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Review of the doctoral dissertation
entitled "***Impact of the High Electric Field on the Crystallization Behavior of a Molecular Liquid, Vinyl Ethylene Carbonate***"
by **M.Sc. Daniel Duarte**
under the supervision of **dr. hab. Karolina Adrjanowicz, assoc. prof.**

Doctoral dissertation of **M.Sc. Daniel Duarte** "***Impact of the High Electric Field on the Crystallization Behavior of a Molecular Liquid, Vinyl Ethylene Carbonate***", under the supervision of dr. hab. Karolina Adrjanowicz, assoc. prof., was performed at the August Chełkowski Institute of Physics, Faculty of Science and Technology, University of Silesia in Katowice. The doctoral thesis was supported by the National Science Center (NCN) under the SONATA BIS project "*Zachowanie materiałów formujących stan szklisty w obecności silnego pola elektrycznego – dynamika w obszarze odpowiedzi nieliniowej i indykowane zewnętrznym polem elektrycznym zmiany w tendencji do krystalizacji*", coordinated by dr. hab. Karolina Adrjanowicz. Mr. Daniel Duarte is the co-author, in addition to the four articles constituting this doctoral dissertation, a total of seven scientific papers published in very good journals (listed in the Journal Citation Report) for which the value of the Impact Factor is within the range of 3.430 to 6.710. The results of the research, being the subject of the doctoral dissertation, were presented at international conferences in the form of a poster and an oral talk. Mr. Duarte received an award for the best oral talk presented. The dissertation submitted for review consists of a total of 83 pages: including a guide (ten unnumbered pages and pages 1-44), four scientific articles presented on pages 45-69 and the author's and co-authors' statements shown on pages 70-73. The thesis contains 35 drawings, of which 9 are single-panel and 13 are two-panel ones.

The dissertation consists of: an abstract in English (two pages), an abstract in Polish (two pages, called *Streszczenie*), contents (one page), motivation (two pages, pages 1-2 of this scientific work), the aim of the work (one page, page 3), list of publications constituting the thesis (one page, page 4), other scientific activity containing a list of other published scientific papers and conference presentations on which research results were presented (one page, page

5), introduction containing three subsections (as chapter 1, pp. 6-17), chapter 2 in which the results are collected and a discussion conducted, consisting of three subsections (pp. 18-38), chapter 3 containing conclusions and summarizing the results obtained (pp. 39-41), a list of references (pp. 42-44) – containing 40 positions (only 9 articles cited there they were published before 2000, and they are references to the original works, for example, articles by M. Avrami), enclosed four papers being part of the thesis, namely: (*i*) article entitled "*Frequency of the AC Electric Field Determines How a Molecular Liquid Crystallizes*" by D.M. Duarte, R. Richert, K. Adrjanowicz, published in J. Phys. Chem. Lett. **11** (2020) 3975-3979 (hereinafter referred to as [A1], labeling adopted from reviewed dissertation) on pp. 46-50 of the thesis; (*ii*) article entitled "*Watching the Polymorphic Transition from a Field-Induced to a Stable Crystal by Dielectric Techniques*" by D.M. Duarte, R. Richert, K. Adrjanowicz, published in Cryst. Growth Des. **20** (2020), 5406-5412 (as [A2]) on pp. 51-57; (*iii*) article entitled "*AC versus DC field effects on the crystallization behavior of a molecular liquid, vinyl ethylene carbonate (VEC)*" by D.M. Duarte, R. Richert, K. Adrjanowicz, published in Phys. Chem. Chem. Phys. **23** (2021) 498 (as [A3]) on pp. 58-64; (*iv*) article entitled "Bimodal Crystallization Rate Curves of a Molecular Liquid with Field-Induced Polymorphism" by D.M. Duarte, R. Richert, K. Adrjanowicz, published in J. Mol. Liq. **342** (2021) 117419 (as [A4]) on pp. 65-69, and the author's statement (page 71) and statements of two co-authors – dr. hab. Karolina Adrjanowicz (p. 72) and dr. hab. Ranko Richert (page 73). The doctoral thesis is written in English, except for *Streszczenie* (in Polish).

DESCRIPTION OF THE THESIS:

The motivation of the reviewed thesis, according to the Author of the scientific work, was, inter alia, the presentation of an in-depth description of how the high amplitude electric field (alternating or direct ones) affects the process of crystallization of simple molecular materials. Here, the term "simple" means compounds having a simple molecular structure. Mr. Daniel Duarte strived the presented articles [A1-A4] and the doctoral thesis would be, in some sense, a "comprehensive guide" that can stimulate future experiments on how a high-amplitude electric field can be applied to control the crystallization of various molecular compounds. In my opinion, the reviewed doctoral dissertation is not only a kind of "a guide" or a detailed report on the numerous well-planned experiments but also a valuable scientific work presenting the results obtained and describing the so far poorly understood influence of the electric field on the process of crystallization, nucleation and crystal growth, as well as a field induction of a new polymorph of the material under study. The main goals of the reviewed doctoral thesis are, inter alia; characterization of the influence of electric fields, caused by an alternating current with high voltage amplitude and different frequencies (value of the current/voltage changes like a sine function), at various temperatures lower than the melting temperature and higher than the vitrification temperature (glass transition temperature); comparison of crystallization processes carried out at different temperatures in the presence of an alternating or direct electric field (with high amplitude); investigating whether the external electric field has an influence on the process of nucleation and crystallite growth and whether it is possible to induce a formation of a new polymorph by applying an electric field (alternating or direct) and how stable is the electric field-induced polymorph. Investigating the stability of the new form of molecular compounds is of key importance, inter alia, in the pharmaceutical industry. New stable phases of medicines should be more soluble (in water, in gastric acid, etc.) and have better bioavailability. The topic realized by Mr. Daniel Duarte is very interesting, it fits perfectly into the developed directions of science research (not only from a cognitive point of view, but also from a possible application), and, what is worth emphasizing, exploring the so far poorly known area of science, which is a process of crystallization and induction of a new polymorph in the presence of an external electric field. The motivation and the aim of the doctoral thesis are presented in detail in the chapters *Motivation* and *The aim of the thesis*, respectively.

The first chapter, entitled *Introduction*, introduces a potential reader to the topic of the dissertation. Mr. Daniel Duarte described the properties of a glassy state (within subsection *1.1. Glass Transition*), and various methods of obtaining the glassy state (the Author focuses on a glass of the isotropic liquid phase, which may be obtained in the investigated molecular material). In the second subsection, entitled *Crystallization* (subsection 1.2), the Author describes, in detail, the process of crystallization, nucleation, and growth of crystallites, the effect of applying an electric field on the crystallization process (based on literature), and the possible application of this process in the food industry or material engineering. The third section, entitled *Dielectric Spectroscopy* (subsection 1.3), describes the Broadband Dielectric Spectroscopy (BDS) method in detail, and the behavior of polar materials in external electric fields (direct and alternating ones). Moreover, this subsection introduces a reader to the arcana of dielectric response measurements not only for the standard procedures used in the BDS method but also with the use of strong electric fields (high amplitude electric fields). All the mentioned subsections are richly provided with citations to carefully selected literature positions. Unfortunately, the discussed subsections contain minor editorial errors (summarized on pages 7-10 of this review). However, at this point, it should be emphasized that the aforementioned editorial errors do not reduce the scientific importance of the presented doctoral thesis.

Chapter 2, entitled *Results and Discussion*, consists of three subsections and describes the experiments carried out for various external conditions, i.e. for different crystallization temperatures with or without an external electric field, and with the use of various ways of reaching a crystallization temperature, i.e. cooling from the isotropic liquid phase directly to the desired/planned crystallization temperature or a temperature close to the vitrification temperature and heating to the desired/planned crystallization temperature. This chapter is the core of the reviewed thesis. It shows the results published in [A1-A4]. As the experimental material, Daniel Duarte, M.Sc., chose vinyl ethylene carbonate (VEC), which is a very good glassformer.

In subsection 2.1, entitled *Effect of High AC Field on Crystallization*, Mr. Daniel Duarte described the influence of the electric field on the crystallization of the polar molecular compound VEC. He described two procedures, called “protocols”, for measuring the dielectric response, hereinafter referred to as protocol “A” and protocol “B”, for simplicity. The conclusions presented in this subsection were published in [A1] and [A3]. For protocol “A”, the sample from the isotropic liquid phase is cooled directly to 198 K (27 K above the vitrification temperature). At this temperature, crystallization takes place in the presence of an external electric field (with a high amplitude, where several selected electric field amplitudes were used, up to 180 kV/cm, and frequencies from 56.2 mHz to 10 kHz). Then the sample is heated to 243 K (to an initial temperature). The use of such measurement procedure allowed the Author to determine not only a range of time needed to get a fully crystallized sample at 198 K as a function of the amplitude and frequency of the external electric field but also, after adjusting the Avrami equation, to calculate the characteristic crystallization time τ_{cry} (or its inverse – the crystallization rate k) as well as the Avrami coefficient n depending on the dimensionality and geometry of the crystal growth. An important conclusion resulting from the described protocol is the dependence of the characteristic crystallization time and the coefficient n on the amplitude of the external electric field and its frequency. Namely, for low frequency values (tending to 0 Hz) or for high values of the external electric field amplitude (higher than 150 kV/cm), the characteristic crystallization time is one order of magnitude lower than for high frequency values (higher than about 100 Hz) or for a low external electric field amplitude (less than about 50 kV/cm). Moreover, for higher values of the characteristic crystallization time, the coefficient n is about 3.6, which indicates the spherical growth of the crystallites. While, for lower values of the characteristic crystallization time, the coefficient n tends to the value of 1.5, suggesting a rod-like morphology and growing from instantaneously formed nuclei. A very important conclusion, presented by Mr. Daniel Duarte, is also to show an influence of amplitude and frequency of the external electric field on obtaining a new polymorphic form, called '(electric) field-induced polymorph'. As it has been shown for a low value of the electric field amplitude (560 mHz for a field of 80 kV/cm) or a strong electric field (for 130 kV/cm even for a frequency of 56.2 Hz) it is possible to obtain only the polymorphic form, with the melting temperature about 208.5 K (about 19 K lower than the melting point of an "ordinary" polymorph). However, for high frequencies (56.2 Hz for an electric field of 80 kV/cm) or low values of the electric field amplitude, only the "ordinary" polymorph is obtained (the same as obtained for crystallization without an external electric field). It is also possible to obtain a mixture of both polymorphs. It is worth noting here, which, unfortunately, has not been described in detail in the thesis, that the stability of the mixture of both forms, as well as the percentage content of the individual components of the mixture, strictly depends on the value of both parameters of the external electric field – its amplitude and frequency. Measurements were made for electrodes made of stainless steel and titanium. The material from which the electrodes are made slightly affects the values of the parameters obtained, i.e. the characteristic crystallization time as well as the dimensions and geometry of the crystallization process. The next described procedure (protocol "B") consisted of cooling the sample from 243 K to a temperature 2 K higher than the vitrification temperature (cooling with the high rate), switching on an external electric field with various values of amplitudes (130 or 180 kV/cm) and frequency (10 or 30 mHz) for one hour. Then the sample was heated to 198 K, at this temperature crystallization of the sample was expected. Finally, the slow heating rate was applied to reach 243 K. The BDS method was used to observe the behavior of the sample in individual steps of the protocol used. As shown for the 10 mHz frequency (for both values of the electric field amplitudes), only the electric field-induced polymorph was obtained. While for the frequency of 30 mHz – only an "ordinary" polymorph was present. In the reviewed subsection, the Author showed how the amplitude and frequency of the applied external electric field affect the kinetics of crystallization and the morphology of growing crystallites. In addition, Mr. Daniel Duarte has shown that it is possible to 'interfere' with the "end product" – exposing the VEC sample to alternating electric fields with a certain amplitude or frequency value not only induces crystallization but also favors the formation of a new, so far unobserved, polymorph.

Subsection 2.2, entitled *Effect of Electric Field on Crystallization Rate Curves*, presents conclusions published in [A4]. The described measurement procedure – protocol "C" – is constructed as the protocol "B" with one exception – after the sample was kept for an hour at 173 K in the presence of an external alternating electric field with different amplitude (100, 160 kV/cm) and frequency (10 mHz, 100 mHz, 1 Hz) or a direct electric field (with an amplitude of 100 or 200 kV/cm), it was heated up to various temperatures, ranging between 193 K and 223 K, at which crystallization was expected. For external electric fields for frequencies lower than 100 mHz it is possible to obtain an electric field-induced polymorph. Therefore, two maxima of the crystallization rate are observed. The rate of crystallization increases when the amplitude of the external (direct or alternating) electric field increases (for a fixed value of frequency) or when the frequency of the electric field decreases (for a fixed value of electric field amplitude). However, the value of the parameter *n*, describing the dimensionality and the geometry of the crystallization/crystallite growth process, is only significantly influenced by the value of the external electric field amplitude – with the increase of the aforementioned amplitude, the value of the parameter *n* increases. The studies of the dielectric response of VEC for a slow heating rate (of 1 K/min) from temperatures at which complete crystallization was expected to 243 K bring very important information. In the case of the absence of an external electric field and for external electric fields with a high frequency value, i.e. 1 Hz (there is no annotation in the thesis "and higher frequencies"), only one melting process was observed for selected crystallization temperatures – characteristic for the "ordinary" polymorph (at 227 K). However, for external electric field frequencies lower than 100 mHz and crystallization temperatures lower than 208 K, i.e. for 193 K, 198 K, and 203 K, an additional melting process was observed at 208 K – being a characteristic melting temperature of the electric field-induced polymorph. Due to the presence of crystallites of the "ordinary" polymorph (the volume of which depends on the amplitude and frequency of the external electric field, as well as the crystallization temperature), further heating shows the melting process at 227 K. It is necessary to emphasize the carefully selected conditions for conducting the experiment so that to avoid, among other, burning of the sample. This proves that Mr. Daniel Duarte has mastered the experimental workshop very well.

The last subsection – *2.3. Stability of the Field-Induced Polymorph* – contains the research results presented mainly in [A2]. In this subsection, the stability of a new polymorph induced by an electric field is described. For this purpose, Mr. Daniel Duarte proposed two protocols. The protocol "D" consisted of very fast cooling of the sample (with a temperature rate of about 10 K/min, information from [A2]) from 243 K to a temperature of 2 K higher than the vitrification temperature, and then heating it to the crystallization temperature of 198 K, in which an external electric field with an amplitude of about 80 kV/cm was turned on with a frequency of 5.62 Hz (for an alternating field) or 0 Hz (for a direct field). After the crystallization process was completed, the sample was annealed with or without an external electric field (with an amplitude of about 80 kV/cm and a frequency of 5.62 Hz) for some time up to 72 hours. The crystallized sample was then slowly heated to 243 K. By planning another protocol, called protocol “E”, Mr. Daniel Duarte wanted to avoid the possibility of obtaining an “ordinary” polymorph. Thus, the VEC sample was cooled quickly (as in the previous protocol with a rate of about 10 K/min) straight to a crystallization temperature of 198 K. Further steps remained the same as in the protocol “D”. At all levels of the planned protocols, the Author used the BDS method to measure the dielectric response of the system. Mr. Daniel Duarte showed that an electric field-induced polymorph can transform over time into a stable “ordinary” VEC crystal. Depending on the external conditions before the crystallization process, an electric field-induced VEC crystal can be obtained as a crystal composed of an electric field-induced polymorph only – the protocol “E” used, bypassing temperatures close to the vitrification temperature – or as a mixture of both polymorphs (protocol “D”). In that case, a polymorphic transition occurs. It is important, and it was strongly emphasized by the Author, that no signs of changes between different polymorphic forms are observed when the electric field-induced crystal structure is obtained in the absence of the “ordinary” polymorph. Leaving the electric field on or switching it off just after crystallization does not affect the kinetics of transformation and the stability of the polymorph.

The last chapter – chapter 3 entitled *Conclusions and Summary* – contains a summary of the obtained results, which are: (*i*) an in-depth description of the influence of the amplitude and frequency of the external electric field (in the case of an alternating field of both quantities, and the case of a direct field – only the amplitude) on the crystallization process and morphology of a crystallite growth of the VEC molecular material; (*ii*) showing that high-amplitude external electric fields (and in the case of alternating fields with correspondingly low frequencies) mainly affect the nucleation and not the crystal growth rate; (*iii*) through the selection of various measuring protocols, Mr. Daniel Duarte demonstrated that it is possible to obtain a VEC crystal composed only of an electric field-induced polymorph. It is very important from the possible application nature of the procedures described, which opens the way to the search for new polymorphs of other substances (for example medicines or compounds used in the food industry) more stable or better absorbed by living organisms; (*iv*) provide clear evidence from experimental data showing the effect of an external electric field (mainly of high amplitude) on the overall crystallization kinetics over a wide temperature range for a molecular system with polymorphism induced by an electric field; (*v*) stating that transformation from an electric field-induced polymorph to an “ordinary” polymorph can only occur in the presence of nuclei of a stable “ordinary” polymorph. If there are no “ordinary” polymorph nuclei in the obtained sample volume, then the transition between the polymorphic forms of VEC cannot be observed; (*vi*) Mr. Daniel Duarte also showed that dielectric spectroscopy can be used (in real time) to observe not only the transition between various polymorphs but also to describe the behavior of materials (under study).

The reviewed doctoral thesis proves that Daniel Duarte, M. Sc., has mastered the research technique, as well as the methods of analyzing results obtained and their interpretation. Planning of the individual measuring protocols, analyzing and interpreting the experimental data, and clearly presenting them, proves that Daniel Duarte, M.Sc., has mastered the researcher's workshop at an advanced level, which is necessary for the implementation of multi-threaded scientific projects. It is impossible not to mention the high substantive level of the issues discussed in the doctoral thesis. Undoubtedly, the commitment of the supervisor – dr. hab. Karolina Adrjanowicz, associate professor, from the excellent school of prof. dr. hab. Marian Paluch, had a significant impact here.

CRITICAL NOTES AND SOME QUESTIONS:

Positively evaluating the doctoral thesis, I have to point out a few critical remarks, which are the editorial errors and not the substantive ones. They should be understood not as allegations for the doctoral thesis but as the guidance for a further improvement of the editorial workshop. The errors and mismatches found are drawbacks of various importance. **(I)** There are very rare misprints/misspellings or imprecise sentences in the thesis, as: (1) in *Streszczenie* (in Polish, in the last paragraph on the first page of this summary) it is "*Jest ono związane z obecnością odmiany polimorficznej indukowanej polem o niższej temperaturze topnienia…*". This sentence, without raising any doubts, could be: "*Jest ono związane z obecnością odmiany polimorficznej o niższej temperaturze topnienia indukowanej polem…*"; (2) p. 10, there is „$\mu E = k_B T$" and it should be „$\mu E \ll k_B T$"; (3) p. 11 there is: "*In the absence of an applied electric field, polar molecules are randomly oriented*". A phase to which this sentence refers should be indicated, because in an ordered crystal phase, even without an external electric field, molecules are oriented; (4) p. 17, Fig. 7 – used colors of the real and imaginary parts of the dielectric permittivity as a function of frequency should be described; (5) p. 18, the first sentence is, being a mental shortcut probably: "(...) *the properties of the external electric field can influence* (...)". A potential reader may have problems with understanding what properties of the electric field are mentioned (it should be indicated "amplitude" and "frequency"); (6) p. 22, there is written: "(...) *the* [*characteristic* – own note] *crystallization times analyzed as a function of the field magnitude (…) also follow an S-shaped dependence. With increasing the magnitude of the applied ac field, the crystallization rate will increase. However, at some point, it also saturates. Thus, the two limiting values of* τ_{cry} [*characteristic crystallization time* – own note] *for VEC are* (…) ". The first and the last sentences cited describe the dependence of the characteristic crystallization time, while the intermediate sentences refer to the crystallization rate. When discussing the data shown in Figure 12 (showing the dependence of the characteristic relaxation time on frequency and amplitude of the external electric field), a potential reader should not meet with sentences describing once τ_{cry} and once *k*; (7) p. 25, there is: "(…) *the lower the frequency or the higher the magnitude of the ac field, the large the volume fraction* (…)", and it should be: "(…) *the lower the frequency or the higher the magnitude of the ac field, the larger the volume fraction* (…) "; (8) p. 25, Mr. Daniel Duarte defines a polymorph obtained in a "traditional" manner (without an external electric field) in a sentence: "*Therefore, it is termed in this thesis as the ordinary or low-field polymorph*" as "*ordinary* *polymorph*" and "*low-field polymorph*". Unfortunately, in the next sentence a potential reader may find the third designation for this polymorph as "*high-temperature polymorph*", and in the description of Fig. 26 (and on the following pages) – also as "*regular polymorph*". It would be better if all designations for a given polymorph were collected in one sentence; (9) p. 33, the caption under Fig. 19, is "245 K" and it should be "243 K"; (10) pp. 34 and 36-37 (8 times) it is written "t_w" and it should be "t_{wt}"; (11) p. 37, Fig. 22 (b) there is "$T_{m,m}$" and it should be "T_{m2}"; (12) p. 38, there is "*Switching the field on/on* (...)" and it should be "*Switching the field on/off* (...)";(13) p. 45 there is "*Bimadal*" and should be "*Bimodal*"; (14) p. 48 (p. 3977 in [A1]) there is "*On the contrary, a field of* E_{rmf} *= 180 kVcm*$^{-1}$ (...) *see Figure 5b*", and it should be "*On the contrary, a field of* E_{rmf} *= 130 kVcm*$^{-1}$ (…) *see Figure 5b*"; (15) the page 500 of [A3] is not included. The above-mentioned page discusses the measurement protocol omitted in the thesis, but it should be noted that this page was omitted; (16) p. 66 (p. 2 in [A4]) in the last paragraph of chapter 3 the Avrami equation (Eq. (4)) is missing. **(II)** The thesis also contains some information discrepancies given in individual sentences, namely: (1) p. 7, Fig. 1 and the Fig. 1 caption: on the figure there is shown two values of vitrification temperatures $T_{g(1)}$ and $T_{g(2)}$, while under the figure the glass transition temperature is described only as T_g; (2) p. 11, there is: "(…) *[BDS technique] analyzes the cooperative movements of molecules in (...) a wide range of temperature 433 K to 673 K*". I think that the Author should indicate a temperature much lower than 433 K (as he himself shows the results for temperatures around 171 K); (3) last paragraph on p. 16 – Mr. Daniel Duarte described the behavior of the real and imaginary part of the dielectric permittivity, ending this paragraph with the sentence "*This is also demonstrated in Figure 7*". Unfortunately, Fig. 7 does not clearly show the behavior of the above mentioned quantities depending on the temperature/phase; (4) p. 19 and later pages – Mr. Daniel Duarte used the "DS" (*Dielectric Spectroscopy*) and "BDS" (*Broadband Dielectric Spectroscopy*) to denote the technique of dielectric response measurements – the nomenclature should be uniform inside the thesis; (5) p. 22, Fig. 12 – the abbreviations "SS" and "Ti" were used to denote the electrodes used for the measurements, but they are not explained. On the next page, a potential reader can find "*Different electrode materials, titanium and stainless steel were used* (...)". It is worth mentioning that instead of "and" it was better to use "or" because mixed types of electrodes were not used; (6) p. 29, Fig. 16 (protocol "C") – there is missing the crystallization temperature 193 K; (7) p. 32 and next pages – to denote the melting temperature of an electric field-induced polymorph the abbreviation T_{m2} was used, but on the previous pages one can find $T_{m,2}$, and for the melting of the "ordinary" polymorph – T_{m1}, but on the previous pages one can find $T_{m,1}$. The used abbreviations for the same temperatures should be uniform within the text of the thesis; (8) p. 35, there is: "*As a reference, the same experiment was also performed in the absence of a high electric field* (...) *(~ 0 kV/cm)*". The same value of the electric field is used in Fig. 2, p. 53 ([A2], p. 5408). However, in Figure 21(a) the same measuring electric field is described as "*10 kV/cm*" (full red circle). A potential reader can find that the measuring fields are smaller than 16 kV/cm and can be treated as zero one. Would not it be better to introduce the abbreviation for the standard value of the measuring field as $E_{meas.}$ and use it consistently within the thesis? **(III)** Preparing of some figures should be more careful: (1) General remark – Daniel Duarte, M.Sc., uses large markers to show measured or calculated values/quantities so that they often overlap with others and do not allow for in-depth analysis of the presented data; (2) p. 15, Fig. 6 (BDS measuring cell shown): individual elements should be indicated/described on the figure; (3) p. 21, Fig. 11; p. 31, Fig. 17 – a comma is used instead of a point, on the vertical axis, as a separator for the integer and the fractional part; (4) p. 32, Fig. 18(a) – some symbols used: full brown hexagon (for measurements for 100 kV/cm, 1.0 Hz) and full olive star (for measurements for 160 kV/cm, 1.0 Hz), which are not visible in the presented figure at all. **(IV)** There are also minor substantive errors: (1) p. 31, Fig. 17 – in the description of the figure there is "*The characteristic time of crystallization*", while the figure shows the dependence of the crystallization rate *k* – therefore it should be "*The crystallization rate*"; (2) p. 35, Fig. 20 – in both figures the notation "$80\ kV_{rms}/cm$", where "*rms*" means "*root-mean-square (amplitude)*" is incorrectly used! Here "*V*" stands for the **volt unit**, not a voltage "*V*", and a unit, such as a volt, has the same meaning for instantaneous or average value, without any subscripts!

After reading the doctoral thesis submitted for review, several questions arise. Namely: (1) p. 21, there is information that the Avrami equation has been fitted to the data obtained, but any fitted curves were not shown on, for example, Fig. 11. What are the fits of the Avrami equation to the experimental data? (2) p. 23, Fig. 12 and p. 24, Fig. 13 – it can be seen that the electrode material (SS or Ti) has a greater influence on the value of the parameter *n* (dependence on frequency) than on the value of the characteristic crystallization time. Here I would like to mention that a similar effect was observed for an influence of the electrode material on the electric polarization of electrodes (the change of the exponent describing a contribution of material close to the electrode surfaces to the real part of the electric permittivity as a function of frequency) – e.g. see T. Ragheb, L.A. Geddes, "*The polarization impedance of common electrode metals operated at low current density*", Ann. Biomed. Eng. **19** (1991) 151-163 (this effect was described for the first time in cited paper); (3) p. 34, there is written: "*All other melting curves associated with crystallization temperatures between 208 K and 223 K follow the same behavior as the non-field case, indicating a melting process of the ordinary polymorph* (T_{m1})." Would it be correct to say/write: "Selected crystallization temperatures above 208 K, because they are higher than T_{m2} (or $T_{m,2}$) – the temperature of melting of the electric field-induced polymorph, then it is to be expected that mentioned polymorph will not be observed"? It would be interesting to check if an electric field-induced polymorph would be observed if the crystallization temperature would be a few K below T_{m2}, e.g. 206 K; (4) some questions arise – for the case where a pure electric field-induced polymorph was obtained. How stable is the polymorph obtained (it is hours or days)? and How does a storage temperature affect the stability of the electric field-induced polymorph obtained?

FINAL CONCLUSIONS:

I would like to emphasize that despite the above mentioned some critical remarks, the doctoral thesis, submitted for review, contains very valuable and original results. It is also a pioneering description of the influence of an external electric field on the crystallization of molecular materials. Mr. Daniel Duarte has proven, in some sense, a very good knowledge of literature. It is worth emphasizing the comprehensive design/planning of individual measurements in such a way as to achieve the goals set at the very beginning. In this way, the measurements carried out by Mr. Daniel Duarte, and, what is more important, the conclusions resulting from these measurements, provided many interesting and promising results, which are worth paying attention to when looking for new forms, for example, medicines. In my opinion, the results presented in the thesis do a significant contribution to the development of innovative solutions for, inter alia, the pharmaceutical or food industries, and to the understanding of phenomena related to crystallization, the formation of crystallites, or the formation of new polymorphs. Considering the importance of the doctoral thesis, the form of planning and preparation of experiments, analysis and presentation of the obtained research results, I am confident that the doctoral dissertation meets the requirements for doctoral dissertations.

I think that the reviewed doctoral dissertation by M.Sc. Daniela Duarte meets the requirements of the Act of July 3, 2018 – Przepisy wprowadzające ustawę – Prawo o szkolnictwie wyższym i nauce (Dz. U. 2018 r. poz. 1669, as amended). On this basis, I am applying to the Council of the Institute of Physics of the University of Silesia in Katowice for the admission of Mr. Daniel Duarte for the public defense of the doctoral dissertation.

REQUEST FOR DISTINCTION OF THE THESIS:

At the same time, I am applying for a distinction to be awarded to the thesis, prepared by M.Sc. Daniel Duarte.

As part of the thesis, Mr. Daniel Duarte planned several measurement procedures/protocols in order to comprehensively investigate the influence of the external electric field on the process of crystallization and crystallite growth. For this purpose, Mr. Daniel Duarte performed five different protocols (published article describes one more protocol being mentioned briefly in the thesis only), in which he carefully examined the influence of the electric field (its amplitude in the case of alternating and direct fields and frequency of alternating field) applied to the compound under study at different temperatures, as well as he chosen various ways of reaching crystallization temperatures of VEC (directly from the isotropic liquid phase or by cooling to a temperature close to the glass transition temperature). A set of various protocols, planned well, proves the scientific maturity of Mr. Daniel Duarte. Moreover, by obtaining a new polymorphic form that is induced by an electric field, he sought to collect as much information as possible that could be obtained based on the method used (BDS) to describe not only the conditions favoring the formation of a new polymorph, but also its stability. It is worth emphasizing that Daniel Duarte, M.Sc., obtained several results that have not been the subject of scientific work in this area so far. The topics described in the doctoral thesis are a unique set of research and results obtained, and, what is more, they are an indispensable guide for further research for other compounds that may be used, inter alia, in the food industry or pharmacology. At this point, it is impossible not to mention the publications that are part of this project, not only due to the high level of the Journals in which they were published but also Mr. Daniel Duarte's contribution. Mr. Daniel Duarte planned and carried out all experiments, analyzed experimental data obtained, and prepared the manuscripts for publication procedures. I conclude that both the subjects undertaken by Mr. Daniel Duarte and the whole of the research carried out and presented in the thesis deserve a distinction.

Mirosław Gałązka