#### Electronic Supplementary Information

### Formation of New Polymorphs and Control of Crystallization in Molecular Glass-Formers by Electric Field

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**Figure S1.** Schematic outline of the dielectric cell used for the high field studies. The main body is made of brass, the electrodes are titanium. The top electrode is held in place via the center hole of a sapphire disk, which is tightened against an o-ring using a steel frame. The lower electrode is pressed against the Teflon ring and upper electrode using a wave spring washer which also acts as electrical contact between lower electrode and main cell body.

## Field-induced changes in the ongoing crystallization of vinyl-PC – in reference to results presented in Figure 3 (main paper).

Figure S2 illustrates the same set of data as that presented in Fig. 3a, but analyzed in terms of normalized dielectric permittivity,  $\varepsilon'_N = [\varepsilon'(t=0) - \varepsilon'(t)]/[\varepsilon'(t=0) - \varepsilon'(t \to \infty)]$  and fitted to the Avrami equation,  $\varepsilon'_N = 1 - \exp(-kt^n)$ , where k is the crystallization rate constant ( $k = 1/t_{cryst}$ ) and n the Avrami exponent [S1, S2]. The parameters  $t_{cryst}$  and n obtained in this this manner are plotted in Fig. S3 as a function of the applied dc bias field.



**Figure S2.** Time evolution of the normalized dielectric permittivity,  $\varepsilon'_N = [\varepsilon'(t=0) - \varepsilon'(t)]/[\varepsilon'(t=0) - \varepsilon'(t)]/[\varepsilon'(t=0) - \varepsilon'(t \to \infty)]$ , at T = 198 K after interrupting zero-field crystallization of vinyl-PC by applying dc bias field of different magnitudes. The solid line shows crystallization kinetics in the absence of a static field. Here, t = 0 is a time at which the dc bias voltage was applied, while  $t = \infty$  refers to the time when transformation was completed. The inset enlarges the changes in  $\varepsilon'_N(t)$  after turning the dc bias field on and off. For the zero-field case t=0 is time when the temperature was reached.



**Figure S3**. Characteristic crystallization time (main figure) and Avrami exponent (inset) plotted as a function of dc bias field applied upon crystallization of vinyl-PC at T = 198 K. Both variables were determined based on fitting of the experimental data presented in Fig. S2 with the use of the Avrami equation,  $\varepsilon'_{\rm N} = 1 - \exp(-kt^{\rm n})$ , where k is the crystallization rate constant ( $k = 1/t_{\rm cryst}$ ) and n the Avrami exponent.

# The effect of dc bias on nucleation rate of vinyl-PC – in reference to results presented in Figure 4 (main paper).

Fig. S4 illustrates that after complete melting of the field induced polymorph at  $T_{m2}$ , crystallization of the zero-field polymorph takes place. At this temperature, the nucleation rate of the type 1 crystal is extremely long and cannot account for relatively fast recrystallization of the liquid.



**Figure S4.** Temperature evolution of the real part of the dielectric permittivity at v = 10 kHz during heating of the crystalline material with nucleation stage modified by applying bias field of 210 kV/cm at T = 173 K for 1 hour. The inset shows results of the time-dependent measurements performed after melting of the high-field polymorph at  $T_{m2} = 208.5$  K. Crystalline material obtained in this way melts at  $T_{m1} = 227$  K, which refers to zero-field polymorph of vinyl PC.

#### Separating field-induced polymorph of vinyl-PC from its zero-field ordinary form – in reference to results presented in Figure 5 (main paper).

Fig. S5 show the same set of data as that presented in Fig. 5a but analyzed in terms of the normalized dielectric permittivity. Additionally, Fig. S6 demonstrates that the field-induced crystallization of vinyl-PC is a diffusion-controlled process. Therefore, with increasing liquid viscosity, we observe that crystallization of type 2 crystal slows down. Meanwhile, the behavior of Avrami parameter at different temperatures shows a very similar characteristic with respect to the magnitude of the applied dc bias field.

Shortening of the crystallization time indicates faster nucleation and crystal growth rates, whereas a systematic reduction of the Avrami exponent signals fundamental changes in the nucleation process and dimensionality of growing crystals. We envision that a close overlap of nucleation rate and growth rate maxima makes crystallization of the type 2 polymorph to proceed orders of magnitude faster than the zero-field form.



**Figure S5.** Time evolution of the normalized dielectric permittivity at v = 10 kHz ( $\varepsilon'_N$ ) upon fieldinduced crystallization of vinyl PC at T = 198 K (following protocol sketched in Figure 2c, step  $2\rightarrow 3$ ). Solid lines are fits of the experimental data with the Avrami equation.



**Figure S6.** Changes in the characteristic crystallization time (main figure) and Avrami exponent (inset) as a function of dc bias field obtained for vinyl-PC at the two temperatures indicated, T = 198 K and T = 193 K (following the protocol displayed in Figure 2c).

[S2] M. Avrami, J. Chem. Phys. 8, 212-224 (1940).

<sup>[</sup>S1] M. Avrami, J. Chem. Phys. 7, 1103-1112 (1939).