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

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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 vinylene 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 form a polymorph that melts at a temperature \( \sim 20 \) K below that of the ordinary crystal. This lower melting polymorph is not obtained at zero electrical field.

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, that is, in the case of polymorphic solids, it is important to understand how the crystallization process can be tuned toward or away from a number of polymorphic solids, it is important to understand how the crystallization process can be tuned toward 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.\(^1\)\(^\text{-}^9\) The mechanisms considered for the origin of such field effects include contributions from field-dependent thermodynamic potentials\(^10\)\(^\text{-}^12\) and from field-induced orientations.\(^13\)\(^\text{-}^14\) Whereas the existence of the impact of electric fields on the crystallization rate and the polymorph outcome is well established, there is little experimental evidence that helps one decide 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 \( 40\sim210 \) kV cm\(^{-1} \) amplitude range. That study demonstrated a field-induced increase in the crystallization rate of VEC by more than a factor of 10, and it showed that static fields give rise to a previously unknown polymorph that melts at a temperature located \( \sim 20 \) 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 that are at least 5 decades below the peak frequency, \( \nu_{\text{max}} \), of the dielectric loss that characterizes the molecular reorientation time, \( \tau_{\alpha} \). From this unexpected frequency dependence, we conclude that the most likely source of this effect is the 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, \( \epsilon'(\nu) \) and \( \epsilon''(\nu) \), for VEC at the crystallization temperature \( T = 198 \) K are depicted in Figure 1. At this temperature, the primary (\( \alpha \)) structural relaxation process is characterized by a peak at \( \nu_{\text{max}} = 2 \times 10^4 \) Hz, equivalent to a peak relaxation time of \( \tau_{\max} = 8 \times 10^{-7} \) s. The signature of dc conductivity is the increase in \( \epsilon'' \) for \( \nu < 10^3 \) Hz, and the increase in \( \epsilon' \) below \( \nu \approx 1 \) Hz indicates electrode polarization.

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

\[
V_{\text{cry}} / V_{\text{total}} = (\varepsilon_\infty - \varepsilon') / (\varepsilon_\infty - \varepsilon_\infty)
\]

(1a)

\[
V_{\text{liq}} / V_{\text{total}} = (\varepsilon' - \varepsilon_\infty) / (\varepsilon_\infty - \varepsilon_\infty)
\]

(1b)

Here the value of \( \varepsilon_\infty \) is understood as the permittivity of the crystalline state. In the liquid state, \( \varepsilon_\infty \) represents the high frequency limit of permittivity, that is, in the absence of orientational contributions from permanent dipoles. Its magnitude is thus governed by the molecular electronic polarizability and density, values that are very similar in both the crystalline and the liquid states. To monitor the progress of crystallization of a sample subjected to a high field, sinusoidal fields with frequencies 50 mHz \( \leq \nu \leq 10 \text{ kHz} \) and root-mean-square (rms) amplitudes between 60 and 180 kV cm\(^{-1}\) were used. All crystallization curves were recorded isothermally at \( T = 198 \text{ K} \), a temperature situated between the glass-transition temperature \( T_g = 171 \text{ K} \) and the regular melting temperature at \( T_m = 227 \text{ K} \). Prior to cooling to \( T = 198 \text{ K} \), the sample had been melted by holding it at \( T = 243 \text{ K} \) (= \( T_m + 16 \text{ K} \)) for at least 30 min.

The effect of the frequency of an ac field with amplitude \( E_{\text{rms}} = 80 \text{ kV cm}^{-1}\) on the crystallization rate is depicted as \( V_{\text{cry}} / V_{\text{total}} \) versus log \( \nu \) curves in Figure 2. At a frequency \( \nu = 100 \text{ Hz} \) or higher, no significant crystallization is observed for times up to 50 000 s (\( \sim 14 \text{ h} \)). However, at the somewhat lower frequency of \( \nu = 18 \text{ Hz} \), crystallization is practically complete after 10 000 s, and at \( \nu = 56 \text{ Hz} \), the crystallization rate has increased by another factor of 10. Consistent with the frequency dependence at a field of \( E_{\text{rms}} = 80 \text{ kV cm}^{-1}\) outlined in Figure 2, the crystallization curve at the same field for \( \nu = 56 \text{ Hz} \) shown in Figure 3 indicates completion at \( \sim 20 \text{ 000 s} \), that is, twice as long as the 18 Hz case. Moreover, Figure 3 indicates that the crystallization rate at a fixed frequency of \( \nu = 56 \text{ Hz} \) can be tuned a factor of about ten by changing the field amplitude from 80 to 180 kV cm\(^{-1}\). Among others, the crystallization curves of Figures 2 and 3 have been analyzed in terms of the Avrami relation\(^{19,20}\)

\[
V_{\text{cry}} / V_{\text{total}} = 1 - \exp\left[-\left(t / t_{\text{cry}}\right)^n\right]
\]

(2)

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

The field amplitude and frequency impact not only the rate of crystallization but also the polymorph obtained by crystallization. This is demonstrated in Figure 5 by melting curves measured at a very low field (\( E_{\text{rms}} = 0.5 \text{ kV cm}^{-1}\)) at a fixed frequency of \( \nu_0 = 10 \text{ kHz} \) by scanning the temperature from the crystallization temperature of \( T = 198 \text{ K} \) to a value of \( T = 243 \text{ K} \), where the liquid state of VEC is recovered. The curves for selected frequencies and field amplitudes indicate that low frequencies or a high field (where \( t_{\text{cry}} \) is small) lead to a large volume fraction of the lower melting polymorph, with \( T_m,2 = 208.5 \text{ K} \). This large amount of the field-induced crystal

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Only for the zero-point is the crystallization rate and lead to a polymorph whose melting ε drop in dependence of T at fi = 198 K. The field amplitude dependence of 56.2 Hz. The liquid volume fraction is given by ε, where ε is the dielectric constant in the limits of low and high frequencies, respectively. At each temperature, the liquid volume fraction is estimated to match the frequency max = 200 kHz; see Figure 1. The low frequency of 20 Hz is still a safe distance from electrode polarization with an onset frequency of ~1 Hz. Moreover, if space charge accumulation observed as electrode polarization was at the origin of this field effect, then the impact of a dc field should exceed that for ac fields, which is not observed.

To understand this frequency dependence shown in Figures 2 and 4a, we consider the possibility that the orientation of particles larger than the molecules is 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

\[
\tau_{rot} = \frac{4 \pi \eta r^3}{k_B T}
\]

(3)

With the parameters \( T = 198 \text{ K} \) and \( \eta = 70 \text{ Pa s} \) and translating the onset frequency of \( \nu \approx 18 \text{ Hz} \) to \( \omega = 2 \pi \nu = 110 \text{ Hz} \) and further to \( \tau_{rot} = 1/\omega = 8.8 \text{ ms} \), a particle radius of \( r = 3 \text{ nm} \) is estimated to match the frequency \( \nu \approx 18 \text{ Hz} \) according to SED hydrodynamics. This onset frequency is determined from Figure 3a as the frequency below which the crystallization rate is systematically affected by the field, namely, data at \( \nu = 17.8 \text{ Hz} \). This is consistent with aligning or agitating low-melting polymer crystal nuclei of radii \( r < 3 \text{ nm} \), provided these crystallites possess a net permanent dipole moment \( \mu \). Another requirement is that these crystallites are able to rotate to lower their free energy via an external field, namely, the angular term \( \mu E \cos \theta \) in the potential energy. 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 the electrode separation from \( d = 20 \text{ to } 53 \text{ \mu m} \) has little effect.

Apart from the onset frequency information (\( \nu \approx 18 \text{ Hz} \)), Figure 4 suggests that frequency (at a given field of \( E_{rms} = 80 \text{ kV cm}^{-1} \)) modifies the rate of crystallization by a factor of about 30 that separate the high and low frequency plateau values for \( \tau_{cry} \). 25 000 and 800 s, respectively. The low rate (high \( \tau_{cry} \)) level is near the field free case, whereas the high rate (low \( \tau_{cry} \)) is likely a matter of the crystal growth rate and its limitation due to transport coefficients at \( T = 198 \text{ K} \), such as viscosity. Within the transition frequency range, increasing the field amplitude can accelerate crystallization, as shown in

(5)

formed at zero electric field. 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 on this study lies in the unexpected frequency dependence of the field effect. At the crystallization temperature of \( T = 198 \text{ K} \), the molecular reorientation process of this polar liquid is characterized by a dielectric peak at \( \nu_{max} = 2 \times 10^5 \text{ Hz} \). Thus one may expect the absence of a considerable field effect for frequencies in excess of \( \nu_{max} \) but field-assisted crystallization for \( \nu < \nu_{max} \) that is similar to the dc field case previously reported. Instead, Figure 4a reveals that the field effect (at \( E_{rms} = 80 \text{ kV cm}^{-1} \)) becomes considerable at or below about 20–50 Hz, that is, five orders of magnitude below the loss peak at \( \nu_{max} = 200 \text{ kHz} \); see Figure 1.

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

Figure 5. Melting curves of previously crystallized VEC in terms of the permittivity \( \varepsilon' \) measured at a frequency \( \nu = 10 \text{ kHz} \) upon scanning temperature from 198 to 245 K at a rate of 1 K min\(^{-1}\). Crystalization at \( T = 198 \text{ K} \) has been field-induced using various conditions: (a) at a fixed field of \( E_{rms} = 80 \text{ kV cm}^{-1} \) 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 \( \varepsilon_i \) and \( \varepsilon_{cry} \) refer to the dielectric constants in the limits of low and high frequencies, respectively. At each temperature, the liquid volume fraction is given by \( \nu_{tot}/\nu_{mol}= (\varepsilon' - \varepsilon_{inf})/(\varepsilon_{inf} - 1) \).

shows in Figure 5 as \( \varepsilon' \) rising a significant fraction of the \( \varepsilon_{inf} \) to \( \varepsilon_i \) interval, cf. eqs 1a and 1b. The recrystallization seen as a drop in \( \varepsilon' \) for \( T > T_{mol} \) is a matter of the amount of nuclei or crystallites leading to the higher melting polymorph with \( T_{mol} = 227 \text{ K} \) (equal to the standard melting point \( T_m = 227 \text{ K} \)). Only for the zero-field case in Figure 5a is the melting curve free of a signature of the low melting polymorph. On the contrary, a field of \( E_{rms} = 180 \text{ kV cm}^{-1} \) at \( \nu = 56 \text{ Hz} \) yields only the low melting polymorph (see Figure 5b), with no recrystallization due to the lack of nuclei that could form the high melting polymorph.

The present polar and glass-forming material, VEC, has been characterized in detail regarding its low-field (linear response) dielectric properties and structural relaxation. 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 ~20 K below that of the ordinary crystal, which is
Figure 4b. Of course, these results on the rates of crystallization do not specify which fractions of the two distinct polymorphs are being formed. To answer this question, melting curves were recorded after crystallization had practically completed, that is, when $V_{\text{cry}} = V_{\text{total}}$.

Melting curves are recorded at a low field and fixed frequency $k_0 = 10$ kHz, so that $\varepsilon'(T)$ gauges the liquid volume fraction according to eq 1b. A set of $\varepsilon'(T)$ melting curves are compiled in Figure 5a, measured after the sample crystallized while exposed to a fixed field amplitude of $E_{\text{rms}} = 80$ kV cm$^{-1}$ but with various frequencies $\nu$. 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 is formed, as no melting event is observed for $T < T_{m,1}$. As the frequency is lowered toward 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 Figure 5a. In the case of $\nu = 17.8$ Hz, $\sim$46% of the material melts at $T_{m,2}$ which then rapidly recrystallizes due to the large amount of ordinary crystals that melt at $T_{m,1}$. For the two lowest frequencies, $\nu = 5.62$ and 0.56 Hz, practically 100% of the sample melts at the lower temperature $T_{m,3}$. Still, the $\nu = 0.56$ Hz curve reveals a higher volume fraction of the lower melting crystal via the diminished recrystallization for $T > 208.5$ K, which is indicative of a smaller amount of ordinary crystallites. Analogous to this frequency dependence of Figure 5a, the melting curves for different field amplitudes in Figure 5b also point toward 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 than impacting the nucleation or crystallization of the ordinary polymorph that 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 vinylene 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 toward faster rates and toward favoring a lower melting polymorph that is not observed in the absence of an external electric field. Compatible with calculations, 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 the homogeneous nucleation of polar crystals with radii below $\sim$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 nonpolar crystal structure. In conclusion, the amplitude and frequency of external electric fields may serve as new strategies 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 VEC was supplied by Sigma-Aldrich (purity 99%, CAS no. 4427-96-7) and used as received. VEC is a vinyl derivative of propylene carbonate (PC) and is sometimes referred to as “vinyl-PC”. The liquid is loaded into a high-field capacitor cell described in detail in a previous publication. The polished parallel disk pairs are made of SS or Ti and are separated by a Teflon ring of $d = 25$ or 50 $\mu$m nominal thickness, leaving an active inner electrode surface area of $r = 7$ mm radius. For the $d = 25$ $\mu$m spacer, the geometric capacitance is $C_{\text{geo}} = \varepsilon_r \pi r^2 / d = 54.5$ pF. By comparing the observed permittivity, $\varepsilon = \varepsilon' - i\varepsilon''$, with reference data, the actual electrode separations were determined to be 20 and 53 $\mu$m. The 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 of up to 500Vp 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 of 30 mHz to 120 kHz for fields up to 240 kV cm$^{-1}$.

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 Notes

 The authors declare no competing financial interest.

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