The Dow Chemical Company
Core R&D, Analytical Sciences
Michigan Operations
Midland, MI, 48667, U.S.A.
Florin Dan, Research Scientist
e-mail: Fdan@dow.com
phone work: +1 989-636-6299

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Review of PhD thesis: Kinetics of Ring-Opening Polymerization of Lactones and Epoxides at Various Thermodynamic Conditions by **Andrzej Dzienia**

It was conveyed to my attention that on June 1st, 2020, I was appointed by the Scientific Council of the Institute of Chemistry of the University of Silesia in Katowice to review the doctoral dissertation of Andrzej Dzienia, MA. The supervisor of this doctorate is dr hab. Miroslaw Chorazewski and the co-supervisor is dr Eng. Paulina Maksym.

The doctoral dissertation titled 'Kinetics of Ring-Opening Polymerization of Lactones and Epoxides at various thermodynamic conditions' has been elaborated in the form of a guidebook on the collection of three scientific papers and one granted patent. All included publications are in well-known scientific journals and passed the scrutiny of reviewers and editors. The dissertation contains 124 pages, including the three papers and the patent, it has been divided into three chapters, and is completed by a list of publications with the statements of co-authors on the contribution, list of references (99), and an appendix summarizing the candidate's list of publications. It is worth mentioning that the candidate is a prolific scientific author, with 18 articles published in scientific journals since 2017, which speaks greatly to his dedication to science. In addition, there is a list of other four patent applications, six oral presentations and six poster presentations at national and international scientific manifestations. Finally, Andrzej Dzienia was awarded with a grant.

In the Introduction section, the Candidate first clarifies concepts like catalyst and activator, the role of such additional substances in accelerating the desired processes, in particular polymerization reactions, and classifies them as 'internal' catalytic forces of driving the desired reactions. Then he

introduces the reader to the 'external' driving forces, e.g. heat, pressure, ultrasonic waves, microwaves, light radiation, etc., and defines the multiactivation concept as a combination of 'internal' and 'external' driving forces. The multiactivation concept is a key component in the further work included in the thesis. A special emphasis is placed on the pressure as an 'external' driving force, highlighting that High-Pressure Processing is not a high energy consuming process, because the energy is consumed mostly during the compression stage. The pressure effect is explained through the transition state theory, which correlates the reaction rate constant to the activation volume, pressure, and temperature, respectively. Here the author clarifies that the mechanistic features of a given process affects the activation volume differently, and consequently the reaction rate can be either accelerated or decelerated under high-pressure conditions, respectively. In the second part of the Introduction, a review of polymer synthesis is given. The Author distinguishes between step-growth polymerization (SGP) and chain-growth polymerization and offers examples of the most representative polymers in each class. Free radical polymerization (FRP) and reversible deactivation radical polymerization (RDRP) are comparatively discussed, with highlights of the most versatile RPDP methods, i.e. atom transfer radical polymerization (ATRP) and reversible addition and fragmentation chain transfer (RAFT), respectively. The pressure effect in assisting the free radical polymerization is critically reviewed, too. A special part is dedicated to the ionic methods, and their significance in ring-opening polymerization (ROP), including the compounds with heteroatoms in ring, such as lactones. At this point the topic is shifted toward the synthesis of biologically active polyesters, especially poly(ε-caprolactone), thanks to the use of ecologically-friendly, metal-free, catalysts alongside pressure-assisted ROP of ε-caprolactone. Finally, the production of epoxy resins is briefly reviewed. The mechanism of epoxy thermosets synthesis using amines as hardener is presented and the advantages of calorimetry to acquire data and further use of them to estimate the kinetic parameters by model-free and model fitting methods is discussed.

The first paper included in this thesis, entitled 'High pressure water-initiated ring opening polymerization for the synthesis of well-defined α-hydroxy-ω-(carboxylic acid) polycaprolactones' as well as the granted patent 'Sposób ciśnieniowej polimeryzacji ε-kaprolaktonu. *PL 232892B1*' deals with the ROP polymerization of ε-caprolactone initiated by water, under high-pressure. The Author is to be commended for selecting eco-friendly initiators and alternative route of synthesis biodegradable polymer with well-defined structure and narrow polydispersity index. To gain insights into the process

conducted in such conditions, the author makes use of Broadband Dielectric Spectroscopy (BDS). This on-line technique allows for monitoring the reaction progress but also differentiation between the polymerization and pressure-induced monomer crystallization, allowing the selection of optimal pressure range for obtaining polyester. An array of analytical techniques have been used in order to elucidate the structure of polyesters, including ^{1}H NMR, MALDI-TOF, and GPS-LASSL chromatography. It was found that in the presence of water and under high pressure, polymers of low and moderate molecular are obtained. However, under the careful selected reaction conditions, one can obtain PCL of a given molecular weight and low molecular dispersity. The NMR spectra revealed that the produced polyesters consist of telechelic carboxyl and hydroxyl end groups, which should enhance their hydrophilicity as well as both biocompatibility and biodegradability properties. Using high-pressure as an 'external' physical interaction allows for nearly complete monomer conversion and production of medical-grade polymer for biomedical applications. This means that high-pressure polymerization can be a very promising alternative method for ROP polymerization using one of the green methods reported so far, avoiding both toxic catalysts and solvents. The fact that a patent protects this method is a clever decision of the authors.

In the third paper, entitled 'Studying the catalytic activity of DBU and TBD upon water-initiated ROP of ε-caprolactone under different thermodynamic conditions' the author tries to correct some of the shortcomings of water-initiated ROP at high-pressure, namely - long times required to achieve high polymer conversions, by adding ecofriendly organocatalysts, i.e. non-nucleophilic bases DBU and TBD. One can mention that DBU is an effective organocatalyst for ROP of lactides, whereas TBD, due to its bifunctional activity, also presents high catalytic activity toward lactones and they are both nontoxic. This 'multiactivation' mode allowed for obtaining polymers with moderate molecular weight and low molecular dispersity under optimal conditions with both catalysts. However, it was found that DBU-catalyzed ROP proceeds only at elevated temperatures, close to the decomposition temperature of the catalyst, reaching around 50% monomer conversion within 24 hours. Unfortunately, at those reaction conditions, only polyesters with low M_n were produced. With TBU as catalyst, the reaction rate was much higher, even at lower temperature (323K) and almost complete monomer conversion was achieved when TBD/H_2O molar ration was higher than 1.25. However, the molecular weights of these polymers were up to 12 kg/mol with Đ = 1.39, which is far from the desired high-molecular weight PCLs. It was found that the catalytic activity of the selected organocatalysts is directly linked to the presence of water and the termination process is correlated to the catalyst/initiator ratio. To probe these interactions, the Author made use of FTIR spectroscopy. In the case of a slight excess of TBD with respect to water, the formation of TBDH$^+$ was confirmed, which interacts with water molecules via hydrogen bonds. The TBDH$^+$-H_2O complexes cannot effectively catalyze ε-caprolactone

ROP and only low monomer conversion can be reached. The same technique has been used to explain the observed catalytic activity of DBU at high-temperatures. It was concluded that the high-temperature/high pressure combination leads to possible protonation of DBU. Thus, if both protonated and non-protonated forms are present in the reaction mixture, the pair can mimic the catalytic activity of bifunctional catalysts and interact with both monomer and water, respectively. The authors propose a plausible mechanism of DBU/water activity via acid-conjugated base pair, to explain the ROP of ε-caprolactone. Finally, it is worth mentioning, that under optimal reaction conditions, one can reach a 'pseudo-living' polymerization character. This feature was evidenced by 1) linear evolution of polymer M_n with ε-CL conversion; and 2) low to moderate molecular dispersities of resulted polymers. In my opinion, hydrolytic ROP of lactams, especially ε-caprolactam, and its copolymers with ε-caprolactone at high-pressure is an open field to investigate in the future for the team.

In the paper entitled 'Direct insight into the kinetics of the high-pressure step-growth polymerization of DGEBA/aniline model system' (P4), the Author uses high-pressure calorimetry to monitor the heat of the polymerization of bisphenol-A diglycidyl ether (DGEBA) mixed with a stoichiometric amount of aniline over a wide range of pressure, p = 0.1–350 MPa, at constant temperature, 298.15 K. Calorimetry is the second technique used by the author to online monitor the progress of polymerization reaction under high pressure. Calorimetry is probably the most used technique to monitor the progress of epoxy resin cure and for kinetic modeling. The instrument records the heat flow during the whole process, including the compression and decompression stages as well as the volume change associated to compression/decompression and the shrinkage during the isobaric cure. As expected, it was found that ultimate conversion decreases with increasing pressure due to the increase in T_g of the formed polymer with pressure, which moves the system earlier in the diffusion controlled regime. Due to the low temperature, the full conversion was not achieved even under atmospheric conditions. To account for the total heat of cure, the samples exposed to pressure were further analyzed by DSC, under linear temperature ramping, from ambient temperature to 225 °C. The Author correctly identifies the Kamal kinetic model as the most suited to fit the calorimetric data, i.e a serial combination of nth order autocatalytic model. In the first step, the data are fitted to a conversion, α, equal to 1 to obtained the Kamal rates constant for the chemical process, and in the second step, the Kamal equation was modified to account for the diffusion-controlled process in the

latter stage of epoxy cure reaction. Thus, introducing the constant 'C', i.e. the maximum degree of cure, α_{max}, allows to obtain 'the real' (lit. effective) Kamal rate constants. As expected, the nth order rate constant is a function solely of n reaction order, the autocatalytic rate constant depends on both m and n parameters. Moreover, through mathematical treatment a correlation between the effective and the chemical Kamal rate constants was made via the reaction orders and maximum degree of cure. The ratio of the effective to chemical rate constants, $k_e/k_c = f(\alpha)$, where $f(\alpha)$ is the diffusion factor. To my knowledge, this is the first scientific publication in which the diffusion factor is correlated to reaction orders. However, while $f(\alpha)$ varies with conversion according to the classical Fournier or Cole diffusion factors, it is a constant in the proposed model. Thus, with diffusion-limited models of the nth order, the effective and chemical rate constants are the same since they are measured at the beginning of process when the diffusion effect is not manifested, while with the proposed equation this is true only if the reaction order is equal to 1. Analyzing the obtained rate constants, one can conclude that the benefit of pressure-assisted epoxy cure is the speed of reaction, in an exponential manner, with some expense on the final conversion. This is in agreement with the calculated activated volumes, ΔV, for both non-catalyzed and catalyzed reactions. It was found that the determined rate constants are sensitive to pressure and model dependent, resulting in different activation volumes, which fall within the range from -16 cm^3/mol to -26 cm^3/mol, which are close to those reported for the epoxide ring-opening polymerization reaction, which changes in the range between -15 cm^3/mol to -20 cm^3/mol. The reaction order parameters, m and n, were found to vary with pressure, too. However, up to 100 MPa the ratio of the two rate constants is about the same, suggesting a similar reaction mechanism. The ratio decreases at 200 MPa to become close to 1 at 350 MPa, when the rate function is almost symmetrical, and the overall reaction order becomes higher than 3, which supports the assumption of change in mechanism in this range of pressure. In this part, I would expect to see the temperature effect, the activation energy, on the overall reaction rate, too. I understand that this type of measurements are time consuming, but, at least, the temperature effect on the investigated process should be investigated by DSC at atmospheric pressure, and an overall kinetic equation given. In this context. I would like to ask the Candidate what it takes, in his opinion, to get and comprehensive kinetic equation including both the temperature and pressure effect as well as incomplete cure?

In conclusion, I assess the PhD thesis presented by Andrzej Dzienia highly favorably. Taking into account the sound scientific results, successful combination of experimental measurements, careful analysis and interpretation of variety of analytical techniques, and the elegant kinetic modelling approach, as well as potential for applications I must state that the thesis presented by Andrzej is an important contribution to our knowledge in pressure-assisted ROP. In my opinion, the presented dissertation fulfills the statutory and customary requirements for PhD theses, constitutes original

solution to the scientific problem, presents general theoretical knowledge of the PhD Candidate in polymer chemistry and demonstrates the ability for independent scientific work. Therefore, I am recommending – to the Scientific Council of the Institute of Chemistry, Faculty of Science and Technology of University of Silesia – admittance of MSc eng. Andrzej Dzienia to the next stages of the doctoral process.

<div align="center">Award request</div>

It is my pleasure to ask for a distinction of the doctoral dissertation of Mr. Andrzej Dzienia, if the statutory conditions of distinctions at the Faculty of Science and Technology, University of Silesia are met. The nomination is supported by the following arguments:

a) Skills: High-pressure chemical synthesis requires very specialized and highly skilled personnel. There are few worldwide laboratories across the globe able to do it at high scientific standards. Most of the young scientists are mastering one online technique to monitor the progress of the process. Andrzej has good command on Broadband Dielectric Spectroscopy and Calorimetry;

b) Creativity & originality: The candidate proposed an original and plausible mechanism of DBU/water activity via acid-conjugated base pair, to explain the ROP of ε-caprolactone. The modified Kamal kinetic equation for the limited conversion, correlated to the reaction order parameters, m and n;

c) Scientific prolificacy: From 2017 to the date, Andrzej has coauthored 18 scientific publications, 4 as first author, in well-recognized, peer-reviewed journals. In addition, he has four granted patents and patent applications, many oral and poster presentations and was awarded with a grant. His supervisors, mentors, and co-workers are commendable for this achievement, too.

Kind regards,

Florin Dan, PhD