ABSTRACT

Control of the crystallization process has great importance in material engineering and pharmaceutical industry. Using electric fields for this purpose shows strong potential. However, the effect of electric field on crystallization is rather poorly recognized. In this Ph.D. Thesis, using dielectric spectroscopy, the effect of the alternating (ac) and direct current (dc) high-electric field on the crystallization of a molecular system with field-induced polymorphism, vinyl ethylene carbonate (VEC) is explored.

Among research that was performed, the importance of the sinewave properties of the applied alternating signal on crystallization kinetics was investigated. As it turned out, it is possible to control the crystallization rate or the morphology of the growing crystal by changing the amplitude or frequency of the applied electric field. The crystallization rate increases when the amplitude of the electric field increases or its frequency decreases. Moreover, by changing the properties of the applied time-dependent electric field, we can control the polymorph outcome. To be more specific, a high electric field can suppress the ordinary polymorphic form and induce the appearance of a new one.

Additionally, this study was extended to a broad temperature range to examine how the presence of a high electric field influences the temperature dependence of the crystallization rate. It was observed that the position of the maximum of the overall crystallization rate is not affected by the external electric field. However, the rate of crystallization increases when the field magnitude is increased or either the frequency of the ac field is decreased. Applying high amplitude time-dependent electric fields from a specific low-frequency region is responsible for generating an additional low-temperature maximum in the overall crystallization rate-temperature dependence. Interestingly, it is not observed in the absence of a high electric field.

As a final point, the stability of the field-induced VEC polymorph was investigated. It happens that if the field-induced polymorph is created along with the regular polymorph, it is unstable and will transform with time into a stable form. At this stage, applying a high-electric field does not affect the time transformation. On the other hand, if only the high-field polymorph is generated, the polymorphic transformation does not take place. The high-field polymorph does not convert with time into the regular form.

The research work that constitutes the basis of this doctoral thesis has been published in the following series of publications:

1. 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
2. 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
3. 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
4. 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

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