Wrocław University
of Science and Technology

Department of Experimental Physics

dr hab. inż. Adam Sieradzki, prof. PWr
Deputy Dean for cooperation and promotion
Faculty of Fundamental Problems of Technology
Departament of Experimental Physics
Wrocław University of Science and Technology

Wrocław, 24.01.2022 r.

Review report of the PhD dissertation

Name of the PhD student: *Daniel Duarte*

Title of the dissertation: *Impact of the High Electric Field on the Crystallization Behavior of a Molecular Liquid, Vinyl Ethylene Carbonate*

Supervision: *dr hab. Karolina Adrjanowicz*

Institution: Institute of Physics, Faculty of Science and Technology, Silesian University

The formal basis

The report of the dissertation was commisioned by the prof. Elżbieta Stephan – Deputy Director of the Institute of Physics of the Silesian University by the formal letter from 2021.11.23. The corresponding dissertation was submitted by MSC Daniel Duarte in fulfillment of the requirements for the doctoral degree. The submitted dissertation consists of the results obtained during the ongoing SONATA BIS project, headed by dr hab. Karolina Adrjanowicz.

The dissertation consists of four three-author scientific publications, as well as an additional description constituting a guide to these works. In each paper Daniel Duarte is the first author and his independent contribution can be distinguished. Daniel Duarte has also submitted statements by the co-authors in which their individual contributions have been defined. The author also defined his individual input to each of the publication, on the basis of which his dominant contribution in their creation can undoubtedly be discerned. The author's statements are consistent with those of all the other co-authors. Therefore, the formal requirements regarding the form of the doctoral dissertation have been fulfilled. The publications constituting the doctoral dissertation of Mr. Daniel Duarte are:

HR EXCELLENCE IN RESEARCH

Wrocław University
of Science and Technology

Faculty of Fundamental Problems
of Technology

Department of Experimental Physics

Wybrzeże Wyspiańskiego 27
50-370 Wrocław, Poland

T: +48 71 320 25 79
F: +48 71 328 36 96

wppt.kfd@pwr.edu.pl
www.pwr.edu.pl

REGON: 000001614
NIP: 896-000-58-51
Bank Zachodni WBK S.A.
37 1090 2402 0000 0006 1000 0434

Wrocław University
of Science and Technology

Department of Experimental Physics

A1. Daniel M. Duarte, Ranko Richert, and Karolina Adrjanowicz, *Frequency of the AC Electric Field Determines How a Molecular Liquid Crystallizes*, J. Phys. Chem. Lett. 2020, 11, 10, 3975–3979

A2. Daniel M. Duarte, Ranko Richert, and Karolina Adrjanowicz, *Watching the Polymorphic Transition from a Field-Induced to a Stable Crystal by Dielectric Techniques*, Cryst. Growth Des. 2020,20, 5406-5412

A3. Daniel M. Duarte, Ranko Richert, and Karolina Adrjanowicz, *AC versus DC field effects on the crystallization behavior of a molecular liquid, vinyl ethylene carbonate (VEC),* Phys. Chem Chem. Phys., 2021, 23, 498

A4. Daniel M. Duarte, Ranko Richert, and Karolina Adrjanowicz, *Bimodal Crystallization Rate Curves of a Molecular Liquid with Field-Induced Polymorphism*, J. Molecular Liquids, 2021, 342, 117419

Mr. Daniel Duarte declared that in all the presented papers, he acquired, analysed and interpreted the data and wrote the manuscript.

Evaluation statement

Controlled crystallization is undoubtedly an important aspect of materials science in actual pharmaceutical applications. Controlling of crystallization parameters is crucial to avoid the transformation to an ordered solid phase when supercooled or glassy materials are desired. Moreover, understanding of crystallization process allows to control the polymorphic phases which may often exhibit various physico-chemical properties. One of the investigation manner is the controlled crystallization utilizing the external electric field application in supercooled or glassy materials. Despite widespread interest, however, many aspects of controlled crystallization are still unclear. Just to mention such an issue as predicting how an electric field parameters affects crystallization. The presented dissertation, based on the results obtained by the dielectric spectroscopy technique, deals with solving this problem for pure dipolar liquid, vinyl ethylene carbonate (VEC).

In the presented doctoral dissertation, three main approaches to the problem of the influence of the electric field on the parameters of VEC crystallization and its stability can be distinguished:

1. Effect of high ac field on crystallization (articles A1 and A3)
2. Effect of electric field on crystallization rate curves (A4)
3. Stability of the field-induced polymorph (A3)

In all the three approaches some special paths (called protocols) in the temperature-time diagram were used, where the variables were the frequency and the magnitude of the applied alternating electric field.

To understand the way the parameters of the applied external electric field influence crystallization process, two different thermal protocols (*A* and *B*) were used. In protocol *A* the changes in the crystallization of VEC, described in terms of the crystal volume fraction were analyzed. It was

HR EXCELLENCE IN RESEARCH

Wrocław University
of Science and Technology

Faculty of Fundamental Problems
of Technology

Department of Experimental Physics

Wybrzeże Wyspiańskiego 27
50-370 Wrocław, Poland

T: +48 71 320 25 79
F: +48 71 328 36 96

wppt.kfd@pwr.edu.pl
www.pwr.edu.pl

REGON: 000001614
NIP: 896-000-58-51
Bank Zachodni WBK S.A.
37 1090 2402 0000 0006 1000 0434

assumed that, two limiting values of ratio between the crystal volume and the total volume V_{cry}/V_{total}, 0 and 1, denote pure liquid and fully crystallized material, respectively. For both the fixed magnitude of electric field or applied frequency the characteristic step-like on the normalized volume vs time can be observed. In the investigated time scale such a behaviour occurs just for some critical frequency and magnitude of field ranges. The author observed in Fig. 11a that, for frequencies higher than 100 Hz, no crystallization was detected and then stated that crystallization is induced in the presence of the altered field when a frequency value of approximately 18 Hz is reached, calling it as a threshold. Then, the measurements for different values of the electric field for protocol A (Fig 11 b) were performed for a constant value of the frequency equal to 56.2 Hz. Moreover, the analysis of the time constant obtained from the Avrami relation, led the author to the conclusion that the threshold is located in the frequency range of 20 to 50 Hz. Thus, the question arises, what does the author understand by the notion of a threshold? In my opinion, this is inconsistent with the commonly used definition in which it is described as a value that determines the boundary (limit) of an effect. At the same time, I am aware that the threshold should be defined for the given range of measured parameters, the time scale, in particular.

In my view, an interesting part of the research of the influence of an alternating electric field on crystallization presented in protocol *A* is the analysis of the morphology of crystal growth. The interpretation was based on the analysis of Avrami parameters, which contain the information on the arrangement of the molecular systems in crystalline structures. It was shown that the morphology is sensitive to the frequency and amplitude of the ac field. At low amplitude or high frequencies, the system prefers to grow as spherical crystallites with sporadic nucleation events. While, at low frequencies or high field magnitude, the crystallites adopt a more rod-like morphology and grow from instantaneously formed nuclei.

The effect of a high ac field on the nucleation of VEC was explored in protocol *B*. It was shown that crystallization speeds up when the ac field is applied during the nucleation period. The high ac field have an impact on the crystallization of VEC only when it is consistent with the time scale of reorientation of much bigger structures like crystal nuclei. The interesting conclusion from protocol *B* is that the nucleation rather than the crystal growth rate is mainly affected at high electric fields.

Influence of the electric field on the overall crystallization rate for VEC was analyzed using the protocol *C*, in which different magnitude or frequencies of the ac or dc field were applied close to T_g. Similarly, as demonstrated in the previous protocols, the crystallization data were analyzed using the Avrami approach. It was observed that, the location of the overall crystallization rate maximum corresponding to the ordinary VEC polymorph remains unaffected by the electric field. It was observed, however, that the rate of crystallization slightly increases with increasing field size. Static

HR EXCELLENCE IN RESEARCH

Wrocław University
of Science and Technology

Faculty of Fundamental Problems
of Technology

Department of Experimental Physics

Wybrzeże Wyspiańskiego 27
50-370 Wrocław, Poland

T: +48 71 320 25 79
F: +48 71 328 36 96

wppt.kfd@pwr.edu.pl
www.pwr.edu.pl

REGON: 000001614
NIP: 896-000-58-51
Bank Zachodni WBK S.A.
37 1090 2402 0000 0006 1000 0434

electric fields influence VEC crystallization in the same way as high alternating electric fields of very low frequency.

The last issue discussed in the dissertation concerned the stability of the field-induced polymorph of VEC. To deal with this problem two different thermal protocols were utilized. The first protocol, protocol *D*, aims to induce the nucleation of the regular polymorph via decreasing the temperature to 173 K. In the second protocol, protocol *E*, in order to avoid the formation of the regular polymorph, the liquid sample was cooled down straight to the crystallization temperature, 198 K, without any further cooling to the temperature region close to T_g. By selecting the temperature protocol introduced before crystallization, the field-induced crystals of VEC can be obtained either with high polymorphic purity or mixed with seed crystals of the ordinary stable polymorph, depicted as polymorphic phase transition. In contrast, when the field-induced crystal structure is obtained in the absence of the ordinary form, no sign of any phase transition is observed. Moreover, the inclusion/exclusion of the electric field after crystallization has no other effect on the transformation kinetics or polymorph stability.

The unpleasant duty of the reviewer is to point out the shortcomings in the work. Nevertheless, I did not find any significant errors in the submitted dissertation. The only general question arising is the one concerning the definition of strong and weak electric fields. Can such a classification of electric fields be defined in the investigated materials?

Final evaluation statement

This dissertation represents a great deal of work. The results are well presented and their interpretation is at a high scientific level. I really appreciate the candidate expertise in the field of materials characterization. the presented research is of the international standard.. This thesis is ready to be defended orally and certainly meets the requirements laid down for the degree of Ph.D. in physics.

HR EXCELLENCE IN RESEARCH

Wrocław University
of Science and Technology

Faculty of Fundamental Problems
of Technology

Department of Experimental Physics

Wybrzeże Wyspiańskiego 27
50-370 Wrocław, Poland

T: +48 71 320 25 79
F: +48 71 328 36 96

wppt.kfd@pwr.edu.pl
www.pwr.edu.pl

REGON: 000001614
NIP: 896-000-58-51
Bank Zachodni WBK S.A.
37 1090 2402 0000 0006 1000 0434

Politechnika Wrocławska

dr hab. inż. Adam Sieradzki, prof. ucz.
Katedra Fizyki Doświadczalnej
Wydział Podstawowych Problemów Techniki
Politechnika Wrocławska

Wrocław, 21.01.2022 r.

Rada Instytutu Fizyki
Uniwersytetu Śląskiego
w Katowicach

Wniosek o wyróżnienie pracy doktorskiej p. mgr Daniela Duarte

Niniejszym wnioskuję o przyznanie wyróżnienia przedłożonej mi do oceny rozprawy doktorskiej pana magistra Daniela Duarte, pt: *„Impact of the High Electric Field on the Crystallization Behavior of a Molecular Liquid, Vinyl Ethylene Carbonate"* wykonanej w Instytucie Fizyki Wydziału Nauk Ścisłych i Technicznych Uniwersytetu Śląskiego pod kierunkiem dr hab. Karoliny Adrjanowicz.

Tematyka badawcza w/w rozprawy doktorskiej stanowi ważny element światowych badań nad kontrolą procesu krystalizacji z prostych cieczy molekularnych. Krystalizacja ta ma ogromne znaczenie m.in. w zastosowaniach farmaceutycznych, chemii materiałowej czy biotechnologii. Dzieje się tak, ponieważ zachowanie krystalizacyjne determinuje najbardziej krytyczne właściwości fizyczne, chemiczne, a nawet biologiczne produktu końcowego. Ostateczne właściwości materiału krystalicznego będą zależeć od stopnia krystaliczności, polimorfizmu, wielkości i jakości otrzymanych kryształów.

Na wyróżnienie zasługuje szczegółowe podejście do problemu kontroli krystalizacji w pole elektrycznym oraz wysoki poziom interpretacji danych otrzymanych metodą spektroskopii dielektrycznej zarówno w domenie temperaturowej jak i częstotliwościowej. Potwierdzeniem bardzo dobrego warsztatu badawczego zaprezentowanego w rozprawie doktorskiej jest lista zaprezentowanych 4 publikacji w renomowanych czasopismach naukowych.

Biorąc powyższe argumentacje pod uwagę, jako recenzent z pełną odpowiedzialnością stwierdzam, że całokształt prac badawczych pana mgr Daniela Duarte zasługuje na wyróżnienie.

z poważaniem,

HR EXCELLENCE IN RESEARCH

Politechnika Wrocławska
Wybrzeże Wyspiańskiego 27
50-370 Wrocław
www.pwr.edu.pl
REGON: 000001614
NIP: 896-000-58-51
Bank Zachodni WBK S.A.
37 1090 2402 0000 0006 1000 0434