with pressure increments indicated for each isotherm in Fig. 5, ranging from 0.1 MPa to ~650 MPa. Additionally, one isobaric measurement at 625 MPa was performed for the DMS14C5 sample. The complex dielectric permittivity was measured within the same frequency range as in the case of ambient pressure experiments.

3. Results and Discussion

3.1. Thermal analysis

As a fundamental analysis, we performed DSC measurements for the examined compounds, and the obtained thermograms recorded during the first heating cycle, immediately after cooling down to 130 K, are shown in the insets of each panel of Fig. 2 with the specified sample name. From these data, it is evident that all systems exhibit only one heat flow step (as indicated by the “endo” arrow in the plot) corresponding to the glass transition at T_g . As can be seen, T_g systematically increases with the size of the molecule (please see also Table 1). This observation confirms the glass-forming nature of the samples, demonstrating their ability to be supercooled without crystallization.

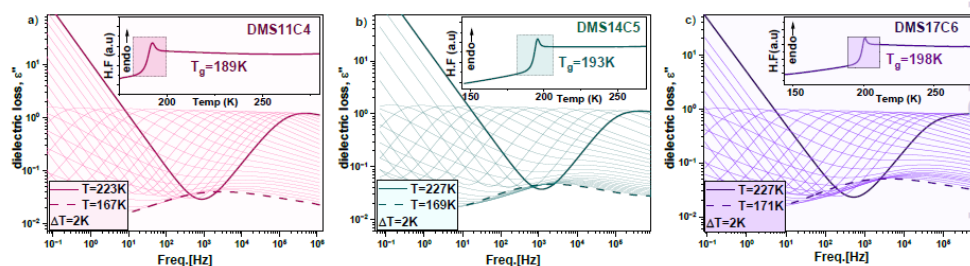


Figure 2. The dielectric loss spectra of a) DMS11C4, b) DMS14C5, and c) DMS17C6 collected at ambient pressure. The insets represent their respective DSC thermograms obtained during the first heating run, with the endothermic step (glass transition event) indicated.

3.2. Dielectric data at ambient pressure

Fig. 2 (a–c) presents frequency-dependent dielectric loss of DMS11C4, DMS14C5, and DMS17C6 over a range of temperatures (~230 K to 165 K) with a temperature step of 2 K, upon cooling. Each dielectric spectrum reveals three distinct dynamic processes: (i) the α -

relaxation ($T > T_g$), corresponding to cooperative structural dynamics and reflecting the overall molecular mobility; (ii) the β -relaxation, discernible even above T_g and associated with localized or intramolecular motions; and (iii) the DC conductivity contribution at low frequencies (f). As the temperature decreases, all relaxation modes systematically shift toward lower f , demonstrating the progressive slowing down of molecular dynamics upon approaching the glass transition.

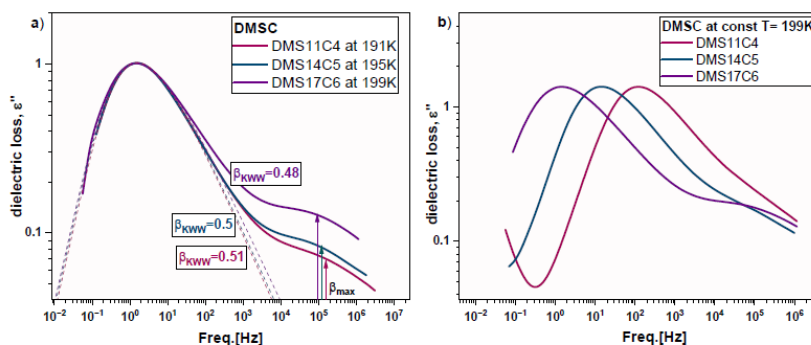


Figure 3. (a) The comparison of the spectral shape of all examined systems at $f_{\max}=1$ Hz, and (b) at constant temperature of 199 K.

To gain deeper insight into the molecular dynamics of the studied systems, dielectric loss spectra of each sample having identical relaxation time, τ (the same maximum peak frequency, ~ 1 Hz) were superimposed; **Fig. 3a**. This approach enables a direct comparison of the spectral shape as the system approaches the glass-transition region. The experimental spectra were analyzed using the frequency-domain response corresponding to the Kohlrausch-Williams-Watts (KWW) relaxation function:

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau_a}\right)^{\beta_{\text{KWW}}}\right] \quad (1)$$

where β_{KWW} is the stretched-exponential parameter describing the width of the α -dispersion and the degree of dynamic heterogeneity ($0 < \beta_{\text{KWW}} \leq 1$). Since the KWW function is defined in the time domain, it was converted to the frequency domain through the one-sided Laplace/Fourier transform of the corresponding response function,

$$\varepsilon_{\alpha}^*(\omega) = \Delta\varepsilon_{\alpha} \int_0^{\infty} \left(-\frac{d\Phi(t)}{dt}\right) e^{-i\omega t} dt \quad (2)$$

and the imaginary part, $\epsilon''_{\alpha}(\omega)$, was fitted to the experimental dielectric-loss spectra. The transform was evaluated numerically. In this way, the KWW analysis was used to compare directly the broadening of the structural-relaxation peak under isochronal conditions.

As shown in **Fig. 3a**, all three compounds exhibit very similar α -peak shapes. DMS17C6, possessing the largest cyclic skeleton, comparatively exhibits the broadest α -relaxation peak ($\beta_{KWW} \approx 0.48 \pm 0.01$) indicating slightly a higher degree of dynamic heterogeneity than DMS14C5 ($\beta_{KWW} \approx 0.50 \pm 0.01$) and DMS11C4 ($\beta_{KWW} \approx 0.51 \pm 0.01$). Although the DMS17C6 tend to exhibit a slight tendency to show a broader α -relaxation peak, considering the fitting uncertainty the trend can be treated as modest.

Furthermore, the comparative spectra collected at a constant temperature of 199 K (**Fig. 3b**) reveal a systematic shift of the α -relaxation maximum toward lower f with increasing molecular size. This behavior signifies slower molecular dynamics in the larger cyclic system, which is consistent with the expected influence of chain length on the free volume and intermolecular constraints.

To quantify the shift of the α -peak seen in **Fig. 3b**, BDS spectra collected for the three studied compounds over a wide T -range, both above and below the T_g , were analyzed using the Havriliak-Negami (HN) function, with an additional term describing the dc-conductivity:

$$\epsilon(\omega)^n = \frac{\sigma_{dc}}{\epsilon_0 \omega} + Im \sum_{i=1}^2 \left(\epsilon_{\infty} + \frac{\Delta \epsilon_i}{[1 + (i\omega \tau_i)^{\alpha_i}]^{\beta_i}} \right) \quad (3)$$

where σ_{DC} is a DC-conductivity, ϵ_0 is a vacuum permittivity, ω is an angular frequency ($\omega = 2\pi f$), $\Delta \epsilon$ is a dielectric strength, α_{HN} and β_{HN} are shape parameters, while τ_{HN} is the HN relaxation time, and Im denotes the imaginary part of the complex function. From the latter, one can evaluate τ_{max} (τ_{α} and τ_{β}) using the formula given in Ref. [52]. This approach was also useful to determine precisely both structural and secondary relaxation times close to the T_g where both peaks were close to each other. One has to note that the HN function was used here as an empirical frequency-domain description of the same α -relaxation process over the full temperature range, whereas the KWW analysis discussed above was applied specifically to compare the peak broadening under isochronal conditions. We note that the HN shape parameters and β_{KWW} are known to be approximately related for the same relaxation process, although HN is not the exact Fourier transform of the KWW function.

The obtained τ_α , as well as τ_β , were plotted against the inverse of temperature in Fig. 4a. Additionally, they were presented as a function of T_g/T in panel (b) of Fig. 4. The $\log \tau_\alpha$ vs. T_g/T plot provides information about the fragility of the sample; notably, the examined compounds exhibit nearly identical fragility, as their α -relaxation times collapse into a single curve irrespective of their ring size.

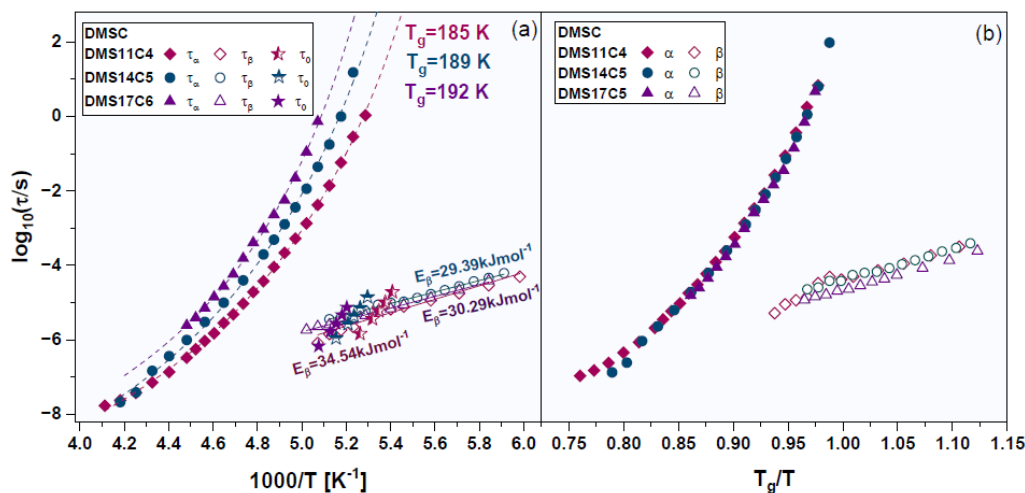


Figure 4. (a) The temperature dependences of relaxation times (τ_α and τ_β) for all the samples, with dashed and solid lines representing VFT and Arrhenius fits, respectively. Colored stars represent primitive relaxation times calculated using Eq. 7. (b) α - and β -relaxation times of the examined compounds, plotted as a function of T_g/T .

To determine the glass transition temperature (T_g), τ_α vs. $1/T$ dependences shown in Fig. 4(a) were fitted using the Vogel-Fulcher-Tammann (VFT) equation[53]:

$$\tau_\alpha = \tau_\infty \exp\left(\frac{D_T T_0}{T - T_0}\right) \quad (4)$$

where τ_∞ is the relaxation time at infinite temperatures, T_0 is the temperature with τ_α approaching infinity, and D_T is the strength parameter. Estimated values of T_g , which is defined as the temperature at which $\tau_\alpha = 100$ s, are presented in Table 1. The values are in good agreement with the T_g determined from DSC studies within the error estimated (± 4 -6 K).

The temperature dependences of β -relaxation times (τ_β) were fitted by the Arrhenius equation:

$$\tau_\beta = \tau_\infty \exp\left(\frac{E_\beta}{k_B T}\right) \quad (5)$$

where E_a is the activation energy, and k_B is the Boltzmann constant. The obtained E_a values are very similar for the studied DMSCs (29–34 kJ/mol). Moreover, as can be seen in **Fig. 4b**, β -relaxation times for different samples overlap, which means nearly the same position of this process in dielectric spectra with respect to the α -process. This means that irrespective of the sample, the molecular nature of the β -relaxation is the same. To determine the origin of the secondary relaxation in a given compound, it is necessary to perform theoretical analyses capable of predicting whether the secondary process has intermolecular (local whole-molecule dynamics) or intramolecular (side-group motions) character. Therefore, we applied the Coupling Model (CM), which is an important tool enabling distinguishing intermolecular JG process from intramolecular non-JG relaxation [54,55]. Importantly, in the case of a JG relaxation, its τ_{JG} should be approximately equal to the primitive relaxation time (τ_0) of the CM:

$$\tau_{JG}(T,p) \approx \tau_0(T,p) \quad (6)$$

τ_0 can be obtained using the equation:

$$\tau_0 = t_c^n \tau_\alpha^{1-n} \quad (7)$$

In the CM framework, t_c represents the transition time from the primitive relaxation to the fully cooperative (α) relaxation. For small-molecular glass formers, this parameter is typically constant and has a value of 1–2 ps[56]. n denotes the coupling parameter, which corresponds to $1 - \beta_{KWW}$ where β_{KWW} was taken from the KWW fit shown in **Fig. 3a**. Using **Eq. 7**, we estimated τ_0 at five temperatures near T_g for each investigated sample. The corresponding τ_α values were taken from the VFT fits, and a fixed $t_c = 2$ ps was used in the calculations. The resulting primitive relaxation times are shown as colored stars in **Fig. 4(a)**. Notably, for all samples, the experimentally determined τ_β values closely match the calculated τ_0 , indicating that the observed β -relaxation is possibly of the JG type. It should be also noted that the τ_0 , estimated within the CM, shows a somewhat stronger temperature dependence than the experimentally determined β -relaxation time. This difference is not unexpected. In the CM, the JG process is identified mainly through the approximate relation $\tau_\beta \approx \tau_0$, whereas a strict equality of activation energies is not required. Moreover, the temperature dependence of the JG β -relaxation is known to change across the glass transition: while $\tau_\beta(T)$ is often close to Arrhenius below T_g , it becomes stronger and typically non-Arrhenius above T_g , where it is more strongly coupled to the structural α -relaxation. Since τ_0 in the present work was calculated from τ_α values determined near and above T_g , the somewhat higher apparent activation energy

of τ_0 is consistent with this crossover and does not preclude assigning the observed β -process to the JG type [57–59].

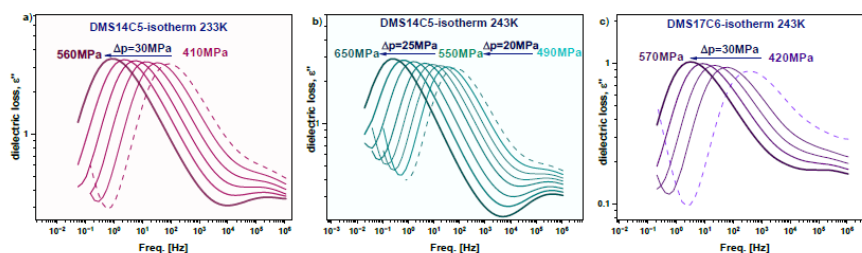


Figure 5. Dielectric loss spectra of the examined compounds measured at the indicated isothermal conditions and pressure steps.

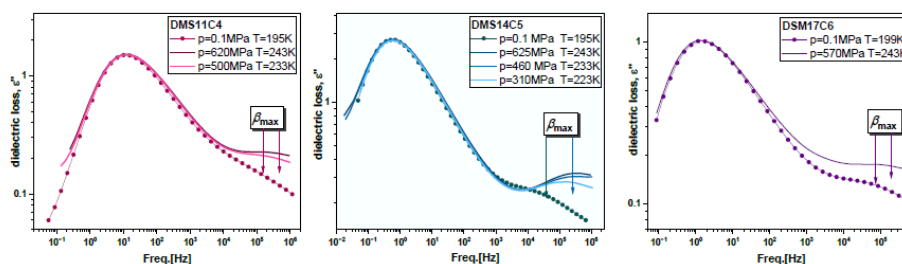
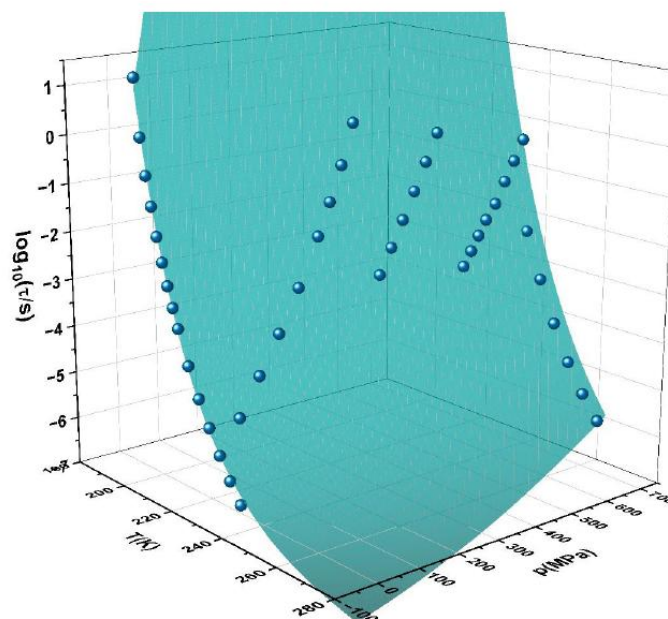


Figure 6. Superimposed dielectric loss spectra of the examined systems measured at the indicated T, p conditions. The arrows represent the maximum of the β -relaxation peak obtained by the HN fit.

3.3. Dielectric data at high pressure

To further validate the predictions of the Coupling Model (CM), we conducted BDS measurements under high-pressure conditions, reaching approximately 650 MPa with increments as indicated in each isotherm, covering a frequency range nearly identical to that during the ambient-pressure experiments. As discussed in the Introduction, HP dielectric studies provide an effective means to test the applicability of the CM. The measurements were performed at various combinations of T and p , and representative isothermal spectra for each sample are presented in **Fig. 5**. As can be observed, the effect of increasing pressure is analogous to the impact of lowering the temperature, namely, a systematic shift of all relaxation processes toward lower f is observed. This trend reflects the enhanced molecular packing and sample densification near the T_g .

To examine the influence of compression on the relaxation dynamics more directly, we compared the dielectric loss spectra obtained at isochronal conditions (i.e., at identical τ_a). It is interesting to note that, while the shape parameters of the structural (α) relaxation remains nearly unchanged under these conditions – indicating that the TTP rule is satisfied – the β -relaxation exhibits a different behavior (**Fig. 6**)^[21]. Specifically, the amplitude of the β -process under high pressure is slightly enhanced and shifted towards higher frequencies compared to that observed at ambient pressure. This phenomenon closely aligns with the findings of Hellwig et al., who showed that in cyclic thioethers, the β -relaxation becomes more pronounced under compression, reflecting its sensitivity to pressure-driven conformational adjustments within the heterocyclic ring structure^[60]. Such findings suggest that secondary relaxations in cyclic systems may respond differently to pressure than the cooperative α -process, potentially due to local intramolecular motions being more directly affected by changes in free volume and internal constraints. Motivated by these observations, we examined whether the pressure-induced shift of the β -relaxation in cyclic dimethylsila crown ethers signifies a breakdown of isochronal superposition, which, according to the CM, would imply a non-JG character. To isolate the β -process and enable a more direct comparison, the α -relaxation contribution was subtracted, and the resulting β -relaxation peaks were superimposed (see **Fig. S1** in the Supporting Information, SI). Although a perfect overlap is not achieved, the observed shift under compression does not exceed one decade in frequency. This limited deviation is still acceptable and enables us to conclude that it is consistent with CM predictions for JG relaxations. Therefore, despite a modest pressure-induced enhancement and frequency shift, the β -relaxation in these cyclic crown ethers retains its JG character. These results indicate that compression slightly modifies the local dynamics associated with the β -process, without inducing a qualitative change in its fundamental nature or its coupling to the structural relaxation.



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DOI: 10.1039/D6CP00287K

Figure 7. The structural relaxation times (τ_α) plotted as a function of T and p for DMS14C5. The colored area present Avramov 3D surface fit.

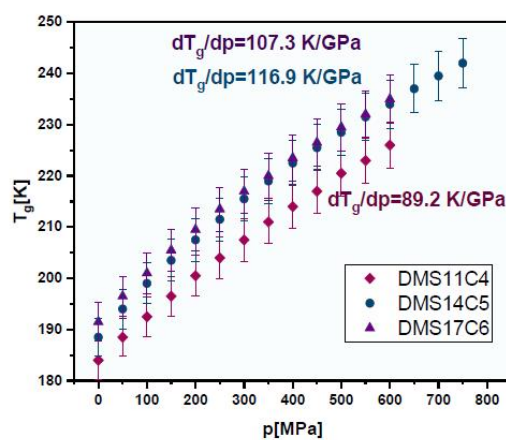


Figure 8. The T_g vs. p dependence for each investigated sample along with the obtained dT_g/dp values. Error bars represent the estimated experimental uncertainties.

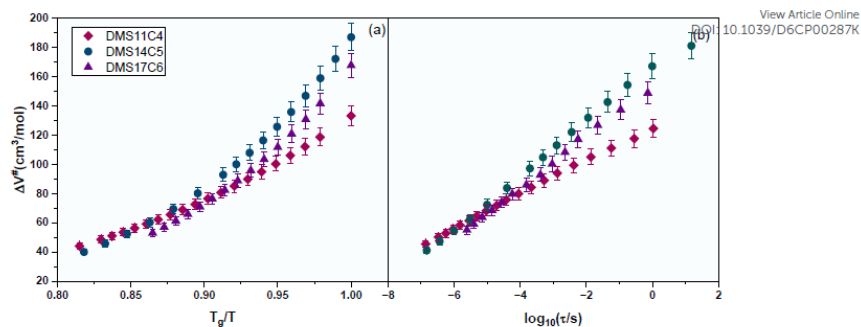


Figure 9. The activation volume plotted against T_g/T (a) and $\log_{10}\tau_\alpha$ (b) for all studied DMSC. Error bars represent the estimated experimental uncertainties.

Table 1. M , T_g (from DSC and BDS), and $\Delta V^\ddagger$ (determined from the Avramov surface fits), the number of correlated molecules calculated using the Donth (N_c^D) (Eq. 12) as well as the Berthier equation (N_c^B) (Eq. 13), and the respective cooperative lengths (ξ) calculated from both modes using Eq. 14.

	M [g/mol]	T_g^{DSC} [K]	T_g^{BDS} [K]	$\Delta V^\ddagger$ [nm ³]	$N_c^D(T_g)$	$N_c^B(T_g)$	ξ^D [nm]	ξ^B [nm]
DMS11C4	206.31	189 ± 1	185 ± 1	0.19 ± 0.02	225	88	2.58	1.88
DMS14C5	250.37	193 ± 1	189 ± 1	0.31 ± 0.02	194	85	2.61	1.99
DMS17C6	294.42	198 ± 1	192 ± 1	0.28 ± 0.02	197	69	2.76	1.95

To gain deeper insight into the dynamics of structural relaxation in the examined cyclic molecules, the dielectric data obtained under various thermodynamic conditions were analyzed using the HN function (Eq. 3). The resulting α -relaxation times were plotted as a function of both T and p in Fig. 7 (DMS14C5) and in Figs. S2 and S3 (DMS11C4, DMS17C6) in the SI. The temperature–pressure dependences of τ_α were further described using the modified Avramov equation (Eq. 8) which relates the structural relaxation time to thermodynamic variables through an entropy-controlled framework[61].

$$\tau_{\alpha} = \tau_{\infty} \exp \left[\ln(\tau_g/\tau_{\infty}) \left(\frac{T_r}{T} \right)^{\alpha_0} \left(1 - \frac{C}{C_{p_0}} \ln \left(1 + \frac{p}{\Pi} \right) \right) \left(1 + \frac{p}{\Pi} \right)^{\beta} \right], \quad (8)$$

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where τ_{∞} is a τ at extremely high T , $\tau_g = \tau(T_g)$, T_r is a reference temperature ($T_r \sim T_g$), C_{p_0} is a specific heat capacity, C is an additional adjustable parameter, Π is a constant with the pressure dimension, and α_0 and β are exponential parameters, which are defined as follows:

$$\alpha_0 = \frac{2C_{p_0}}{ZR}, \quad (9)$$

$$\beta = \frac{2\alpha_p V_m}{ZR} \Pi, \quad (10)$$

where Z describes the degeneracy of the system, α_p denotes a volume expansion coefficient at $p=0.1$ MPa, and V_m is a molar volume. This model assumes that molecular mobility decreases exponentially with increasing density or decreasing temperature, providing a quantitative link between relaxation dynamics and the thermodynamic state of the system.

Subsequently, using the following formula, which was derived from **Eq. 8**:

$$T_g(p) = T_g(p_0) \left(1 + \frac{p}{\Pi} \right)^{\beta/\alpha_0 \left(1 - \frac{C}{C_{p_0}} \ln \left(1 + \frac{p}{\Pi} \right) \right)}, \quad (11)$$

in which Π , β , α_0 , and C_{p_0} are the same parameters as those in **Eq. 8**, the values of T_g at various p were determined. Subsequently, we calculated the pressure coefficient of the glass transition temperature (dT_g/dp) in the limit of ambient pressure for each investigated compound. The obtained values are presented in **Fig. 8**. Typically, dT_g/dp reflects how the structural dynamics is sensitive to the applied compression, i.e., larger values indicate the stronger p -dependence[62]. It can be seen that they are all close to 100 K/GPa, showing rather weak sensitivity of the α -process to pressure. Very similar dT_g/dp are especially in the case of higher ring size molecules (107.3 and 116.9 K/GPa). It has been observed so far that the dT_g/dp values for typical van der Waals liquids is higher than 150 K/GPa, whereas associating liquids, such as hydrogen-bonded systems, exhibit relatively weak sensitivity to pressure (less than 100 K/GPa)[63]. This reduced pressure sensitivity of the α -process is attributed to the higher structural rigidity and strong directional bonding characteristic of hydrogen-bonded systems. Although the present materials are van der Waals liquids, their cyclic molecular geometry imparts greater rigidity than that of typical van der Waals counterparts.

Additionally, from the surface fits of the Avramov equation (**Fig. 7** and **Figs. S2** and **S3** in the SI), the activation volume for the α -process ($\Delta V^\ddagger$), which is another parameter providing information on how sensitive to compression is the structural dynamics, was determined for the examined systems. The calculated $\Delta V^\ddagger$ values were subsequently plotted in two representations: as a function of T_g/T and versus $\log \tau_\alpha$ in panels **a** and **b** of **Fig. 9**. It is evident that, similar to dT_g/dp , $\Delta V^\ddagger$ also shows no tremendous variation with the ring size or molecular volume. The values of $\Delta V^\ddagger$ obtained from the Avramov fits were recalculated to nm^3 and are listed in **Table 1**.

It is worth mentioning that several studies have established that cyclic glass-forming molecules typically show higher $\Delta V^\ddagger$ and greater dT_g/dp compared to their linear analogues, which is attributed to the restricted conformational freedom and enhanced packing efficiency in cyclic systems, which amplify the response of the structural dynamics to pressure. Notably, Hellwig et al. examined cyclic thioethers and reported significantly higher $\Delta V^\ddagger$ and dT_g/dp relative to comparable linear analogues, highlighting that the closed-ring topology limits molecular relaxation and increases cooperative volume (V_c) during vitrification [60]. While the small differences in $\Delta V^\ddagger$ observed particularly for larger DMSC rings fall within the estimated experimental uncertainty, only the smallest cyclic molecule exhibits a noticeably distinct behaviour. This can be rationalized within the framework of Baeyer's theory, suggesting that the ring size influences molecular rigidity. Accordingly, larger rings exhibit slightly higher $\Delta V^\ddagger$, whereas smaller rings appear more rigid and less prone to rearrangement under pressure. Baeyer's strain theory, first proposed in 1885, provides a foundational framework for understanding the stability and reactivity of cyclic compounds by associating molecular strain with deviations of bond angles from the ideal tetrahedral geometry of 109.5° [64]. According to this theory, smaller rings are characterized by significant angle strain, which imparts higher potential energy and reactivity compared to higher-membered rings. Recent mechano-chemical and activation strain models extend Baeyer's ideas to the behaviour of strained molecules under pressure, relating $\Delta V^\ddagger$ to molecular rigidity and deformation energy during bond activations [65]. In this context, to an extent, we can explain the difference in the activation volume as an indication of ring strain and structural rigidity respond to external compression in the smaller and larger ring size of the examined systems. Specifically, rigid, highly strained systems typically display smaller or even negative $\Delta V^\ddagger$ values, reflecting reduced compressibility and resistance to conformational distortion under pressure [66].

With the activation volumes determined, we additionally examined their relation to the number of cooperatively rearranging molecules near T_g . For this purpose, two theoretical approaches were employed:

i) the Donth equation

$$N_c^D(T_g) = \frac{N_A \left(\frac{1}{C_p^{glass}} - \frac{1}{C_p^{liquid}} \right) k_B T_g^2}{M(\delta T)^2} \quad (12)$$

where N_A denotes Avogadro's number, C_p^{glass} and C_p^{liquid} represent the heat capacities of the glassy and liquid states at T_g , respectively, and M is the molar mass. The parameter δT corresponds to the mean temperature fluctuation associated with the glass transition dynamics[67]. Results from the temperature-modulated DSC experiments are presented in Fig. S4 in the SI, from which we calculated the values of C_p^{glass} and C_p^{liquid} , T_g , and subsequently the value of δT . The temperature interval ΔT was defined between the 16 % and 84 % of the total heat capacity change between the glass and liquid phases. For heating experiments, δT was obtained by dividing ΔT by 2.5. The resulting N_c^D values evaluated at T_g are listed in Table 1.

ii) the simplified Berthier equation [68,69]:

$$N_c^B = \frac{k_B}{\Delta C_p} \left[\frac{\beta_{KWW}}{e} \right]^2 \left[\frac{\partial \ln \tau_a}{\partial \ln T} \right]^2 \quad (13)$$

where ΔC_p is the heat capacity jump at T_g , and β_{KWW} is the stretched exponent from Eq. 1, and e is Euler's number. This is a simplified formula of the original equation proposed by Berthier et al. in the framework of the 4-point correlation function approach, as mentioned in Ref. [70].

Further, the correlation lengths (ξ) obtained from both models, quantifying the characteristic spatial scale over which molecular relaxations are cooperatively correlated, were calculated from the determined N_c^B and N_c^D values (considering the cooperative molecules as spheres);

$$\xi = \left[\frac{3V_{cooperative}}{4\pi} \right]^{1/3} \quad (14)$$

whereas

$$V_{cooperative} = \frac{MN_c}{\rho N_A} \quad (15)$$

where, ρ is the density.

The correlation length scale determined for our systems ($\xi^B \sim 1.9\text{--}2.0$ nm and $\xi^D \sim 2.6\text{--}2.8$; see **Table 1**) is in agreement with previously reported literature data[40] as shown in **Fig. 10**, particularly for the values calculated via Berthier approach. This discrepancy between the N_C calculated via both methods is theoretically anticipated. The Berthier formalism provides a rigorous lower bound on the dynamic correlation volume by utilizing experimentally accessible three-point susceptibilities, whereas the Donth model relies on heuristic thermodynamic arguments to define the size of cooperatively rearranging regions (CRRs)[71]. Furthermore, because the two methods depend on different experimental quantities and probes, such as the specific heat capacity jump at T_g versus dielectric relaxation behavior, variations of up to a factor of two are expected. Additionally, one can observe that the Berthier approach confirms that the number of dynamically correlated molecules (N_C) as well as the ξ (see **Fig. S5** in the SI) increases as the material approaches the glass transition. This trend aligns perfectly with theoretical expectations, which predict a growth in cooperativity upon cooling [72].

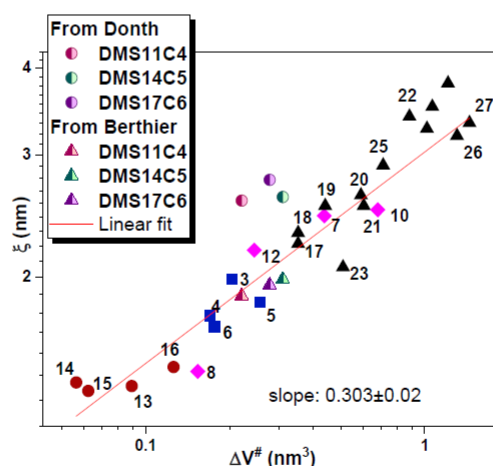


Figure 10. Correlation between the correlation length scale (ξ) and the activation volume ($\Delta V^\ddagger$) at T_g . The data reported by Hong *et al.*[40] were digitized and reused from Blazytko *et al.*[26], with added data for the compounds investigated herein (marked with partially filled triangles and circles, calculated using the Berthier and Donth equations, respectively). The presented numbers refer to different compounds taken from the table of data described in Ref. [40].

Additionally, we examined the relationship between the cooperative length scale, ξ , and the activation volume ($\Delta V^\ddagger$), evaluated under identical isochronal conditions and referenced to ambient pressure for all systems. As shown in **Fig. 11**, a clear linear dependence of ξ on $\Delta V^\ddagger$ is observed across the series. Notably, the smallest cyclic system, DMS11C4, displays a markedly larger slope (≈ 8), whereas the two larger rings exhibit similar slopes of approximately 4. This pronounced difference reflects the enhanced rigidity and stronger intramolecular constraints imposed by the smaller cyclic framework, as mentioned earlier. In such a tightly constrained ring, pressure-induced changes in activation volume translate more efficiently into variations in cooperative length, highlighting the dominant role of molecular topology and internal constraints in governing cooperative dynamics.

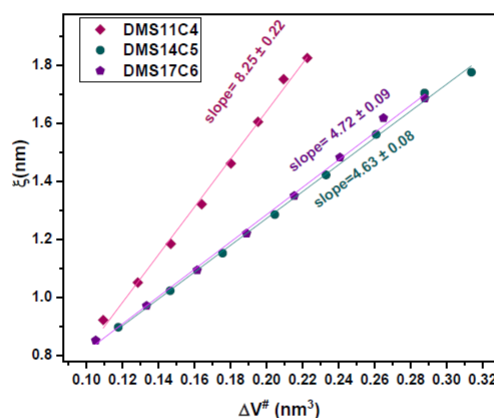


Figure 11. The correlation length scale (ξ) is plotted as a function of activation volume ($\Delta V^\ddagger$), calculated at the same isochronal conditions for all the examined systems. The solid lines represent the linear fit for each system, respectively.

Conclusions

This work presents a comprehensive investigation of relaxation dynamics and molecular cooperativity in cyclic dimethylsila crowns under elevated pressure using complementary dielectric and calorimetric techniques. Two distinct relaxation processes are consistently observed: a structural α -relaxation associated with cooperative molecular rearrangements and a secondary β -relaxation that exhibits the characteristics of a JG process, as predicted by the CM at ambient pressure. It was essential to verify whether these JG characteristics are preserved under compression, since the β -relaxation processes do not fully superimpose under varying T and p conditions. Although a modest pressure-induced

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enhancement and a slight frequency shift are observed at isochronal conditions, these variations remain within an acceptable range so they are consistent with the preservation of JG behavior.

Additionally, the pressure coefficients of the glass transition temperature and the activation volumes reveal moderate compressibility typical of van der Waals glass formers, while clearly reflecting the enhanced rigidity imposed by the cyclic molecular framework. In particular, the smallest cyclic system exhibits the lowest pressure sensitivity of the α -process, underscoring the role of ring size and internal constraints in governing the response of global molecular dynamics to compression. Moreover, the cooperative length scales estimated from calorimetric and dielectric analyses are consistent with literature values, yielding nanometric correlation lengths on the order of 1.9–2.7 nm. Notably, the experimentally obtained ξ values follow the same trend as those determined from purely thermodynamic calculations although the latter (ξ calculated using the Donth approach) yield higher estimates. A linear relationship between the activation volume and cooperative length was also observed at ambient pressure.

Overall, these findings demonstrate that cyclic topology and internal molecular constraints play a decisive role in shaping glassy dynamics, influencing relaxation patterns, cooperativity, and pressure response in van der Waals liquids. The present results provide a molecular-level framework for understanding and tuning glass-forming dynamics through targeted control of ring geometry and molecular stiffness.

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Notes. The authors declare no competing financial interests.

ACKNOWLEDGMENTS. The part of this work was financially supported by the Polish National Science Centre (Opus 24 No. 2022/47/B/ST4/00236). For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission.

CRediT authorship contribution statement

Anjana Krishna Sudhakaran Nair Valsala Kumari: Writing-original draft, Data Curation, Formal analysis, Investigation, Visualization; **Ewa Kaminska:** Validation, Writing-Review

and editing: **Magdalena Tarnacka**: Investigation; **Kamil Kaminski**: Funding acquisition, Resources, Supervision, Writing-Review and editing.

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DOI: 10.1039/D6CP00287K

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Data availability statement

View Article Online
DOI: 10.1039/D6CP00287K

The Data will be made available on request

The supporting data has been provided as part of the Supplementary Information.

Supplementary information: Figures S1, S2, and S3

Supplementary Information

**The Role of Ring Geometry and Rigidity in the
Glassy Dynamics of Cyclic Dimethylsila Crowns
under Elevated Pressure**

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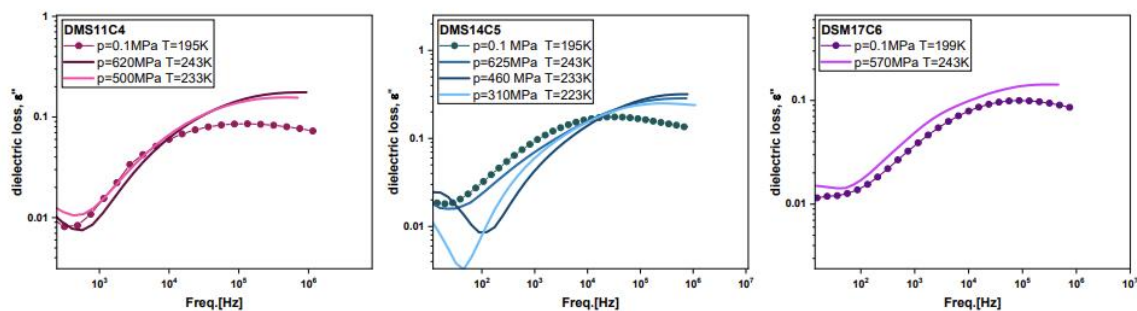


Figure S1. Superimposed β -relaxation peaks (after subtracting the α -process) of the examined systems measured at the indicated T, p conditions.

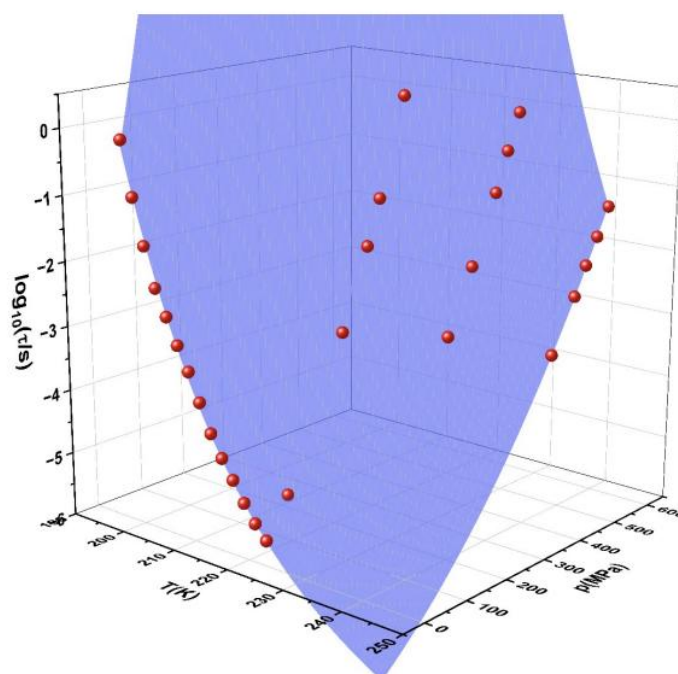


Figure S2. Structural (α)-relaxation times plotted as a function of T and p for DMS17C6. The blue area represents surface fits to eq. 8.

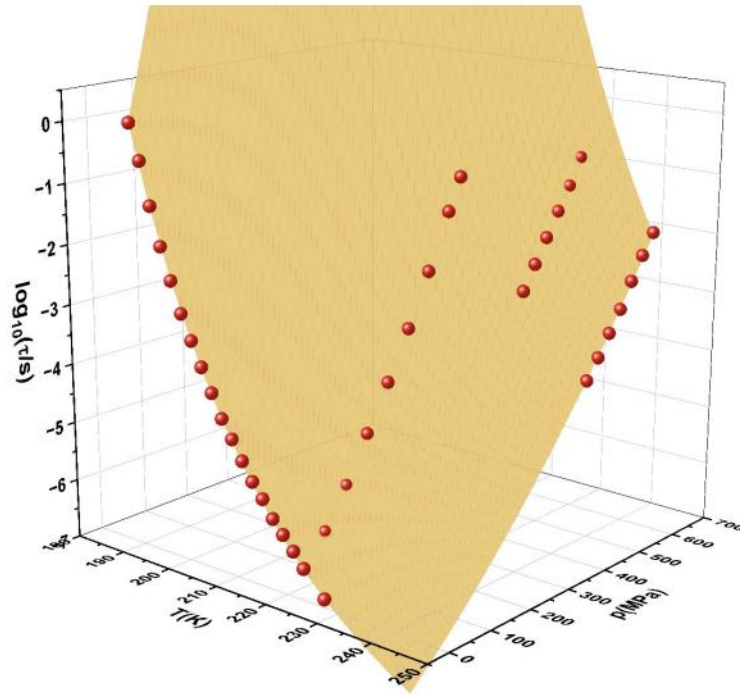


Figure S3. Structural (α)-relaxation times plotted as a function of T and p for DMS14C5. The yellow area represents surface fits to eq. 8.

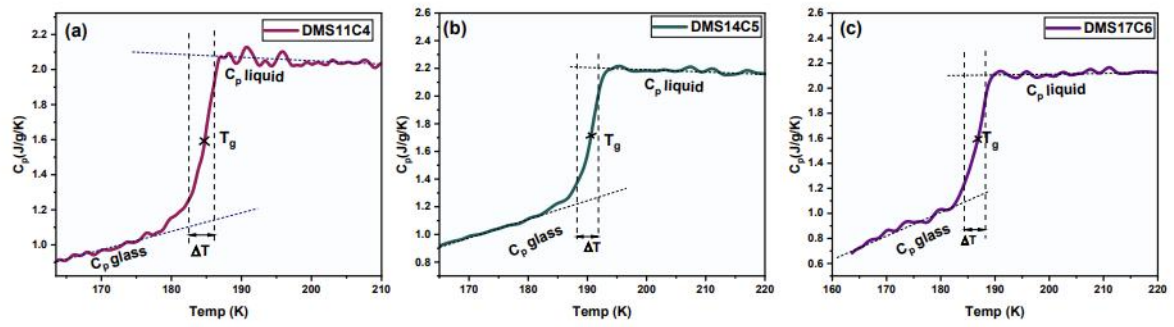


Figure S4. Temperature dependences of quasi-static specific heat capacity C_p for the investigated crowns used to calculate the $N_C(T_g)$ using the Donth method.

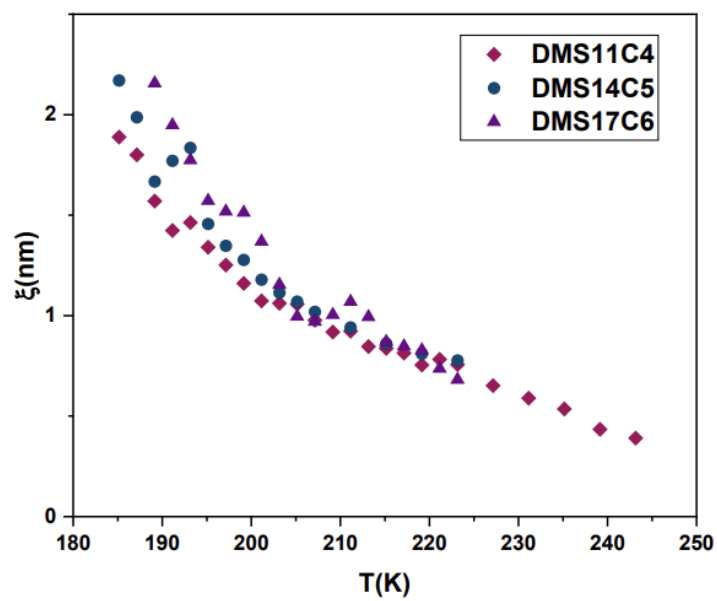


Figure S5. Temperature dependences of the characteristic length scale (ξ) calculated using the Berthier equation (Eq. 13).

4.4. Article 4 (A4) Nanoscale dewetting and unpredictable dynamics of cyclic liquid in curved and rough nanochannels

Journal of Colloid and Interface Science 704 (2026) 139390



Contents lists available at ScienceDirect

Journal of Colloid And Interface Science

journal homepage: www.elsevier.com/locate/jcis



Nanoscale dewetting and unpredictable dynamics of cyclic liquid in curved and rough nanochannels

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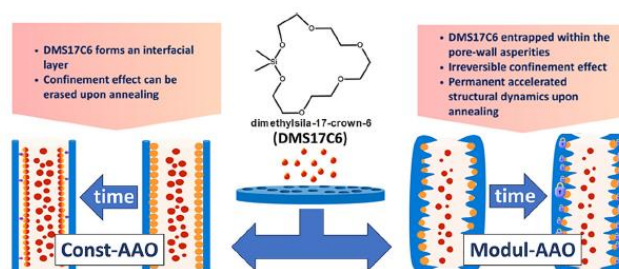
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HIGHLIGHTS

- Irreversible and accelerated structural dynamics in modulated alumina membrane.
- Pore wall roughness speeds up the dynamics of confined sample.
- Double glass transition phenomena in all the confined systems.
- Atomic Force Microscopy reveals the underlying interfacial mechanism.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Dimethylsilila-17-crown-6
Mesoporous confinement
Dynamics
Roughness
Adhesion force

ABSTRACT

Understanding of the behavior of liquids in nanochannels remains a challenging task and unsolved puzzle. Many different approaches/theories are developed to explain physical phenomena such as alteration of dynamics and shift of the glass transition temperature (T_g) reported for nanoconfined systems. Recent studies have linked these effects to the interfacial energy and wettability, typically measured on flat, polished surfaces. However, this approach overlooks a critical factor: under nanoconfinement, liquids interact with highly curved and rough pore surfaces, which can fundamentally alter their behavior. This study explores the thermal, dynamic, and interfacial properties of cyclic dimethylsilila-17-crown-6 (DMS17C6) confined in anodic aluminum oxide (AAO) mesopores with either constant (const-AAO) or modulated diameters (modul-AAO). We found a series of unexpected differences between both systems, i.e., different dynamics of confined liquid and T_g , reversible vs permanent confinement effects, and various time-dependent behavior. Notably, wettability change, inferred from the

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<https://doi.org/10.1016/j.jcis.2025.139390>

Received 5 July 2025; Received in revised form 4 October 2025; Accepted 31 October 2025

Available online 4 November 2025

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measurements of adhesion force within the pores by Atomic Force Microscopy, was found to be highly sensitive to the pore roughness, leading to unexpected behavior of cyclic liquid. These observations correlate with the permanent acceleration of structural relaxation dynamics, suggesting nanoscale dewetting despite apparent wetting at macroscopic scales. This discrepancy highlights the limitations of conventional contact angle measurements and underscores the necessity of nanoscale probes to accurately characterize interfacial interactions. The results also reveal the unique role of DMS17C6's cyclic molecular topology in the behavior of this molecule in nanospatial confinement. These findings provide new insights into nanoconfined liquid behavior, emphasizing the need to account for nanoscale pore roughness in theoretical models.

1. Introduction

The nanoscale spatial restriction of soft materials has gained considerable attention due to the potential application in many fields, including electronics, [1] drug delivery, [2] and sensors. It is because gradual miniaturization induces systematic change in the structural organization, thermodynamic behavior, and dynamic properties of such systems compared to their bulk counterparts. [3,4] So at the end, by varying the scale, and type of spatial confinement, one can try to fine-tune the property of interest for a given application. Usually, notable alterations occur when soft matter is restricted below 100 nm, where, apart from the finite size, the surface interactions become a significant factor controlling the behavior of confined samples. [5,6] Herein, it must be recalled that the spatial nanoscale restriction can be achieved through many different methods. Aside from the investigations of the features of nanoparticles, deposition of a material as a thin layer on a hard substrate (1D) or infiltration of a fluidic system into mesoporous membranes (2D), are the most widely explored and discussed in the literature.

Analysis of the literature data yields a firm reliance of properties of confined materials on the degree of confinement, including geometry, surface roughness, interfacial energy, etc. Dielectric spectroscopic studies on the thin polymer films have demonstrated that the nanoscale confinement influences the segmental dynamics and the glass transition temperature (T_g). [7] Depending on the experimental specifics (i.e., sample preparation, measurement method/time of experiment), T_g of polymers under confinement will either increase, decrease, or remain constant relative to the bulk. [8,9] For example, T_g decreased as film thickness decreased in polystyrene thin films. [10] This phenomenon was attributed to the free surface's growing effect, which increased the polymer chain's mobility. Also, the dynamics of the confined materials are modulated by physical alterations of the interface, such as interaction area, surface roughness, and nanopatterning. [11] Therefore, one should emphasize the significance of the surface interactions when discussing the confinement effect on T_g . By studying the distribution of T_g across the multilayer of polystyrene, it was shown that attractive interactions with the substrates or pore walls might cause a rise in T_g ; whereas, free surfaces often reduce the glass transition temperature due to enhanced mobility. [12] Note that, particularly in vapor-deposited systems, strong (interfacial) interactions might slow down the segmental mobility by forming dense interfacial layers. On the contrary, surface roughness in poly(4-chlorostyrene) films was found to diminish packing density at weakly interacting interfaces, thereby speeding up the α -relaxation (segmental) dynamics. [11] Additionally, research on annealing sheds light on another captivating aspect: the density gradients formed near interfaces that, intriguingly, turned out to be metastable and time/temperature dependent. Over time, the process of equilibration redistributed free volume, recovering the bulk-like dynamics of the thin films.

Further investigations using mesoporous templates highlighted the dual impact of the interfacial energy (γ_{SL}) and pore size (d) on the molecular mobility, demonstrating that in smaller pores, stronger T_g reduction is noted. [13] Although there are cases where pore diameter alone does not show any effect. [14] These data indicated that T_g shifts in confined systems emerge from a delicate balance between the

interplay of confinement dimensions and surface effects quantified by the interfacial energy, wettability, ability to form specific interactions, etc. [15] Recent research has confirmed that γ_{SL} significantly impacts the structural and segmental dynamics of confined materials, including their T_g . [16] Due to their well-defined geometry, tunable thickness, and surface properties, thin polymer films have been widely used to study interfacial effects. [17] At the same time, significant progress has been made in the understanding of the behavior of polymers confined within mesoporous membranes. For instance, Alexandris et al. found that higher solid-liquid interfacial tension correlates with a pronounced T_g reduction. [9] Similarly, studies on a series of poly(propylene glycols) (PPG) derivatives showed that while γ_{SL} remained consistent across them, hydrogen bonding formation capability was the critical factor governing the vitrification temperature of adsorbed layers. [18] The role of surface interactions has also been explored through chemical modifications, such as self-assembled monolayers, polymer brushes, and substrate functionalization. [19] Remarkably, these studies highlight that predicting the behavior of the confined material solely based on the interfacial energy variations is not always reliable.

In this article, we investigated the behavior of a heterocyclic molecule, dimethylsila-17-crown-6 (labeled as DMS17C6, the chemical structure is shown in Fig. 1(a)), infiltrated within anodic aluminum oxide (AAO) membranes characterized by different pore geometries. Herein, we employed two types of AAO templates, (i) standard membranes with a constant pore diameter (both $d = 10$ nm and $d = 40$ nm, labeled as const-AAO) as well as (ii) those with a modified pore diameters ranging from ~ 18 nm to ~ 35 nm (modul-AAO, see Fig. 1(b,c)). The changes in dynamics of all examined systems were followed by Differential Scanning Calorimetry (DSC), Broadband Dielectric Spectroscopy (BDS), which were supported further by contact angle measurements for a better understanding of the observed phenomena. Lastly, Atomic Force Microscopy (AFM) was used to analyze the surface properties, specifically pore roughness and adhesion of the surface with and without the presence of DMS17C6. Measurement of the adhesion forces at the nanoscale helps to understand the interaction of DMS17C6 with the templates and provides an indirect insight into the eventual change in the wettability with respect to the macroscopic measurements carried out on flat surfaces.

2. Experimental section

2.1. Materials

Dimethylsila-17-crown-6 (DMS17C6) with a purity of 95 % with a molecular weight of 294.42 g/mol, was supplied by Gelest, Inc. As the constraining medium, we utilized porous anodic aluminum oxide (AAO) membranes featuring uniaxial channels that are open on both ends. These membranes had well-defined pore diameters, either constant (const-AAO) or modulated (modul-AAO). The const-AAO membranes, obtained from InRedox Technologies, contained uniform porous channels with pore diameters of $d = 10$ nm and $d = 40$ nm.

2.2. Preparation of modul-AAO membranes

Modulated-pore AAO (modul-AAO) membranes were fabricated via

a two-step anodization process in 0.3 M H_2SO_4 at 1 °C, yielding pores with alternating diameters with mild anodization (MA) and hard anodization (HA). Prior to anodization, a high-purity aluminum foil (99.999 %, GoodFellow) was degreased in acetone and ethanol, followed by electrochemical polishing in a chilled ethanol-perchloric acid mixture (3:1 vol.) at 20 V and 0 °C for 2 min. The first anodization step was carried out at 25 V and 1 °C for 12 h in a two-electrode cell. The resulting disordered porous layer was then selectively removed by etching in a 6 wt% H_3PO_4 and 1.8 wt% H_2CrO_4 solution at 60 °C for 1 h. For the second anodization step, a pulsed potential approach was employed, consisting of 50 cycles alternating between a mild anodizing phase (25 V for 3 min) and a high anodizing phase (35 V for 1 s). This process produced modul-AAO membranes with periodically varying pore diameters. The internal nanostructure of these membranes was further characterized in Ref. [20], while field-emission scanning electron microscopy (FE-SEM) confirmed the cross-sectional morphology of the modul-AAO membranes (see Fig. S1 in the Supporting Information, SI). Additionally, we determined the pore-size distribution (PSD) function calculated from desorption branch of nitrogen adsorption/desorption isotherms measured at 77 K by using automatic BELSORP MINI X sorption analyzer (Microtrac BEL Corp., Japan) for investigated sample, see Fig. S2 in SI file. The shape of isotherm (type IV according to IUPAC classification) with well-defined H1 hysteresis loops is typical for mesoporous solids with a sharp increase of adsorption at the point corresponding to the capillary condensation in mesopores. The pore size distribution (PSD) curve for modul-AAO was estimated from the desorption branch of nitrogen isotherm using the Barrett-Joyner-Halenda (BJH) model with cylindrical pores. The PSD plot for the investigated material shows relatively broad pore sizes distribution suggesting that porous structure is not uniform; we observed two population of pores diameters, which are ~18 nm and ~35 nm (see Fig. S2(b)).

2.3. Scanning electron microscopy (SEM)

The cross-section of the AAO membranes was studied using a field-emission scanning electron microscope (FE-SEM Hitachi S-4700, Tokyo, Japan). Prior to FE-SEM examination, the samples were broken and pre-etched in 5 wt% H_3PO_4 at 25 °C for ca. 7 min and then attached to the holder and sputter-coated using a thin conductive Au layer of ~12 nm of thickness using a vacuum sputter coater (Emitech K575X). The imaging was performed at an accelerating voltage of 20 kV, emission current of 9 μA , and a working distance of 12.8 mm.

Collected SEM micrographs (see Fig. S1 in SI file) that clearly illustrate the periodic modulation of pore diameters along the growth direction, which directly results from the applied anodization protocol. The left-hand image shows the AAO prior to etching in phosphoric acid, while the right-hand image depicts the structure after etching. In the latter, the highlighted frames indicate the transition from the HA layers (with larger pore diameters) to the MA layers (with smaller pore

diameters).

2.4. Samples' preparation

The alumina templates were first dried at 373 K under vacuum to eliminate any volatile impurities within the nanochannels. After cooling, they were infiltrated with the target compound. Prior to infiltration, DMS17C6 was freeze-dried in liquid nitrogen to remove any residual water. The system was then maintained at 298 K under vacuum (10^{-2} bar) to facilitate capillary-driven infiltration of the liquid. The process was deemed complete once the sample mass stabilized (no further change over time). Finally, any excess liquid on the surface was carefully removed using a paper towel.

2.5. Surface tension and contact angle measurements

The surface tension (γ_L) of DMS17C6 was determined using the pendant drop method, while contact angles (θ) were measured using a Drop Shape Analysis 100S Krüss Tensiometer (GmbH, Germany) with Advanced software. Contact angle measurements were performed across nine temperatures, beginning at $T = 298$ K and extending to subzero temperatures. A humidity-controlled measurement chamber enabled reliable measurements below 0 °C, circumventing limitations due to water freezing. For statistical reliability, each contact angle measurement on smooth solid surfaces was repeated at least twelve times. The experimental uncertainties were as follows: temperature control (± 0.1 K), contact angle precision (estimated uncertainty: $\pm 2^\circ$), surface tension uncertainty (± 0.1 mN/m). The general methodology has been previously described in Ref. [21].

2.6. Differential scanning calorimetry (DSC)

Mettler-Toledo DSC apparatus equipped with a liquid nitrogen cooling accessory and an HSS8 ceramic sensor (heat flux sensor with 120 thermocouples) was used to perform calorimetric isothermal measurements. The sample was prepared in an open aluminum crucible (40 μL) outside the DSC apparatus. Next, the crucible was sealed with aluminum cover and placed inside the chamber, and then the investigated sample was cooled down to 130 K. Further, it was measured on heating up to 298 K at a constant heating rate of 10 K/min. Measurements were repeated to confirm the accuracy of the obtained values.

2.7. Broadband dielectric spectroscopy (BDS)

Broadband dielectric spectroscopy (BDS) measurements were performed on cooling using a Novocontrol spectrometer system comprising an Alpha Impedance Analyzer with an active sample cell and Quatro Cryosystem, covering a temperature range of 230–170 K and frequency range of 10^{-1} – 10^6 Hz. Bulk samples were measured in a parallel-plate capacitor (15 mm diameter, 0.1 mm gap) as described in Ref. [22];

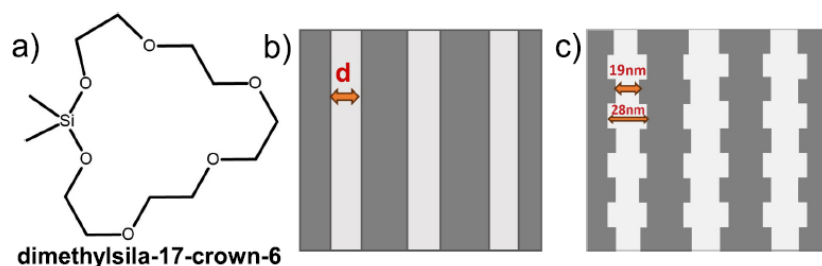


Fig. 1. (a) Schematic representation of the investigated substance, (b,c) The cross-section of commercially available (b) and self-made (c) alumina membranes of applied AAO mesopores, respectively.

while DMS17C6-filled AAO membranes were characterized in a similar configuration (10 mm diameter, 0.05 mm thickness) following Refs. [23, 24]. Given the system's heterogeneous nature, we modeled it considering the electric field parallel to the pore axes, representing it as two parallel capacitors ($\epsilon^{\text{compound}}$ and ϵ^{AAO}) with total impedance following $1/Z^{\text{c}} = 1/Z^{\text{compound}} + 1/Z^{\text{AAO}}$, where the AAO template's contribution is marginal. All dielectric spectra were corrected according to the method presented in Ref. [9].

Structural relaxation process measured for the bulk and confined samples was described by the one-sided Fourier transform of the Kohlrausch-Williams-Watts (KWW) function (the dotted lines in Fig. 4 (a)):

$$\Phi(t) = \exp \left[- \left(\frac{t}{\tau_{\alpha}} \right)^{\beta_{\text{KWW}}} \right] \quad (1)$$

where β_{KWW} is the stretched exponent describing the width of α -dispersion ($0 < \beta_{\text{KWW}} \leq 1$).

The relaxation times, τ , were determined from the fitting of detected loss peaks shown in Fig. 3 with the use of the Havriliak-Negami (HN) function with an additional term describing the dc-conductivity: [25].

$$\epsilon''(\omega) = \frac{\sigma_{\text{DC}}}{\epsilon_0 \omega} + \frac{\Delta \epsilon}{[1 + (i\omega \tau_{\text{HN}})^{\alpha_{\text{HN}}}]^{\beta_{\text{HN}}}} \quad (2)$$

where σ_{DC} is a DC-conductivity, ϵ_0 is a vacuum permittivity, ω is an angular frequency ($\omega = 2\pi f$), $\Delta \epsilon$ is a dielectric strength, α_{HN} and β_{HN} are shape parameters, while τ_{HN} is the HN relaxation time. From the last parameter, one can evaluate τ_{max} using the formula given in Ref. [26].

To determine the glass transition temperature (T_g), $\tau_{\alpha}(1/T)$ dependences presented in Fig. 4(b) were fitted using the Vogel-Fulcher-Tammann (VFT) equation: [27–29].

$$\tau_{\alpha} = \tau_{\infty} \exp \left(\frac{D_T T_0}{T - T_0} \right) \quad (3)$$

where τ_{∞} is the relaxation time at finite temperature, T_0 is the temperature, with τ_{α} approaching infinity, and D_T is the strength parameter. Estimated values of T_g , which is defined as the temperature at which $\tau_{\alpha} = 100$ s, are presented in Table 1. The temperature dependences of β -relaxation times (τ_{β}) were fitted by the Arrhenius equation:

$$\tau_{\beta} = \tau_{\infty} \exp \left(\frac{E_a}{k_b T} \right) \quad (4)$$

where E_a is the activation energy and k_b is the Boltzmann constant.

2.3. Atomic force microscopy (AFM)

AFM measurements were done by a NanoWizard®3 BioScience (Bruker) AFM at ambient conditions. Data was obtained using the ultra-sharp Si tips with a diamond-like spike (approximately 1 nm at the apex)

Table 1
Comparison of glass transition temperatures (T_g) determined by calorimetry and dielectric spectroscopy for bulk and confined systems.

Sample	DSC measurements		BDS measurements
	T_g , core [K]	T_g , interfacial [K]	T_g [K], for $\tau_{\alpha} = 100$ s
Bulk material	198 ± 1	–	193 ± 1
Sample within const-AAO of d = 10 nm (const-AAO-10 nm)	191 ± 1	217 ± 1	186 ± 1
Sample within const-AAO of d = 40 nm (const-AAO-40 nm)	190 ± 1	218 ± 1	188 ± 1
Sample within modul-AAO	189 ± 1	223 ± 1	181 ± 1

from Budget Sensors. The force constant of the tip was close to 5 N/m, with a resonant frequency close to 150 kHz. To determine adhesion, we obtained force-distance curves in the quantitative imaging mode; the images were analyzed using statistical analysis using both the JPK software and the Gwyddion package. Multiple images were recorded, and the data were averaged over several measurements (5–10 typically). The geometry of the experiment was that the membrane was broken in half, exposing the pores. Next, the membrane was attached horizontally, allowing for the AFM investigation from the top. Thus, we were able to investigate the cross-section of both empty and filled porous membranes. The experiment involved the analysis of four samples, the membranes with 40 nm wide pores and 18–35 nm wide (modulated) pores; both empty and filled.

3. Results and discussion

3.1. Thermal investigation

Fig. 2 (a) shows the calorimetric data of bulk DMS17C6 and confined samples. The former material exhibits a single type of thermal effect, attributed to the glass transition (T_g), with no sight of other transitions, i. e., crystallization. At first sight, one can notice that, while it exhibits only a solitary step of heat capacity related to its T_g at 198 K, all the confined systems show two T_g s located below and above the glass transition of the bulk DMS17C6. In the literature, this phenomenon is called the Double Glass Transition (DGT) and has been reported for many low- and high-molecular-weight soft materials infiltrated into cylindrical nanochannels. It originates from the molecular motions of interfacial and core molecules under confinement (so-called “core-shell” model). [13,30] It is postulated that due to additional interactions with the substrate, the interfacial layer shows an increased T_g compared to the bulk, while the core molecules exhibit a reduced T_g . [31] However, unexpectedly, a double glass transition is observed for each studied herein confined sample. Briefly, one should remind that this phenomenon has never been reported in systems infiltrated within membranes of modulated pore size. [32,33] In the further part of this paper, we will try to address this intriguing finding.

3.2. Contact angle measurements

Subsequently we performed temperature-dependent contact angle measurements (Fig. 2(b)) since, as stated in the introduction section, wettability or interfacial energy dictates, to some extent, the behavior of the confined systems. It was found that the investigated crown wets alumina surface very well ($\theta \sim 20^\circ$) at $T = 295$ K, while upon temperature drop, a notable increase in the contact angle up to $\theta \sim 40^\circ$ at $T = 267$ K is observed. It means that wettability gets worse with temperature lowering, but θ is still much below 90° , indicating good wettability of the examined compound even at very low temperatures. Hence, the contact angle investigations revealed that, in contrast to PPG [32] and phenyl alcohols [33] (both having predominantly linear chemical structure), DMS17C6 does not wet the surface of AAO so well.

3.3. Molecular dynamics

Next, we performed dielectric measurements of all examined systems over a broad temperature range ($T = 230$ – 170 K). Note that all samples were measured upon cooling from room temperature. The representative dielectric loss spectra (ϵ'') plotted as a function of frequency are shown in Fig. 3. As one can observe, the spectra obtained for the samples, regardless of confinement, show three processes (appearing from the lowest to highest frequencies), a DC conductivity (related to the ion transport), a dominant structural (α) relaxation process (attributed to the cooperative motions of molecules), and a secondary β -process visible in the vicinity of T_g . As shown, all processes shift to lower frequencies with a temperature drop.

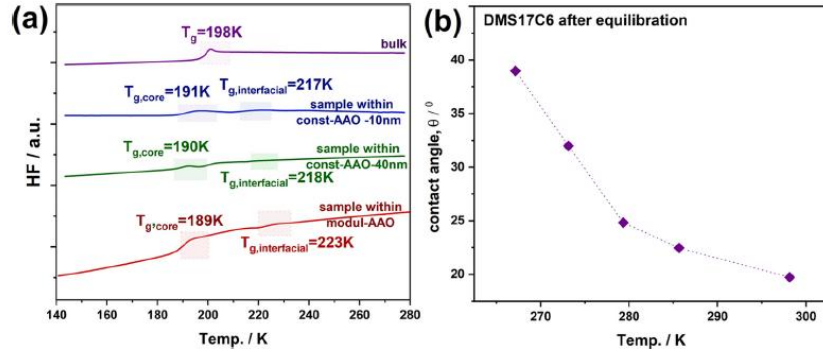


Fig. 2. (a) DSC thermograms for all the examined systems and (b) the contact angle measured for the bulk sample at different temperatures.

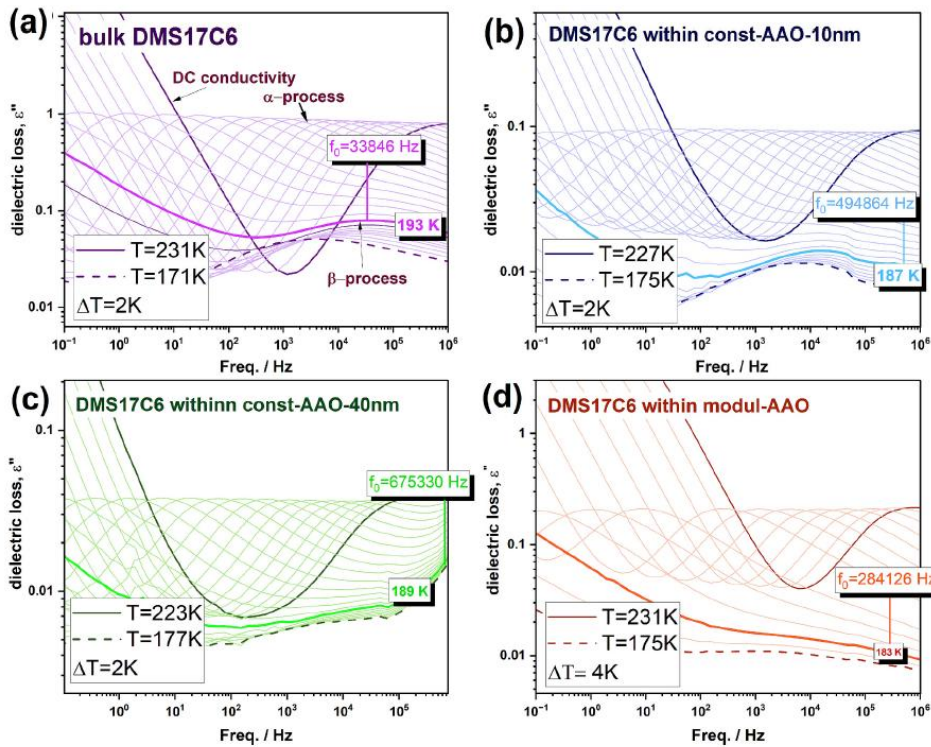


Fig. 3. The dielectric loss spectra of bulk DMS17C6 (a) and the sample confined in const-AAO-10 nm (b), const-AAO-40 nm (c), and modul-AAO templates (d). Vertical solid lines indicate the position of primitive relaxation frequency ($f_0 = 2\pi\tau_0$) calculated for each sample at one representative temperature close to T_g .

Fig. 4(a) presents α -loss peaks measured for the bulk and confined DMS17C6 at a constant frequency of the dominant structural peak's maximum ($f_{max} \sim 1$ Hz). Note that the data were shifted and superimposed on the bulk signal. As seen, the width of the structural process of all the confined systems is broader with respect to the bulk material, which is quantified by the changing value of the stretched exponent (β_{KWW}) of the KWW function (eq. 1) from $\beta_{KWW} = 0.48$ –0.38. This broadening of the α -peak can be explained by the increased

heterogeneity in the molecular mobility, usually observed in confinement, most likely due to interactions with the host AAO substrate pore walls. [34] Additionally, it is worth stressing that the shape of the structural process varies from sample to sample, indicating different interactions between crown and pore surface in constant and modulated AAO.

One can also add that when we compared the loss spectra at the same temperature (see the inset in Fig. 4(a)), it was found that the sample

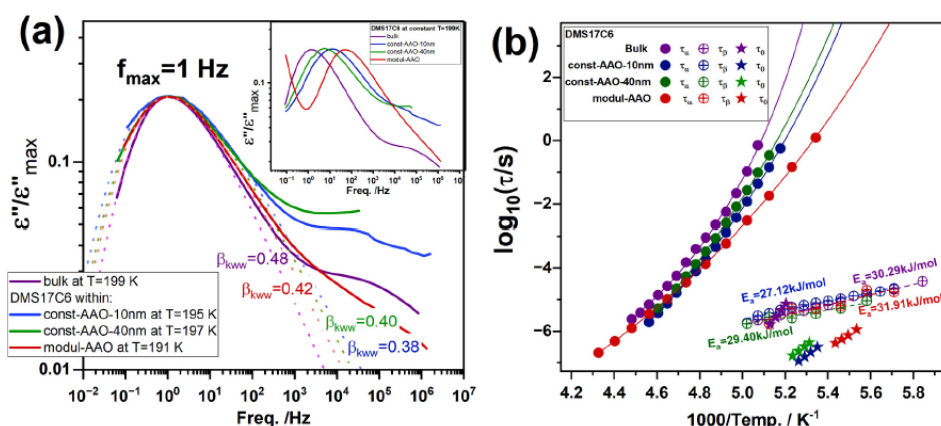


Fig. 4. (a) The dielectric loss spectra of DMS17C6 (both bulk and confined) recorded at the indicated temperatures (to superpose at the maximum of the structural process). The KWW fits are shown by dotted lines. For comparison, in the inset in panel (a), the position of the dielectric loss spectra collected at a constant temperature are also presented. (b) The temperature dependence of the relaxation times (τ_α and τ_β) obtained for all examined samples. VFT and Arrhenius fits are illustrated by solid and dashed lines respectively. Star points represent primitive relaxation times estimated from the CM formula (eq. 6).

within modul-AAO shows more shift in comparison to the ones within const-AAO. This data presentation demonstrates a clear impact of the pore size as well as the pore geometry on the structural relaxation of DMS17C6 within AAO mesopores (see Fig. 4(b)).

To gain further insight into this phenomenon, we analyzed the temperature dependences of relaxation times. The dielectric loss spectra were fitted using the Havriliak-Negami (HN) function combined with the DC-conductivity term (eq. 2). Fig. 4(b) presents the resulting relaxation times as a function of the inverse temperature. Interestingly, α -relaxation times (τ_α) of all confined systems are clearly altered in the whole range of temperature when compared to the $\tau_\alpha(1/T)$ of the bulk crown. As illustrated in Fig. 4(b), all samples maintain their relative shift with respect to the bulk compound even above T_g , indicating long-lasting confinement effects. It seems that the determined $\tau_\alpha(1/T)$ -dependences of spatially restricted systems deviate from the bulk in the following hierarchy (from the biggest to the smallest deviation), DMS17C6 within modul-AAO > samples within const-AAO-10 nm > the one incorporated into const-AAO-40 nm. Especially exciting remains the data collected for the material infiltrated within modul-AAO, for which, surprisingly, the most notable deviation in the dynamics is detected when compared to the other systems. This finding is in clear contrast with previously published data. Just to mention that studies on PPG confined in modul-AAO clearly revealed the bulk-like behavior when compared to the samples within const-AAO templates. [32] A similar trend was also reported for the phenyl derivatives of monohydroxy alcohols. [33] Nevertheless, herein, a strong deviation from the bulk behavior for the system infiltrated within modul-AAO was observed. Such acceleration in the structural dynamics in confined systems might be related to the roughness-induced free volume distribution, where geometric constraints create heterogeneous void distributions that enhance the molecular mobility. Most likely, this effect is even amplified in the examined DMS17C6 due to its flexible cyclic carbon-oxygen backbone, which exploits these free volume hotspots for rapid reorientation, a behavior absent in linear systems like, i.e., PPG and PhA. [32,33] Values of T_g determined using the VFT equation (eq. 3) are listed in Table 1. Good agreement is observed between the dielectric T_g (at which $\tau_\alpha = 100$ s) and calorimetric values of $T_{g,core}$.

3.4. The origin of the β -relaxation

After analyzing the temperature-dependent evolution of structural

(α) relaxation times across all samples, we now focus on the characteristics of the secondary (β) relaxation process. Fig. 4(a) clearly reveals that, even though the α -relaxation peak position shows significant confinement-induced shifts, the β -relaxation remains completely unaffected. Typically, β -processes are sensitive to nanoconfinement, often showing complete suppression due to the restricted molecular mobility or frequency shifts (in the case of β -modes of Johari-Goldstein (JG) type). [35,36] For example, dielectric studies of one-dimensional PMMA nanofibers (35–65 nm) in AAO templates revealed a notable slowdown of the β -relaxation, with its peak shifting to the lower frequencies with respect to the bulk PMMA. This retardation is attributed to the interfacial constraints that impede cooperative molecular motions. The Arrhenius behavior of this relaxation, along with its correlation to the boson peak in Raman spectra, confirms its identity as a collective β -JG relaxation. [37] Similarly, in ibuprofen confined within silica nanopores (2.5–4 nm), dielectric spectroscopy experiments indicated a two-order-of-magnitude increase in β -relaxation times. This slowdown, characteristic of the JG process, results from its sensitivity to density and coupling to α -relaxation. [38] The unaffected persistence of β -relaxation in our systems suggests that localized motions remain fully active even when the large-scale cooperative dynamics are strongly perturbed. To elucidate the molecular dynamics and origin of the β -relaxation process, we analyzed the temperature dependence of β -relaxation times by fitting them to the Arrhenius equation (eq. 4), from which we determined the activation energy (E_a). Interestingly, we found that it shows almost similar values ($E_a \sim 30$ kJ/mol) for all the systems irrespective of the applied confinement.

Thus, the Coupling Model (CM) [39,40] was applied to identify the β -relaxation origin in bulk DMS17C6, distinguishing intermolecular JG motions (whole-molecule dynamics) from intramolecular non-JG processes (side-group motions). Importantly, in the case of a JG relaxation, its τ_{JG} should be approximately equal to the primitive relaxation time (τ_0) of the CM:

$$\tau_{JG} = \tau_0 \quad (5)$$

τ_0 can be obtained using the equation:

$$\tau_0 = \tau_c \tau_\alpha^{1-n} \quad (6)$$

In the above CM formula, τ_c is a transition time from the primitive to the fully cooperative, i.e., α -relaxation (it is a constant equal to 1–2 ps

for small molecular glass-formers), [41,42] while n is the coupling parameter, which is identical to $(1 - \beta_{KWW})$. We applied eq. 6 to calculate τ_0 at four temperatures close to T_g for each examined sample (bulk and confined). Note that respective τ_a were taken from the VFT fits. Moreover, we took $t_c = 2$ ps for the calculations. The determined primitive relaxation times are presented as colored stars in panel b of Fig. 4. Interestingly, in the case of the bulk sample, experimental τ_β are very close to the calculated τ_0 . Hence, it seems that the observed β -process is a JG-type. In turn, unexpectedly, values of τ_0 obtained for all confined systems differ from the experimental τ_β (they are much shorter than τ_β). This is also clearly visible when we compare the location of respective primitive relaxation frequencies, $f_0 = 1/(2\pi\tau_0)$ calculated for each sample at one representative T ($\sim T_g$), see Fig. 3. The good correspondence between the maximum frequency ($f_{max,\beta}$) and f_0 can be seen only for the bulk sample (Fig. 3(a)). For all spatially restricted DMS17C6, f_0 is localized at clearly higher frequencies with respect to $f_{max,\beta}$ (Figs. 3(b-d)). Hence, the question arises: Does the relationship between structural and JG secondary processes found for the majority of bulk systems, irrespective of their character, at varying thermodynamic conditions, hold under confinement? Or maybe, there is only a coincidence of τ_0 computed from the CM and τ_β ? Consequently, the observed secondary relaxation process is not a JG type. To answer these questions, further high-pressure studies on DMS17C6 are required. Nevertheless, at the moment, the second scenario is more probable when we take into the account the temperature evolution of the β -relaxation times determined for the bulk and confined samples. It seems to be quite meaningful that, irrespective of the degree of nanospacial restriction, τ_β are the same at a given temperature. That means that the probable variation in density, free volume, and interactions across the confined sample does not change the dynamics of this process at all. Therefore, it can be treated as a local relaxation mode related to some librational motions of the dipoles within the cyclic ring. Based on this argument, one can hypothesize (worth studying in the future) that aside from the high-pressure investigations, the behavior of the secondary mode in confined samples might be another experimental tool to probe the molecular nature of these relaxation processes.

3.5. The annealing of confined systems

Aside from the temperature-dependent measurements, time-dependent experiments for DMS17C6 confined in constant and modulated AAO pores were done. The main motivation behind these studies was to examine whether confinement-induced alterations in the structural dynamics can be erased due to annealing. These investigations were carried out at temperatures located between high and low T_g (T_g ,

interfacial and $T_{g,core}$) detected in the thermograms presented in Fig. 2. Note that all mesoporous materials filled with the crown were quenched deep below their T_g s, and then heated to the chosen annealing temperature (T_{anneal}). Previous studies have demonstrated that extended annealing of nanoconfined glass-formers results in progressive recovery of bulk-like dynamical properties, most notably through retardation of both structural or segmental mobility. [43,44] This effect is attributed to the variations in the interfacial packing density, which influences the mass exchange between interfacial and core dynamics. What is more, time-dependent changes in molecular dynamics have also been discussed within the framework of adsorption-desorption processes that reduce free volume at the interface, enabling to the restoration of the bulk-like properties/dynamics. [35]

Isothermal time-dependent measurements revealed that only the sample within const-AAO-40 nm seems to recover the bulk-like dynamics (see Fig. 5(a)). On the other hand, DCMI7C6 within both const-AAO-10 nm and modul-AAO reaches equilibrium after annealing with a significantly smaller (or even negligible) shift in the dynamics (see Fig. S2 in the SI). The change in the relaxation time (after annealing at $T_{anneal} = 195$ K) plotted against the inverse of temperature is highlighted in Fig. 5(b). This annealing response of DMS17C6 directly correlates with its unique dynamical behavior. In constant pores, crowns gradually recover toward bulk-like behavior (const-AAO-40 nm > const-AAO-10 nm), whereas samples infiltrated into modulated pores exhibit unexpected spectral stability (with negligible shift). So again, we found very unusual and unexpected behavior of DMS17C6 infiltrated into modulated pores.

Summarizing this part of the paper, one can state that the cyclic crown studied herein behaves completely differently from the linear PPG and phenyl alcohols when infiltrated into modulated AAO pores characterized by higher roughness. Just to list the most important observation: (i) two glass transition temperatures detected in the calorimetric data, (ii) strong deviation of the structural dynamics from the bulk sample, (iii) confinement-induced changes, which seem to be permanent and cannot be erased by the annealing experiments. Hence, to understand these experimental observations and find the origin of such atypical dynamics of DMS17C6 infiltrated in modulated pores, we employed a surface-sensitive technique - the AFM. Unfortunately, the insight into the const-AAO-10 nm porous cross-section was not feasible at this point, but we carried out experiments for const-AAO-40 nm and modul-AAO systems.

3.6. AFM analysis

Typical results from the AFM investigation of the samples are

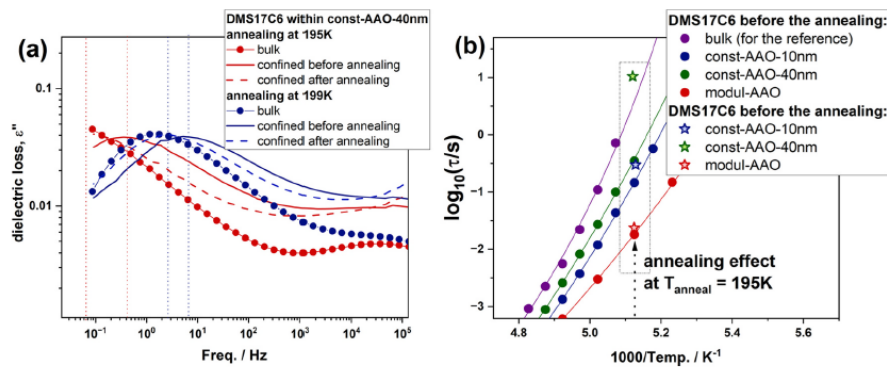


Fig. 5. (a) Time evolution of the loss spectra obtained during annealing of DMS17C6 infiltrated into const-AAO pores of $d = 40$ nm at indicated temperatures. (b) $\tau_a(1/T)$ for the investigated samples. Stars are referred to the structural relaxation times after sample annealing at $T_{anneal} = 195$ K.

illustrated in Fig. 6. The presented images are $1\ \mu\text{m} \times 1\ \mu\text{m}$ in size and show a pseudo 3D (2D image with the third dimension represented by the color change). The topography for both samples reveals perpendicular rows of the porous structure (see Figs. 6(a,c)). Thus, the pores are shown as long, darker depressions in the image. At the same time, the images from the adhesion force map (shown in Figs. 6(b,d)) indicate that the adhesion is the highest exactly at the pore's location, confirming the presence of DMS17C6 inside the pores. We have performed a statistical analysis including a number of images (5–10) and presented the result in the form of a histogram (see Fig. S5 in the SI). Thanks to them, we can distinguish 4 separate components, which correspond to different materials investigated by the AFM tip. The lowest component, with adhesion of around 9 nN, corresponds to the adhesion between the material of the tip (diamond-like spike) and the part of the bulk of the membrane. The highest value component, on the other hand, corresponds to the DMS17C6 inside the pore. The other components (the two middle ones) are related to the loose Al_2O_3 material and DMS17C6, not inside the pores. We believe that this is due to the rather violent process of breaking the membrane; the tension at the break site can move material away from the pore on a nanometer scale. In addition, comparing the roughness (the root mean square (RMS) parameter, measured on $1\ \mu\text{m} \times 1\ \mu\text{m}$ images) of the empty and filled membranes, one can notice that the roughness of empty samples (27.7 nm) is almost three times bigger than that of a full sample (10.43 nm). This is because the material inside the pore stabilizes the pore, and breaking the membrane is much cleaner and produces a much smoother surface. Further analysis, especially between the const-AAO-40 nm and modul-AAO membranes, revealed notable deviations in the adhesion of the AFM tip to the DMS17C6. To avoid membrane-membrane differences, we have decided to present the data for the adhesion for each sample as a difference between the highest and lowest adhesion component. Thus, we found a relatively large difference between the const-AAO-40 nm and modul-AAO samples. In the first case, the average adhesion to the DMS17C6 was 38.45 nN, while in the second, we obtained a value of only 17.60 nN (see Fig. 6). This shows a significant variation in the close-range interaction for the same material (DMS17C6) inside the pores having much different geometry and roughness.

The difference in adhesion force (the force required to separate/pull off the AFM tip from the liquid examined) can originate from different factors, such as differences in (i) roughness-induced molecular packing and conformation at the substrate surface, (ii) the curvature of the interactive surface, etc. Since the straightforward and widely discussed

relationship is that the surface tension (γ_L) of a liquid decreases with an increase in nano curvature, attributed to the low adhesion force, one may hypothesize that here the variation in adhesion force could be due to the difference in γ_L of the liquid, induced by the difference in the interface. [45] But here one has to remember that the effect is pronounced either when we have nano curvature around Tolman length $\delta \sim 0.3\ \text{nm}$ or when it changes over a wide range of pore diameter, for example, 10 nm–150 nm. [46] Here, the examined systems differ only by $\sim 10\ \text{nm}$, even though the adhesion force varies by twice. Hence, by ruling out the role of nano curvature, we emphasize the role of the roughness of the interface on the low adhesion force. From the previously published data, [32] one can recall that the roughness value of the surface of the modulated pore walls (~ 1.7 – $6.2\ \text{nm}$) is significantly higher than that of constant pore walls ($\sim 2.5\ \text{nm}$, see Table 2). Although there is no evident and direct correlation between roughness and the surface tension, we know that it depends on many factors, like hydrophobicity, chemistry of the substrate and substance, their specific interactions, etc. [47]

This difference in adhesion force can be rationalized by two factors: (i) the increased pore wall roughness of modul-AAO, which might increase the contact angle of the confined DMS17C6, and (ii) the roughness-induced dewetting likely reduces the effective contact area between the AFM tip and the liquid. Together, these effects suggest that DMS17C6 within modul-AAO might adopt a Cassie-Baxter or even a metastable Cassie-Baxter wetting state, whereas in const-AAO-40 nm the liquid more uniformly wets the surface, favoring a lower-energy Wenzel state. In the Cassie-Baxter state, a key determinant of wettability is where the liquid rests on a composite interface of solid asperities and trapped air, amplifying the apparent contact angle and thereby reducing the effective contact area, [48] or in a particularly relevant case for dynamic systems, a metastable Cassie-Baxter state. This metastable state is a kinetically trapped configuration, where the droplet remains

Table 2

The line RMS (the roughness measured along with pores) for the different AAO membranes.

Sample	Pore size (nm) [32]	Line RMS (nm) [32]
Modul-AAO	Smaller pore diameters	1.7
	Larger pore diameters	6.2
Const-AAO-40 nm	40 ± 2	2.5

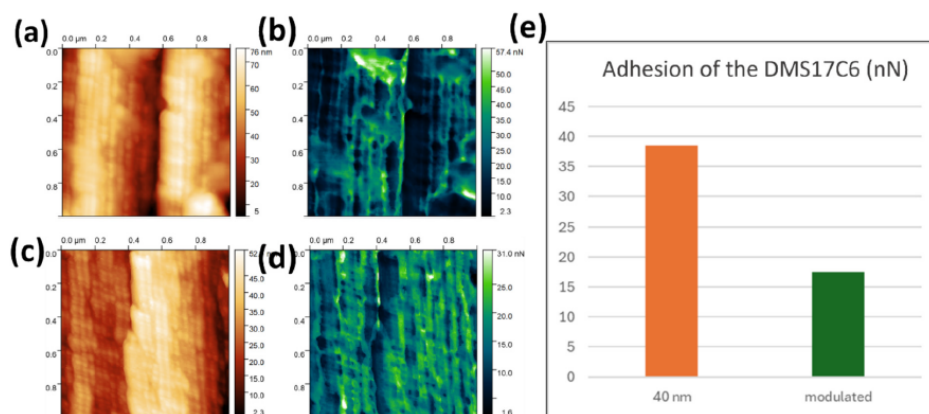


Fig. 6. (a,c) AFM topographic images and (b,d) adhesion force maps of a cross-sectioned const-AAO-40 nm membrane with DMS17C6-filled pores. Note the inverse contrast between images, where nanochannels (dark in topography) exhibit enhanced adhesion (bright in force maps). (e) The comparison of the adhesions determined for DMS17C6 within two systems: const-AAO-40nm and modul-AAO.

suspended over the micro/nano-structures, by partially filling the air pockets, stabilized by an energy barrier, despite the existence of a lower-energy fully wetting Wenzel state. [49] This postulate can account for the low adhesion force observed from AFM, since the Cassie-Baxter state induced by nano-patterning is reported to have low adhesion force, due to the minimal solid-liquid contact area, and the compliance of the underlying air pockets results in low contact line pinning. This enables facile meniscus retreat with minimal force, in contrast to the Wenzel state, where the extensive solid-liquid adhesion necessitates a higher pull-off force to separate the tip from the uniform liquid film than that on the flat surface, where the liquid is in the Wenzel state. [50] Hence, to some extent, we can utilize the Wenzel and Cassie-Baxter models to describe how the roughness impacts wettability and the difference in adhesion force observed in AFM (the schematic representation is shown in Fig. 7). Moreover, even if the liquid is the same, the effective contact between the AFM tip and the liquid might be diminished on a rough substrate due to the presence of asperities (projections) and valleys on a rough surface, which reduces the area where the tip can make direct contact. [51] The observed reduction in adhesion forces might also stem from decreased tip-surface contact area, which weakens interfacial interactions. These effects are particularly enhanced in cases of limited liquid wetting on the surface with a moderately high contact angle. [52] Hence, we hypothesize that the low adhesion (pull-off force) observed from AFM measurements for the modulated system may arise from the specific interactions of the examined DMS17C6 on a rough substrate, where the liquid does not form a continuous film; instead, it might dewet or form islands, reducing the contact area with the AFM tip. Hence, it means that the picture of continuous layer formation of the bulk crown deposited on the flat alumina surface (low contact angle at room temperature $\theta \sim 20^\circ$) does not hold in the pores. It seems that due to roughness variation, the confined DMS17C6 does not wet the pore surface well anymore. What is more, this effect is especially dominant in the case of modulated AAO pores. Therefore, AFM experiments carried out along the cross-section of the pores are so crucial because they provide a unique opportunity to get a real, although indirect insight into wettability (inferred from the measurements of the adhesion force) of the examined compound in pores, which, as shown herein, can be much different than that deduced from the macroscopic measurements.

Thus, it is crucial to have a deeper insight into the pore cross-section, which remains largely unexplored issue for uncovering the localized interfacial interactions within nanoscale pores, where capillary trapping and reduced tip-surface contact significantly alter adhesion behavior. Such phenomena are invisible to macroscopic probes, underscoring the need for nanoscale investigations to fully understand the complex interplay between confinement, surface morphology, and liquid dynamics in porous systems. Additionally, the findings point toward potential future applications in nanofluidic design. Specifically, engineering channels with nanoscale roughness could be a viable strategy to significantly enhance liquid transport efficiency by reducing

interfacial friction due to poor wetting, as reported by Wagemann et al., The authors showed that intentionally engineering misalignments between graphene layers (similar to inducing roughness) in nanofluidic channels presents a powerful method to enhance water transport efficiency by orders of magnitude through a fundamental reduction of interfacial friction. [53]

Hence, taking into account the results of AFM investigations, it can be argued that the unique dynamical behavior of DMS17C6 in modulated pores is due to poor wetting of the much rougher AAO modulated surface. As a consequence of that, inside pores, cyclic crowns form some islands, filling asperities or valleys that act as molecular traps. This would explain the presence of $T_{g,interfacial}$ in the collected thermograms, which most likely is related to the vitrification of interfacially entrapped molecules. What is more, the weaker wettability and molecule entrapment hints might also explain the lack of any shift of the α -process with time for the sample infiltrated into modulated AAO. Since there are fewer molecules entrapped at the interface, there is no or very negligible mass exchange between interfacial and core molecules. Thus, confined effects observed for DMS17C6 infiltrated into modulated AAO seem to be permanent and cannot be erased during isothermal time-dependent measurements. To support our argumentation, one can also refer to Ref. [11], where the authors showed that the higher roughness of the substrate accelerates segmental dynamics of spin-coated poly(4-chlorostyrene). They claim that strong alteration of the surface creates free volume at the interface, leading to a decrease in density packing in the vicinity of the substrate. Consequently, segmental dynamics speed up. This is exactly what we observed in our dielectric investigations, supported by AFM imaging performed on the low molecular weight cyclic molecule infiltrated into modul AAO pores. Herein, one can also comment that DMS17C6, which is a molecule of cyclic topology, behaves completely differently in modulated pores (characterized by the larger roughness) with respect to the linear PPG. In this case, a bulk-like dynamics was observed for the samples infiltrated into rougher pores. It is probably because on the rougher surface, PPG does not adsorb strongly and the number of contact is smaller with respect to the flatter surface. As a consequence of that, the segmental dynamics of this polymer is barely affected in pores characterized by a rougher surface. Moreover, PPG cannot penetrate the voids or surface imperfections due to its large size. That is why it reveals bulk-like dynamics. On the other hand, the cyclic molecule lacks chain ends that may reduce the tendency of the molecules to adsorb on the rougher surface. As a result of that, some dewetting can occur more readily compared to the linear polymers, where chain ends or conformational entropy considerations might promote local pinning. Moreover, DMS17C6 molecules are small enough to get entrapped into the asperities or imperfections on the rougher surfaces, which act like molecular traps. What is more, the hint about molecule entrapments it is a probable explanation why we observe two glass transition temperatures and no recovery of the bulk-like dynamics of DMS17C6 infiltrated into modulated pores upon annealing

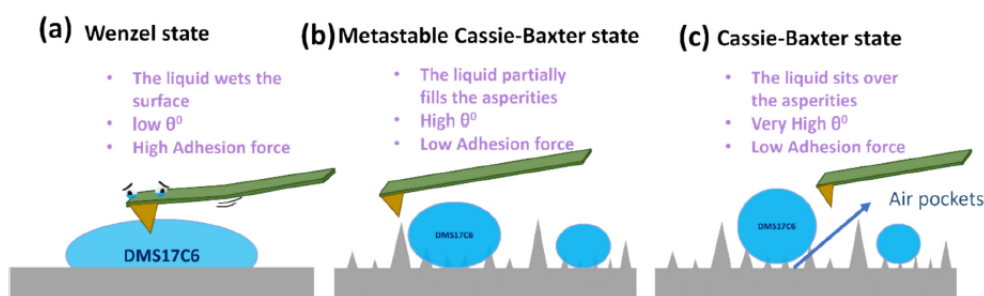


Fig. 7. Schematic representation of (a) Wenzel state, (b) Metastable Cassie-Baxter state, and (c) Cassie-Baxter state.

experiments (no mass exchange between interfacial and core molecules).

4. Conclusions

Recent studies have made attempts to quantify the confinement effect by linking it with the interfacial energy and wettability, [7,9] typically measured on flat, polished surfaces. Therefore, herein, we investigated the 2D mesoporous confinement effects on van der Waals cyclic compound DMS17C6 within two types of AAO mesoporous membranes, characterized by both constant (const-AAO) and modulated (modul-AAO) pore diameters, using BDS, DSC, and AFM techniques. Remarkably, we observed the occurrence of two distinct T_g s ($T_{g, \text{core}} = 191 \pm 1$ K, 190 ± 1 K, and 189 ± 1 K; $T_{g, \text{interfacial}} = 217 \pm 1$ K, 218 ± 1 K, and 223 ± 1 K respectively for the samples confined within the const-AAO-10 nm, const-AAO-40 nm, and modul-AAO respectively) in all systems studied under confinement, which challenges the prevailing assumption that surface roughness suppresses interfacial effects in such systems. [32,33] To explore this finding in more detail, we conducted contact angle measurements. They revealed that DMS17C6 exhibits good wettability on the AAO substrate at room temperature, which decreases upon cooling, explaining the formation of some interfacial layer and the presence of a double glass transition phenomenon. Additionally, dielectric analysis showed that modul-AAO causes broadening of the α -relaxation peak and speeds up the structural relaxation dynamics compared to the bulk and sample infiltrated into const-AAO pores. Importantly, this effect persists even after annealing, indicating its permanent and irreversible character. Furthermore, AFM adhesion force mapping at the AAO interface demonstrated approximately 20 nN lower adhesion force with the substance within modulated pores compared to the sample infiltrated into const-AAO-40 nm nanochannels. This suggests a specific interaction between the cyclic molecular structure of DMS17C6 and the rough substrate morphology, where the liquid may dewet or form discontinuous islands instead of a uniform film, creating geometrical frustrations that more likely support the irreversible and faster dynamics observed via dielectric spectroscopy. Hence, the nanoscale investigation using AFM explains the hidden interfacial mechanism, which is in discrepancy with the good wettability observed via macroscopic contact angle measurements. Subsequently, we propose using AFM as a promising methodology over macroscopic techniques to tackle the issue of the effect of wetting (probed indirectly by the measurements of adhesion force) on the behavior of confined liquids, especially when they are in contact with strongly curved and rough surfaces. The findings reported herein provide fundamental insights into confinement effects, challenging established assumptions about the role of wettability and interfacial energy determined from macroscopic investigations on the flat, well-polished surfaces. However, future studies should investigate similar systems and extend the research to ionic liquids or polymers to further validate the proposed dewetting hypothesis. We believe this will provide valuable guidance for the design of nanomaterials, particularly in contexts where interfacial control is critical. In particular, the irreversible molecular trapping induced by nanoscale roughness offers tangible application potential. Such behavior could be leveraged for passive nanofluidic gating, [54] molecular retention systems, and anti-fouling surfaces that sequester contaminants in non-critical regions. Exploring these possibilities will be an important direction for future work.

CRediT authorship contribution statement

Anjana Krishna Sudhakaran Nair Valsala Kumari: Writing – original draft, Investigation, Formal analysis, Data curation. Magdalena Tarnacka: Writing – review & editing, Investigation, Formal analysis. Ewa Kaminska: Writing – review & editing, Funding acquisition, Formal analysis. Marcin Wojtyniak: Writing – original draft, Investigation. Monika Geppert-Rybczyńska: Investigation. Kinga Biliska:

Investigation. Agnieszka Brzózka: Investigation. Kamil Kamiński: Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The part of this work was financially supported by the Polish National Science Centre (Dec. no 2022/47/B/ST4/00236). For the purpose of Open Access, the author has applied a CC-BY public copyright license to any Author Accepted Manuscript (AAM) version arising from this submission. E.K. is thankful for financial support from the Medical University of Silesia (Poland), Contract No. BNW-1-048/N/4/F.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2025.139390>.

Data availability

Data will be made available on request.

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Nanoscale Dewetting and Unpredictable Dynamics of Cyclic Liquid in Curved and Rough Nanochannels

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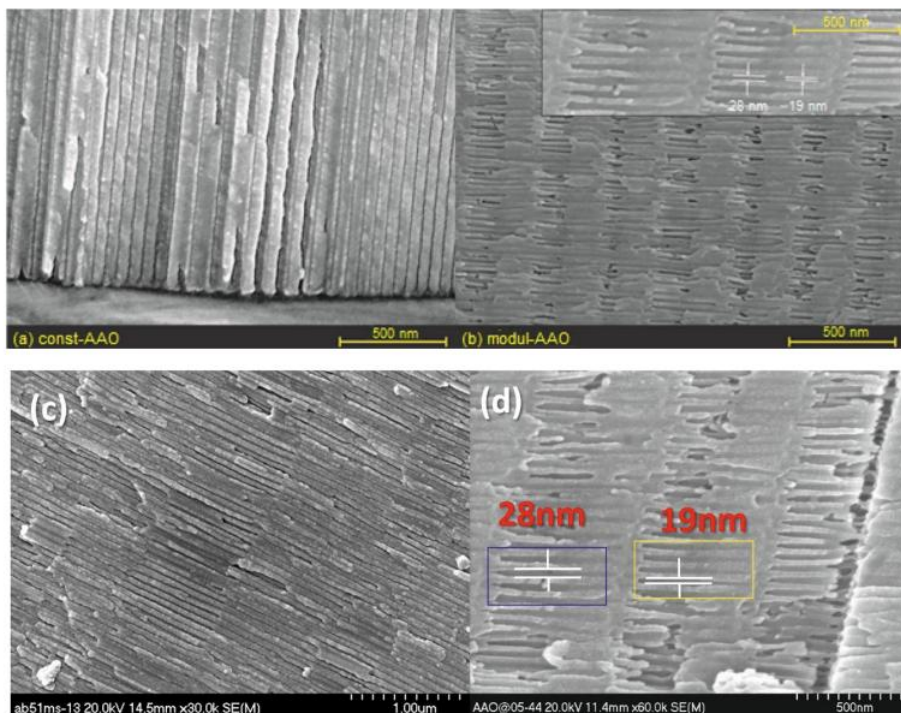


Figure S1. FE-SEM micrographs collected for the cross sections of applied (a) const-AAO and (b) modul-AAO membranes.[1]

Figure 1(c) shows the AAO prior to etching in phosphoric acid, and **Figure 1(d)** depicts the structure after etching. In the latter, the highlighted frames indicate the transition from the HA layers (with larger pore diameters) to the MA layers (with smaller pore diameters).

N₂ adsorption/desorption isotherms.

The porosity as well as pore diameter of modul-AAO templates have been determined on the low temperature nitrogen adsorption/desorption isotherms measured at 77K by using automatic BELSORP MINI X sorption analyzer (Microtrac BEL Corp., Japan). Prior to the measurement, the established amount (0.18g) of modul-AAO support was outgassed (2μmHg) at 453 K for 48 h under vacuum in the degas port of the sorption analyzer. The obtained adsorption/desorption isotherms were used to evaluate the structure of the studied material. Data analysis was assessed by means of BELLMaster7 software (Microtrac BEL). The calculations of the pore size distribution (PSD), and the average BJH desorption pore diameter ($D_{av,des}$) and the maximum pore diameter ($D_{mo,des}$) were obtained from the desorption branches of the nitrogen isotherm by means of the Barrett–Joyner–Halenda (BJH) procedure for cylinder pores with Halsey–Faas correction without smooth differentials.[2] The experimental nitrogen adsorption/desorption isotherms and pore-size distribution (PSD) function calculated from

desorption branch of isotherm for investigated sample are illustrated in **Figure S2(a)** and **Figure S2(b)**, respectively. The shape of isotherm (type IV according to IUPAC classification) with well-defined H1 hysteresis loops is typical for mesoporous solids with a sharp increase of adsorption at the point corresponding to the capillary condensation in mesopores.

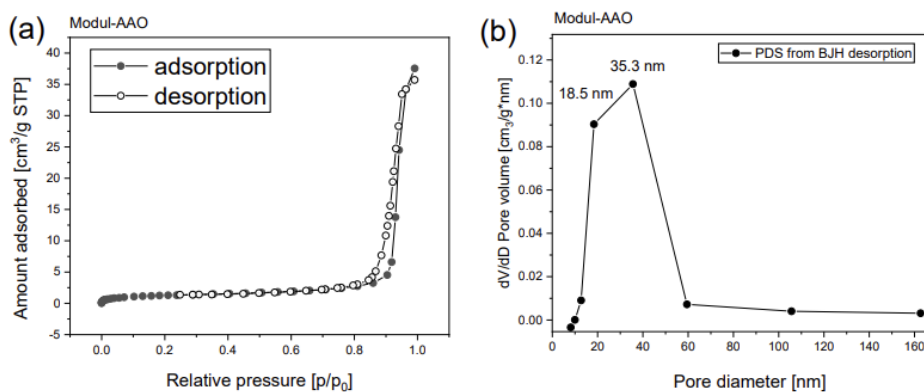


Figure S2. (a) Nitrogen adsorption/desorption isotherms for modul-AAO material. (b) Pore size distribution (PSD) for modul-AAO calculated from desorption branches of isotherm.

The pore size distribution (PSD) curve for modul-AAO was estimated from the desorption branch of nitrogen isotherm using the Barrett–Joyner–Halenda (BJH) model with cylindrical pores. The PSD plot for the investigated material shows relatively broad pore sizes distribution suggesting that porous structure is not uniform; we observed two population of pores diameters, which are ~18.5 nm and ~35.3 nm (see **Figure S2(b)**).

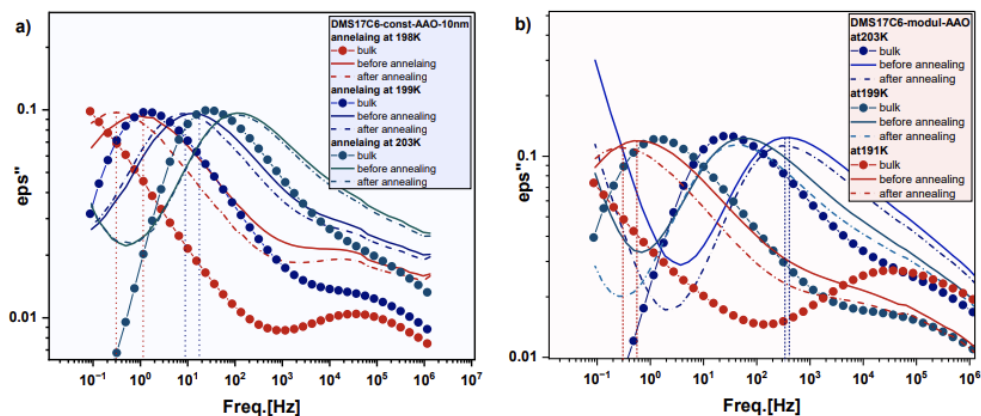


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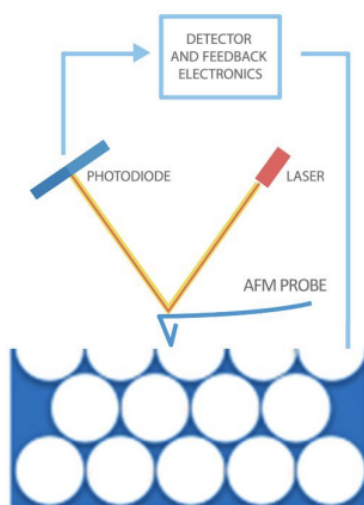


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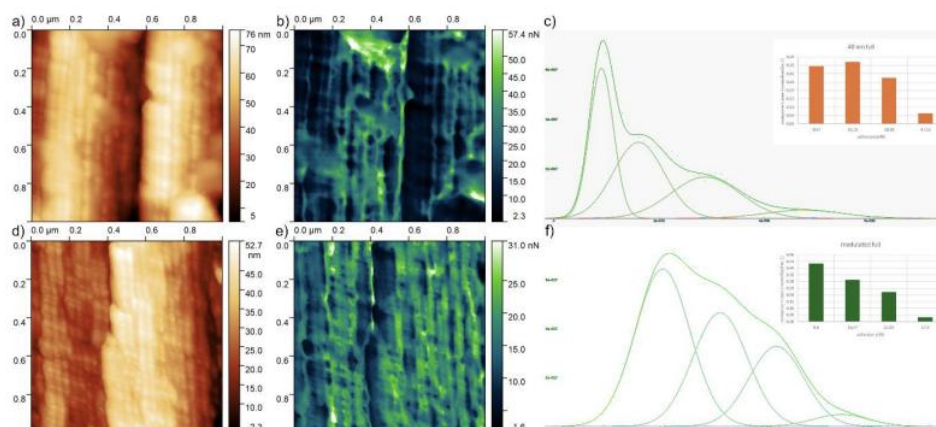


Figure S5. Typical data for the AFM topography, adhesion, and the statistical analysis. The images (a) and (d) are the topography of the filled const-AAO-40nm and modul-AAO, respectively. Accordingly, images (b) and (e) are adhesion maps, and (c) and (f) are the analysis of the multiple components found on the adhesion maps.

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5. Declaration of co-authors

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STATEMENT

I declare that for the following works:

- A1. A.K. Sudhakaran Nair Valsala Kumari, B. Hachuła, M. Tarnacka, E. Kamińska, J. Grelska, T. Lamrani, K. Jurkiewicz, P. Włodarczyk, K. Grzybowska, K. Kamiński, **Specific interactions and mechanism of association in highly viscous aldehyde 3-phenylpropanal**, J. Chem. Phys. 163 (2025).
- A2. A.K. Sudhakaran Nair Valsala Kumari, B. Hachuła, P. Włodarczyk, M. Tarnacka, K. Witkiewicz, R. Wrzałik, E. Kamińska, K. Kamiński, **Pressure-Induced Self-Assembly in 3-Phenylpropanal: Distinct Clustering via π -Stacking and Distorted Hydrogen Bonds**, J. Phys. Chem. Lett. 17 (2026) 736.

My participation consisted of conducting the Raman and FTIR measurements, analyzing and visualizing the obtained data, and co-writing the manuscripts.

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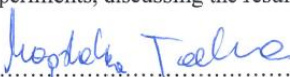
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- A3. A.K. Sudhakaran Nair Valsala Kumari, E. Kamińska, M. Tarnacka, K. Kamiński, **The Role of Ring Geometry and Rigidity in the Glassy Dynamics of Cyclic Dimethylsila Crowns under Elevated Pressure**, Physical Chemistry Chemical Physics, (2026).
- A4. A.K. Sudhakaran Nair Valsala Kumari, M. Tarnacka, E. Kaminska, M. Wojtyniak, M. Geppert-Rybczyńska, K. Bilska, A. Brzózka, K. Kamiński, **Nanoscale dewetting and unpredictable dynamics of cyclic liquid in curved and rough nanochannels**, J. Colloid Interface Sci. 704 (2026) 139390.

My participation consisted of conducting the calorimetric experiments, discussing the results, and proofreading the manuscripts.


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- A2. A.K. Sudhakaran Nair Valsala Kumari, B. Hachuła, P. Włodarczyk, M. Tarnacka, K. Witkiewicz, R. Wrzalik, E. Kamińska, K. Kamiński, **Pressure-Induced Self-Assembly in 3-Phenylpropanal: Distinct Clustering via π -Stacking and Distorted Hydrogen Bonds**, J. Phys. Chem. Lett. 17 (2026) 736.
- A3. A.K. Sudhakaran Nair Valsala Kumari, E. Kamińska, M. Tarnacka, K. Kamiński, **The Role of Ring Geometry and Rigidity in the Glassy Dynamics of Cyclic Dimethylsila Crowns under Elevated Pressure**, Physical Chemistry Chemical Physics, (2026).
- A4. A.K. Sudhakaran Nair Valsala Kumari, M. Tarnacka, E. Kamińska, M. Wojtyniak, M. Geppert-Rybczyńska, K. Bilska, A. Brzózka, K. Kamiński, **Nanoscale dewetting and unpredictable dynamics of cyclic liquid in curved and rough nanochannels**, J. Colloid Interface Sci. 704 (2026) 139390.

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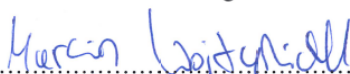
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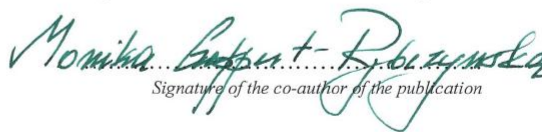
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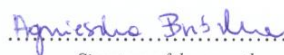
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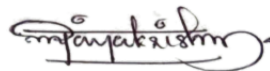
- A4. A.K. Sudhakaran Nair Valsala Kumari, M. Tarnacka, E. Kaminska, M. Wojtyniak, M. Geppert-Rybczyńska, K. Bilska, A. Brzózka, K. Kamiński, **Nanoscale dewetting and unpredictable dynamics of cyclic liquid in curved and rough nanochannels**, J. Colloid Interface Sci. 704 (2026) 139390.

My participation consisted of producing the nanostructured mesoporous membranes, performing the microscopic imaging, and visualizing the obtained data.


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My contributions to this research consisted of the following:

- **Conceptualization & Preparation:** Collecting literature data, co-developing the research hypothesis, and preparing samples.
- **Investigation:** Performing dielectric measurements on the phenyl systems and cyclic dimethylsila crown (under ambient pressure and high-compression conditions) and on DMS17C6 (under confinement).
- **Data Analysis:** Analyzing the collected data and participating in the discussion of the results.
- **Visualization:** Creating the graphs and figures for the publication.
- **Writing & Editing:** Co-editing the manuscript text, preparing responses to reviewers, and executing all necessary revisions.



Anjana Krishna Sudhakaran Nair Valsala Kumari

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6. Summary and Conclusion

The work presented in this dissertation was motivated by the need to understand how molecular mobility in soft glass-forming systems is shaped not only by temperature but also by molecular architecture, specific intermolecular interactions, pressure-induced densification, and nanoscale confinement. The investigated systems, 3P1Pal and cyclic dimethylsila crowns, served as model systems in which weak association, dipolar organization, cyclic topology, rigidity, and conformational flexibility could be examined through complementary thermal, high-pressure, and confinement pathways. Using BDS as the central experimental method to probe the molecular relaxations, complementary calorimetric, structural, spectroscopic, surface-sensitive, and simulation approaches were used to provide additional insight into the observed relaxation behavior.

The results obtained within this framework provide the following answers to the questions formulated in the research objectives:

- The dominant interaction motifs near T_g were found to depend directly on molecular architecture. In 3P1Pal, weak formyl-related dipolar correlations, aromatic interactions, and nonclassical C–H $\cdots$ O contacts contribute to transient supramolecular organization and the appearance of a D-like response. In cyclic dimethylsila crowns, where no analogous D-like mode was observed, the relaxation behavior is governed mainly by ring topology, conformational flexibility, and packing constraints.
- HP studies showed that compression is not equivalent to cooling. In 3P1Pal, pressure modified the D-like process and its separation from α -relaxation, indicating reorganization of weak supramolecular associates. In cyclic dimethylsila crowns, compression revealed topology-dependent differences in α – β dynamics, pressure sensitivity, and cooperative behavior rather than inducing new supramolecular modes.
- TPS was found to be system- and process-dependent. While the α -relaxation showed largely preserved spectral shape under compression, the α –D relationship in 3P1Pal and the α – β relationship in cyclic crowns were more sensitive to pressure, showing that different dielectric mobilities do not necessarily respond to compression in the same way.
- The comparison between α - and D-like dynamics shows that the slow D-like process in 3P1Pal cannot be assigned to classical hydrogen-bonded chain dynamics. Instead, it reflects collective dipolar fluctuations of weak, transient supramolecular associates stabilized by dipole–dipole interactions, aromatic contacts, and weak nonclassical

hydrogen bonds. High pressure further demonstrated that these weak associates can be reorganized into distinct pressure-stabilized arrangements.

- For cyclic dimethylsila crowns, the pressure coefficient of T_g , $\Delta V^\#$, and cooperative length scale (ξ) were found to be mutually connected and dependent on ring architecture. The observed trends follow the general correlation between $\Delta V^\#$ and ξ proposed for other glass-forming liquids, but the differences within the crown series indicate that cyclic topology, rigidity, and conformational flexibility modulate this relationship.
- In cyclic crowns, the behavior of β -relaxation remains more complex. CM analysis, high-pressure measurements, and confinement studies suggest that secondary dynamics in cyclic systems may contain either JG-like or more local, topology-sensitive contributions. Therefore, a universal assignment of the nature of the β -process cannot be made based on the present systems alone.
- Nanoconfinement of DMS17C6 revealed that cyclic molecular liquids cannot be treated as simple confined analogues of previously studied linear systems. Surface-sensitive investigations showed that local molecule–surface interactions may differ from expectations based on macroscopic wettability alone, and that nanoroughness does not necessarily suppress the interfacial dynamic fraction.

Overall, the dissertation shows that thermal cooling, pressure, and nanoconfinement are connected through their influence on molecular packing, density, and available free volume, but they are not equivalent routes to slow dynamics. By following the relations between α -, β -, and Debye-like processes under these different conditions, the work provides a coherent view of how molecular structure and environment control relaxation mechanisms in soft glass-forming systems. At the same time, it leaves open important questions concerning the peculiar behavior of β -relaxation under confinement, which should be addressed in future studies on systematically varied cyclic and non-cyclic glass formers, ideally by combining high-pressure and nanoconfinement approaches.

7. Literature

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8. List of scientific achievements not included in the doctoral dissertation

1. S. V. Anjana Krishna, S. Umadevi, C.D. Midhun Dominic, J. Parameswaranpillai, A. V. Asha Bhanu, J. Susan George, T. Sreedevi, S. Thomas, P. Poornima Vijayan, Biomass derived cellulose nanofiber loaded PVA-nanocurcumin coating for extending the shelf life of Mandarin oranges (*Citrus reticulata*), *Hybrid Advances* 5 (2024).
2. S. Koymeth, S. V. Anjana Krishna, S. Thomas, J. Parameswaranpillai, C.D. Midhun Dominic, J. Susan George, R.S. Reshmi, P. Poornima Vijayan, Biowaste-derived chitosan nanocomposite coatings for the preservation of banana, *Biomass Conversion and Biorefinery* 2023 14 (2023). Ministry points -70, IF- 4.1.
3. M. Tarnacka, R. Bielas, A. Krishna S V, Z. Wojnarowska, P. Maksym, D. Neugebauer, M. Paluch, K. Kamiński, The impact of architecture on the behavior of siloxane-grafted polymethacrylate, *Polymer (Guildf)*. 297 (2024). Ministry points -100, IF-4.5.
4. P. Vijayan P, P.G. Chithra, A. Krishna S V, E.B. Ansar, J. Parameswaranpillai, Development and Current Trends on Ion Exchange Materials, *Separation & Purification Reviews* 53 (2024). Ministry points -140, IF-5.6.
5. Presentation-10th International Conference meeting on complex relaxation systems 20-25 July, Barcelona, Spain.
Title of Presentation- Molecular Dynamics Investigation of Specific Interactions in 3-Phenyl-1-propanal
6. Presentation- in the 6th General Academic Seminar- Physicochemical Methods in Scientific Research-
16th of April 2025, Sosnowiec, Poland.
Title of Presentation- Molecular Dynamics Investigation of Debye Relaxation Origin in 3-Phenylpropanal.
7. Presentation- in European meeting on Physical Organic chemistry- 01– 05 June 2026, Wojcieszce, Poland.
Title of Presentation - Rigid Cage, Variable Nature: Spectroscopic Study of Phase Transitions in Adamantane-Based Active Pharmaceutical Ingredients.
8. Short-term research internship at the University of Leipzig, Germany, at the lab of Prof. Dr. Friedrich Kremer, 16 - 20 February 2026.