Frequency of the AC Electric Field Determines How a Molecular Liquid Crystallizes

Daniel M. Duarte,[1,2] Ranko Richert[3] & Karolina Adrjanowicz [1,2]*

[1]Institute of Physics, University of Silesia, 75 Pulku Piechoty 1, 41-500 Chorzow, Poland

[2]Silesian Center for Education and Interdisciplinary Research (SMCEBI), 75 Pulku Piechoty 1a, 41-500 Chorzow, Poland

[3]School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, USA

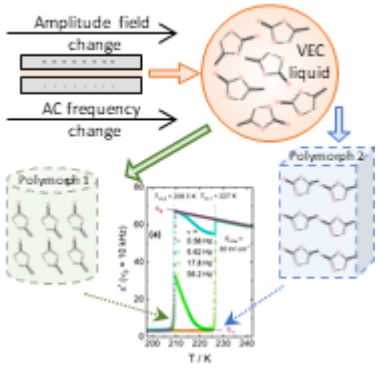
*** Corresponding Author**

Correspondence and requests for materials should be addressed to Karolina Adrjanowicz (email. kadrjano@us.edu.pl)

ABSTRACT

The ability to control crystallization is of central importance to many technologies and pharmaceutical materials. Electric fields have been shown to impact crystallization, but little is known about the mechanism of such effects. Here, we report on our observations of how the frequency of an external electric (ac) field changes the crystallization rate and the partitioning into distinct polymorphs of vinylethylene carbonate. We find that the field effects are pronounced only for frequencies below a certain threshold, which is orders of magnitude below that characterizing molecular orientation, but consistent with the reorientation of polar crystal nuclei of radius $r < 3$ nm. We conclude that the electric field opens an additional nucleation pathway by lowering the free energy barrier to forming a polymorph which melts at a temperature about 20 K below that of the ordinary crystal. This lower melting polymorph is not obtained at zero electrical field.

TOC GRAPHICS



KEYWORDS Dielectric spectroscopy; Crystallization; Electric field; Frequency

Crystallization is an important aspect of materials science, numerous technologies, and pharmaceutical applications. Understanding the parameters that affect crystallization is critical either to enhance crystallization rates or to avoid this phase transition to an ordered solid when a supercooled or glassy material is desired. In case a compound can crystallize into two or more distinct crystal structures, i.e., in the case of polymorphic solids, it is important to understand how the crystallization process can be tuned towards or away from a certain polymorph. In general, distinct polymorphs of the same molecular compound differ with respect to their solubility, bioavailability, and shelf life, with implications for medicinal use.

A number of experimental as well as theoretical studies have revealed that a sufficiently high electric field affects crystallization [1–9]. The mechanisms considered for the origin of these field effects include contributions from field dependent thermodynamic potentials[10–12], and from field induced orientations[13,14]. While the existence of an impact of electric fields on crystallization rate and polymorph outcome is well established, there is little experimental evidence that helps deciding which mechanism is at the origin of this field effect.

Recently, the field induced crystallization of a pure dipolar liquid, vinyl ethylene carbonate (VEC), has been studied using static electric fields in the 40 to 210 kV cm^{-1} amplitude range. That study demonstrated a field induced increase of the crystallization rate of VEC by more than a factor of 10, and that static fields give rise to a previously unknown polymorph that melts at a temperature located about 20 K below the ordinary melting temperature[15]. However, the path by which the electric field promoted this new polymorph of VEC remained unclear.

In the present work, we address the origin of such field effects by studying the dependence of crystallization outcomes on the frequency of the alternating (ac) electric fields that the sample is subjected to. Our main observation is that the field induced change in crystallization behavior sets

in only for frequencies which are at least 5 decades below the peak frequency, ν_{max}, of the dielectric loss that characterizes the molecular reorientation time, τ_α. From this unexpected frequency dependence, we conclude that the most likely source of this effect is field assisted orientation of small (r < 3 nm) crystallites, whose free energy reduction in the presence of a field assists the nucleation process of that lower melting polymorph by virtue of their polar structure.

The low field (linear response regime) dielectric spectra, $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$, for VEC at the crystallization temperature T =198 K are depicted in Fig. 1. At this temperature, the primary (α) structural relaxation process is characterized by a peak at $\nu_{max} = 2\times10^5$ Hz, equivalent to a peak relaxation time of $\tau_{max} = 8\times10^{-7}$ s. The signature of dc-conductivity is the rise of ε'' for $\nu < 10^3$ Hz, and the rise of ε' below $\nu \approx 1$ Hz indicates electrode polarization.

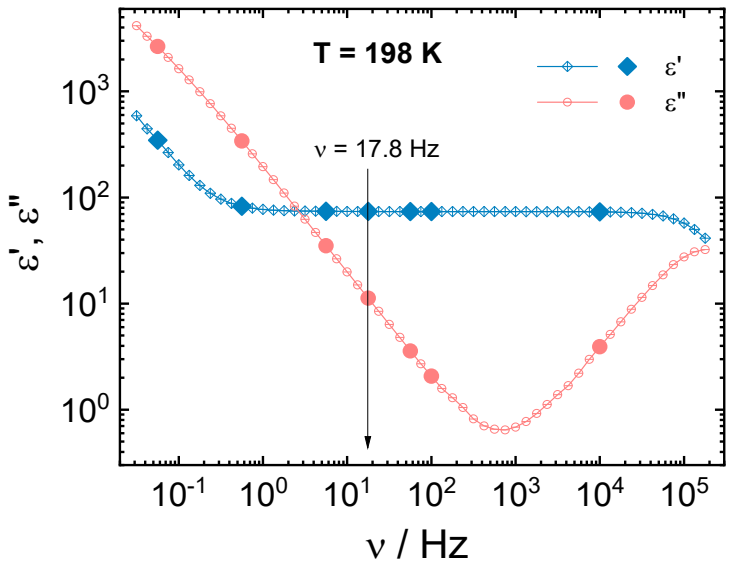


Figure 1. Linear response (E_{rms} < 10 kV cm^{-1}) dielectric susceptibility of VEC at T = 198 K. The ε'' peak near $\nu = 2\times10^5$ Hz originates from the primary (α) structural relaxation, the rise of ε'' for ν < 10^3 Hz is the result of dc conductivity, the rise of ε' below $\nu \approx 1$ Hz indicates electrode

polarization. Solid symbols identify frequencies used for high electric field experiments shown below.

In the absence of a high electric field, crystallization progress is monitored via the real part of permittivity, $\varepsilon'(\nu_0)$, with the fixed frequency ν_0 = 10 kHz, selected such that $\varepsilon'(\nu_0)$ represents the static dielectric constant, ε_s, of the liquid. The basis for assessing crystallization via dielectric techniques is that the dielectric constant, ε_s, of polar liquids is governed by rotational motion of permanent dipoles, which is suppressed in the crystalline state. Thus, as a good approximation[16–18], this value of ε' gauges the crystal (V_{cry}/V_{total}) or liquid (V_{liq}/V_{total}) volume fraction according to:

$$V_{cry}/V_{total} = (\varepsilon_s - \varepsilon')/(\varepsilon_s - \varepsilon_\infty)\,, \qquad (1a)$$

$$V_{liq}/V_{total} = (\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty)\,. \qquad (1b)$$

Here, the value of ε_∞ is understood as the permittivity of the crystalline state. In the liquid state, ε_∞ represents the high frequency limit of permittivity, i.e., in the absence of orientational contributions from permanent dipoles. Its magnitude is thus governed by the molecular electronic polarizability and density, values that very similar in both the crystalline and the liquid state. For monitoring the progress of crystallization of a sample subject to a high field, sinusoidal fields with frequencies 50 mHz ≤ ν ≤ 10 kHz and rms amplitudes between 60 and 180 kV cm^{-1} were used. All crystallization curves are recorded isothermally at T = 198 K, a temperature situated between the glass transition temperature T_g = 171 K and the regular melting temperature at T_m = 227 K[15]. Prior to cooling to T = 198 K, the sample had been melted by holding it at T = 243 K (= T_m + 16 K) for at least 30 minutes.

The effect of frequency of an ac field with amplitude E_{rms} = 80 kV cm^{-1} on the crystallization rate is depicted as V_{cry}/V_{total} versus log$t$ curves in Fig. 2. At a frequency ν = 100 Hz or higher, no

significant crystallization is observed for times up to 50,000 s (approx. 14 h). However, at the somewhat lower frequency of $\nu = 18$ Hz, crystallization is practically complete after 10,000 s, and at $\nu = 56$ mHz, the crystallization rate has increased by another factor of 10. Consistent with the frequency dependence at a field of $E_{rms} = 80$ kV cm^{-1} outlined in Fig. 2, the crystallization curve at the same field for $\nu = 56$ Hz shown in Fig. 3 indicates completion at around 20,000 s, i.e., twice as long as the 18 Hz case. Moreover, Fig. 3 indicates that the crystallization rate at a fixed frequency of $\nu = 56$ Hz can be tuned a factor of about ten by changing the field amplitude from 80 to 180 kV cm^{-1}.

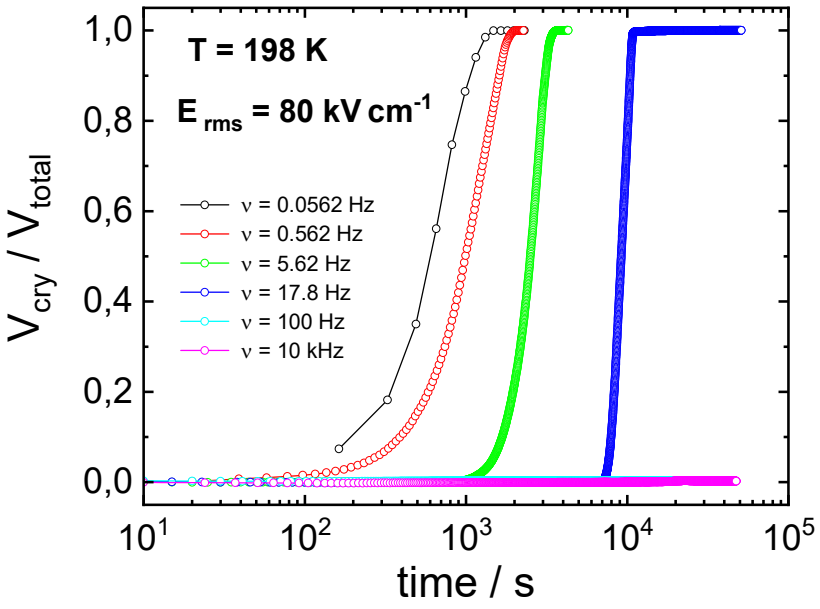


Figure 2. Isothermal crystallization of VEC after cooling the melt, reported as the volume fraction of crystalline material, V_{cry}/V_{total}. After reaching $T = 198$ K, the sample is exposed to an ac electrical field of $E_{rms} = 80$ kV cm^{-1} at different frequencies ν as indicated. For frequencies $\nu \geq 100$ Hz, no crystallization is observed during the first 50,000 seconds.

Among others, the crystallization curves of Fig. 2 and Fig. 3 have been analyzed in terms of the Avrami relation[19,20],

$$V_{cry}/V_{total} = 1 - \exp\left[-\left(t/\tau_{cry}\right)^{n}\right] . \qquad (2)$$

Here, τ_{cry} is a characteristic crystallization time and n an exponent that depends on the dimensionality and geometry of crystal growth. The time t is taken to start at the onset of crystallization, thus diregarding the incubation time of the process. The resulting respective dependencies of τ_{cry} on frequency ν and on field amplitude E_{rms} are compiled in Fig. 4, with all data referring to crystallization at $T = 198$ K after cooling the liquid from $T > T_m$. Note that τ_{cry} is associated with an effective rate which includes the zero-field and the field induced paths to the crystal state.

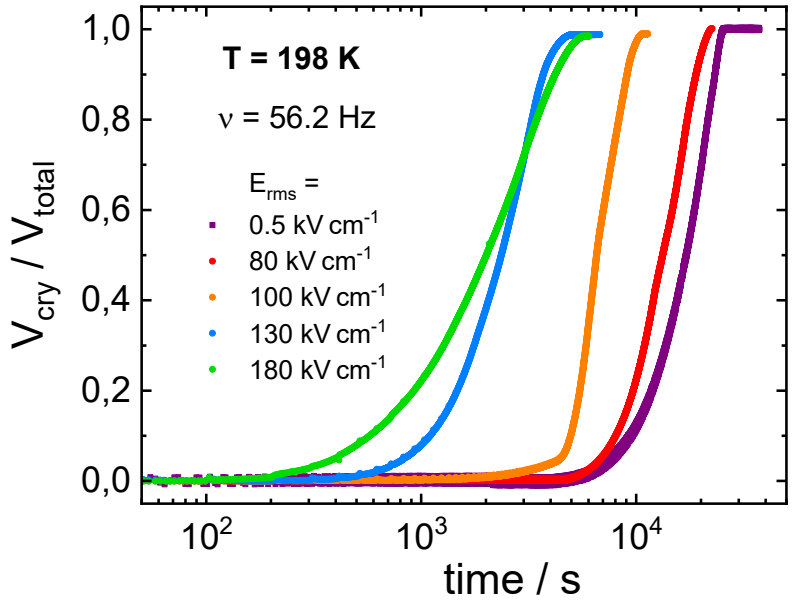


Figure 3. Isothermal crystallization of VEC after cooling the melt, reported as the volume fraction of crystalline material, V_{cry}/V_{total}. After reaching $T = 198$ K, the sample is exposed to an ac electrical field of frequency $\nu = 56.2$ Hz at different field amplitudes E_{rms} as indicated.

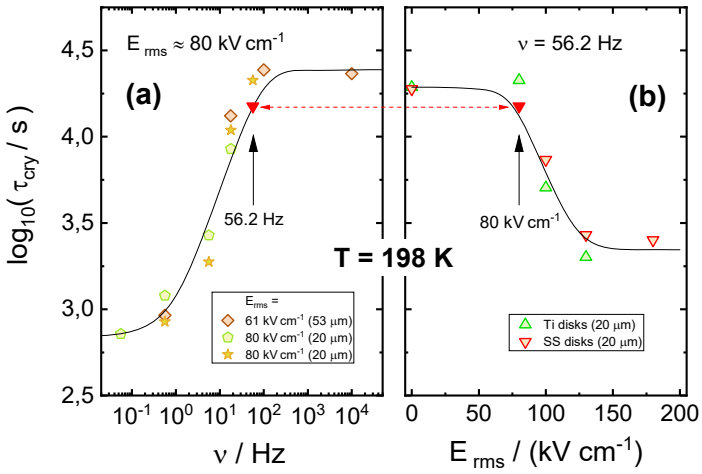


Figure 4. Time constants τ_{cry} characterizing the rate of the crystallization process of VEC at T = 198 K. (a) Frequency dependence of τ_{cry} at a practically constant field of $E_{rms} \approx 80$ kV cm-1. (b). Field amplitude dependence of τ_{cry} at a constant frequency of $\nu = 56.2$ Hz. The $E_{rms} = 80$ kV cm-1 data point of panel (b) is reproduced in panel (a) to show consistency.

Field amplitude and frequency not only impact the rate of crystallization, but also the polymorph obtained by crystallization. This is demonstrated in Fig. 5 by melting curves measured at a very low field (E_{rms} = 0.5 kV cm^{-1}) at a fixed frequency of ν_0 = 10 kHz by scanning temperature from the crystallization temperature of T = 198 K to a value of T =243 K, where the liquid state of VEC is recovered. The curves for selected frequencies and field amplitudes indicate that low frequencies and/or high field (where τ_{cry} is small) lead to a large volume fraction of the lower melting polymorph, with $T_{m,2}$ = 208.5 K. This large amount of the field-induced crystal shows in Fig. 5 as ε' rising a significant fraction of the ε_∞ to ε_s interval, cf. Eq. (1). The recrystallization seen as drop of ε' for $T > T_{m,2}$ is a matter of the amount of nuclei or crystallites leading to the higher melting polymorph with $T_{m,1}$ = 227 K (equal to the standard melting point T_m = 227 K). Only for the zero-

field case in Fig. 5a is the melting curve free of a signature of the low melting polymorph. On the other hand, a field of E_{rms} = 180 kV cm^{-1} at ν = 56 Hz yields only the low melting polymorph, see Fig. 5b, with no recrystallization due to the lack of nuclei that could form the high melting polymorph.

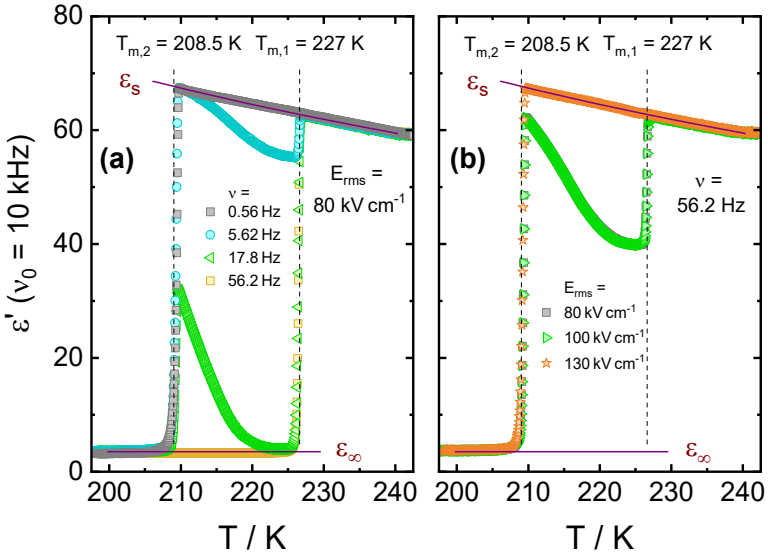


Figure 5. Melting curves of previously crystallized VEC in terms of the permittivity ε' measured at a frequency ν = 10 kHz upon scanning temperature from 198 K to 245 K at a rate of 1 K min^{-1}. Crystallization at T = 198 K has been field induced using various conditions: (a) at a fixed field of E_{rms} = 80 kV cm^{-1} for a range of frequencies, and (b) at a fixed frequency of 56.2 Hz for a range of fields, as indicated in the legends. Lines labeled ε_s and ε_∞ refer to the dielectric constants in the limits of low and high frequencies, respectively. At each temperature, the liquid volume fraction is given by $V_{liq}/V_{total} = (\varepsilon' - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty)$.

The present polar and glass forming material, VEC, has been characterized in detail regarding its low-field (linear response) dielectric properties and structural relaxation[21,22]. With respect to

the crystallization behavior of VEC, it had already been shown that dc-fields between 40 and 210 kV cm^{-1} accelerate the crystallization rate and lead to a polymorph whose melting point is about 20 K below that of the ordinary crystal which is formed at zero electric field[15]. As a result, it is not surprising that similar changes in crystallization outcomes can be achieved with alternating fields (at zero bias) of similar magnitudes, which is what the present results demonstrate. The novel information of this study lies in the unexpected frequency dependence of the field effect. At the crystallization temperature of T = 198 K, the molecular reorientation process of this polar liquid is characterized by a dielectric peak at ν_{max} = 2×10^5 Hz. Thus, one may expect the absence of a considerable field effect for frequencies in excess of ν_{max}, but field assisted crystallization for $\nu < \nu_{max}$ that is similar to the dc field case reported earlier[15]. Instead, Fig. 4a reveals that the field effect (at E_{rms} = 80 kV cm^{-1}) becomes considerable at or below about 20 - 50 Hz, i.e., five orders of magnitude below the loss peak at ν_{max} = 200 kHz, see Fig. 1. The low frequency of 20 Hz is still a safe distance from electrode polarization with an onset frequency of about 1 Hz. Moreover, if space charge accumulation observed as electrode polarization were at the origin of this field effect, the impact of a dc field should exceed that for ac fields, which is not observed.

In order to understand this frequency dependence shown in Fig. 2 and Fig. 4a, we consider the possibility that orientation of particles larger than the molecules are responsible for only low frequencies modifying the crystallization process. To clarify this idea, we use the Stokes-Einstein-Debye (SED) relation to establish a connection between the experimentally determined viscosity of VEC at the crystallization temperature and the rotation time for a given particle size:

$$\tau_{rot} = \frac{4\pi\eta r^3}{k_B T}. \qquad (3)$$

With the parameters T = 198 K, η = 70 Pa s, and translating the onset frequency of $\nu \approx$ 18 Hz to $\omega = 2\pi\nu$ = 110 Hz and further to $\tau_{rot} = 1/\omega$ = 8.8 ms, a particle radius of r = 3 nm is estimated to

match the frequency $\nu \approx 18$ Hz according to SED hydrodynamics. This onset frequency is determined from Fig. 3a as frequency below which the crystallization rate is systematically affected by the field, cf. data at $\nu = 17.8$ Hz. This is consistent with aligning or agitating low-melting polymorph crystal nuclei of radius $r < 3$ nm, provided these crystallites possess a net permanent dipole moment μ. Another requirement is that these crystallites are able to rotate in order to lower their free energy via an external field, cf. the angular term $\mu E\cos\theta$ in the potential energy[23]. This would not be the case with heterogeneous nucleation. In the present case, homogeneous nucleation seems more likely, as the use of titanium (Ti) versus the more highly polished stainless steel (SS) electrodes (majority of surface) shows very similar crystallization behavior, except for very long crystallization times. Moreover, increasing the sample volume by a factor of 2.65 by changing electrode separation from $d = 20$ to 53 μm has little effect.

Apart from the onset frequency information ($\nu \approx 18$ Hz), Fig. 4 suggests that frequency (at a given field of $E_{rms} = 80$ kV cm^{-1}) modifies the rate of crystallization by a factor of about 30 that separate the high and low frequency plateau values for τ_{cry}, 25,000 s and 800 s, respectively. The low rate (high τ_{cry}) level is near the field free case, whereas the high rate (low τ_{cry}) is likely a matter of the crystal growth rate and its limitation due to transport coefficients at $T = 198$ K, such as viscosity. Within the transition frequency range, increasing the field amplitude can accelerate crystallization, as shown in Fig. 4b. Of course, these results on the rates of crystallization do not specify which fractions of the two distinct polymorphs are being formed. In order to answer this question, melting curves were recorded after crystallization had practically completed, i.e., when $V_{cry} = V_{total}$.

Melting curves are recorded at a low field and fixed frequency $\nu_0 = 10$ kHz, so that $\varepsilon'(T)$ gauges the liquid volume fraction according to eq. (1b). A set of $\varepsilon'(T)$ melting curves are compiled in Fig

5a, measured after the sample crystallized while exposed to a fixed field amplitude of E_{rms} = 80 kV cm^{-1} but with various frequencies ν. For a relatively high frequency of 56.2 Hz, where the crystallization rate is modified only marginally relative to the zero field case, only the ordinary crystal that melts at $T_{m,1}$ = 227 K had been formed as no melting event is observed for $T < T_{m,1}$. As the frequency is lowered towards values that result in significant elevations of the crystallization rate, an increase in the volume fraction that melts already at $T_{m,2}$ = 208.5 K is seen in Fig. 5a. In the case of ν = 17.8 Hz, about 46% of the material melts at $T_{m,2}$, which then rapidly recrystallizes due to the large amount of ordinary crystals which melt at $T_{m,1}$. For the two lowest frequencies, ν = 5.62 Hz and ν = 0.56 Hz, practically 100% of the sample melts at the lower temperature $T_{m,2}$. Still, the ν = 0.56 Hz curve reveals a higher volume fraction of the lower melting crystal via the diminished recrystallization for $T > 208.5$ K, indicative of a smaller amount of ordinary crystallites. Analogous to this frequency dependence of Fig. 5a, the melting curves for different field amplitudes in Fig. 5b also point towards a larger fraction of the low-melting field-induced polymorph for situations in which the crystallization rate is faster. This suggests that the crystallization rate of the low-melting polymorph depends on the amplitude and frequency of the strong electric field, whereas the ordinary high-melting polymorph crystallization rate is largely field invariant. In turn, this implies that the field effect on the crystallization rate is matter of adding a further crystallization route leading to the low-melting polymorph, rather that impacting the nucleation or crystallization of the ordinary polymorph which melts at T_m = 227 K.

In summary, we have observed the overall crystallization rate and the resulting volume fractions of the ordinary and field induced polymorphs of vinylethylene carbonate while the sample is subjected to electric fields of varying amplitudes and frequencies. Only for sufficiently high field amplitudes and for frequencies below a certain threshold does the field modify the crystallization

behavior towards faster rates and towards favoring a lower melting polymorph that is not observed in the absence of an external electric field. Compatible with calculations,[12] the results suggest that the field acts via lowering the free energy of formation of crystal nuclei by their orientation along the field, a picture consistent with homogeneous nucleation of polar crystals with radii below about 3 nm. Situations of faster crystallization correlate strongly with the selective formation of the field-induced lower melting polymorph, indicating that the field opens a new path to a distinct polymorph, rather than modifying the crystallization that results in the ordinary and probably non-polar crystal structure. In conclusion, amplitude and frequency of external electric fields may serve as new strategies to for controlling and tuning crystallization outcomes in the context of materials engineering and pharmaceutical applications.

Methods

The compound 4-vinyl-1,3-dioxolan-2-one or vinyl ethylene carbonate (VEC) was supplied by Sigma-Aldrich (purity 99%, CAS Number 4427-96-7) and used as received. VEC is a vinyl derivative of propylene carbonate (PC) and sometimes referred to as 'vinyl-PC'. The liquid is loaded into a high-field capacitor cell described in detail in a previous publication[15]. The polished parallel disk pairs are made of stainless steel (SS) or titanium (Ti), and are separated by a Teflon ring of d = 25 or 50 μm nominal thickness, leaving an active inner electrode surface area of r = 7 mm radius. For the d = 25 μm spacer, the geometric capacitance is $C_{geo} = \varepsilon_0 \pi r^2/d = 54.5$ pF. By comparing the observed permittivity, $\varepsilon = \varepsilon' - i\varepsilon''$, with reference data, the actual electrode separations were determined to be 20 and 53 μm. Temperature regulation of the sample cell was achieved by a Novocontrol Quatro temperature control system.

For dielectric measurements using large ac electric fields, a Trek PZD-700 high-voltage amplifier boosts the output voltage of a Solartron SI-1260 gain–phase analyzer by a factor of 200.

The current was determined from the voltage drop across a calibrated RC-shunt connected to the analyzer via a buffer amplifier that tolerates voltages up to 500 V_p, employed to protect the system from sample failure. This setup facilitates dielectric response measurements within the frequency range from 30 mHz to 200 kHz at low fields and for frequencies 30 mHz to 120 kHz for fields up to 240 kV cm^{-1}.

AUTHOR INFORMATION

Corresponding Author

Correspondence and requests for materials should be addressed to Karolina Adrjanowicz (email. kadrjano@us.edu.pl)

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Competing Interests

The authors declare no other competing interests.

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