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Molecular Dynamics and Kinetics of Isothermal Cold Crystallization in the Chiral Smectogenic 3F7FPhH6 Glassformer

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Abstract: An investigation of the glass transition of the antiferroelectric smectic C_A^* phase and cold crystallization of (S)-4'-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[7-(2,2,3,3,4,4,4-heptafluorobutoxy)heptyl-1-oxy]-3-fluorobenzoate (denoted as 3F7FPhH6) by differential scanning calorimetry, polarizing optical microscopy and broadband dielectric spectroscopy is presented. The fragility index $m_f = 72$, classifying 3F7FPhH6 as a glassformer with intermediate fragility, was obtained from the temperature dependence of the α -process relaxation time, measured upon cooling. Duplication of the α -process was observed exclusively upon heating, before the onset of cold crystallization, and is connected with the pre-transitional effect. The presence of two crystal phases likely influences the kinetics of cold crystallization; the idea stems from a comparison with previous results for the 3F7HPhF6 and 3F7HPhH7 compounds. Additionally, the presence of the smectic C_A^* sub-phase in a narrow temperature range was proved based on the differential scanning calorimetry and broadband dielectric spectroscopy results, as well as the fractal dimension analysis of the textures obtained by polarizing optical microscopy.

Keywords: antiferroelectric; glass transition; cold crystallization



Citation: Deptuch, A.; Jasiurkowska-Delaporte, M.; Juszyńska-Gałązka, E.; Drzewicz, A.; Zajac, W.; Urbanska, M. Molecular Dynamics and Kinetics of Isothermal Cold Crystallization in the Chiral Smectogenic 3F7FPhH6 Glassformer. *Crystals* **2021**, *11*, 1487. <https://doi.org/10.3390/cryst11121487>

Academic Editor: Borislav Angelov

Received: 10 November 2021

Accepted: 28 November 2021

Published: 30 November 2021

Corrected: 8 November 2022

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1. Introduction

Chiral liquid crystalline substances with three aromatic rings in a molecular core and partially fluorinated alkoxy chain [1–8] are desired materials in liquid crystal display (LCD) technology as they often exhibit a smectic C_A^* (SmC_A^*) phase, showing antiferroelectric properties in the surface-stabilized geometry [9]. Moreover, the tilt angle in these compounds often approaches 45° , which leads to the optical uniaxiality and, consequently, far better quality of the dark state compared to the SmC_A^* phase with the smaller tilt angle [10,11]. For a few of the mentioned fluorinated smectogens, the glass transition of the SmC_A^* phase was reported, even for slow cooling (1 K/min or at an even lower rate, enough to avoid crystallization) [12–18]. It allows for the obtainment of glass with anisotropic properties, whose practical application was already proposed both for smectic and nematic glassformers [19–23]. In this study, we report results regarding the vitrification of the SmC_A^* phase and kinetics of the isothermal cold crystallization on subsequent heating for (S)-4'-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[7-(2,2,3,3,4,4,4-heptafluorobutoxy)heptyl-1-oxy]-3-fluorobenzoate, denoted in short as 3F7FPhH6. This compound belongs to a family of $3FmX_1PhX_2r$ compounds [4–6], with a general formula presented in Figure 1a. Differences in the molecular structure within the $3FmX_1PhX_2r$ family exist in the length of the alkoxy chain ($m = 0, 2–7$) and chiral alkyl chain ($r = 4–9$), as well as the fluoro substitution of the benzene ring ($X_1, X_2 = \{H, F\}$). The 3F7FPhH6 compound, chosen in

this paper, was investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and broadband dielectric spectroscopy (BDS). The obtained results were compared with those already reported for the 3F7HPhF6 [12,13] and 3F7HPhH7 [16–18] compounds with a similar molecular structure, in order to discuss the influence of the F substituent and the length of the $-C_rH_{2r+1}$ chain on the glassforming properties and cold crystallization kinetics. It was shown that 3F7FPhH6 has a smaller fragility index and crystallizes slower than the two previously studied compounds. The relationship between the molecular structure of the 3FmX₁PhX₂r compounds and the mentioned properties is still not fully explained and, therefore, it requires wide, systematic studies.

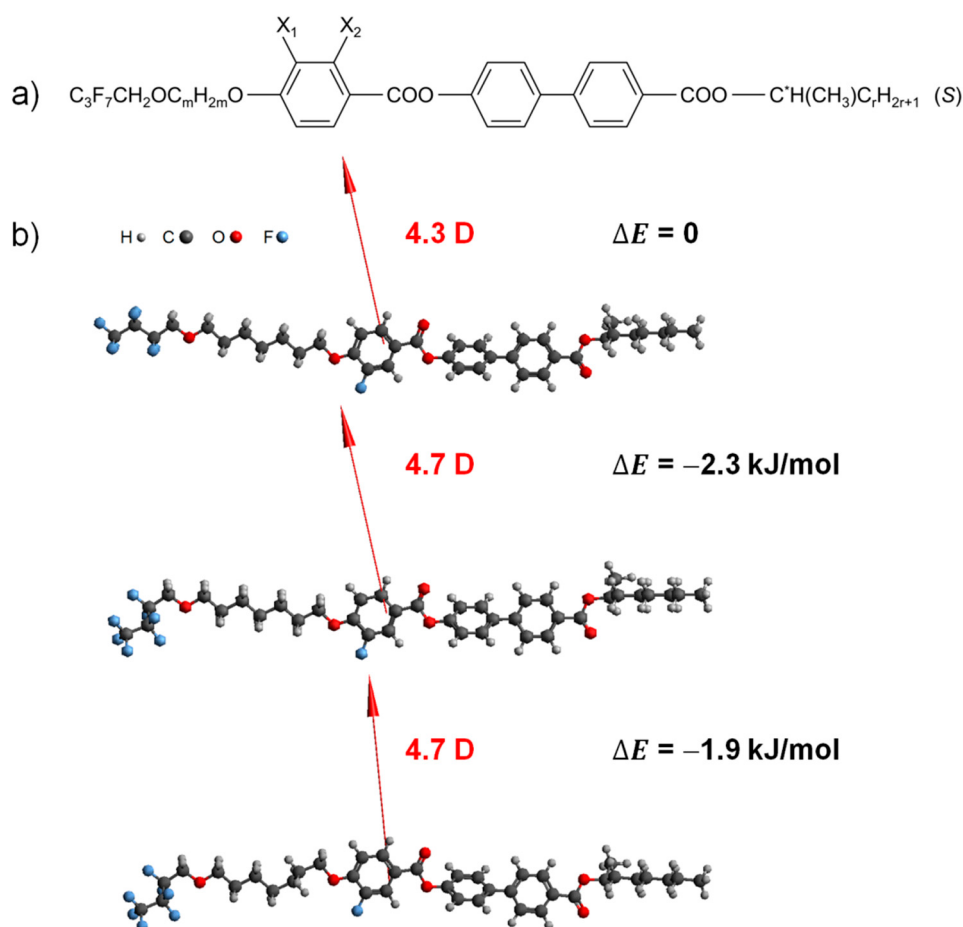


Figure 1. General molecular formula of the 3FmX₁PhX₂r family (a) and 3F7FPhH6 molecules optimized with the DFT method (B3LYP/def2TZVPP) in an extended and two exemplary twisted conformations (b). The dipole moment vectors are shown, and the relative energy of each conformation is given in respect to the extended conformations in a figure.

2. Materials and Methods

(S)-4'-(1-methylheptylcarbonyl)biphenyl-4-yl 4-[7-(2,2,3,3,4,4,4-heptafluorobutoxy)heptyl-1-oxy]-3-fluorobenzoate, abbreviated as 3F7FPhH6, was synthesized according to the method described in [4,5] from the Institute of Chemistry of Military University of Technology in Warsaw, Poland.

DFT calculations for an isolated 3F7FPhH6 molecule were conducted in Gaussian 09 [24] with a B3LYP exchange-correlation potential, def2TZVPP basis set and Grimme's 3D dispersion with Becke–Johnson damping. Preliminary calculations were performed in MOPAC2016 [25] with the semi-empirical PM7 method (see Figure S1 in the Supplementary Materials). Visualization was performed in Avogadro [26].

DSC measurements were performed for a sample weighing 8.460 mg, contained in a standard aluminum pan with the DSC 2500 (TA Instruments) calorimeter during cooling and subsequent heating, at rates of 2, 5, 10, 15, 20 K/min in the 153–413 K range. For the investigation of isothermal cold crystallization, the sample was cooled for each crystallization temperature from 393 K to 193 K at a rate of 10 K/min, heated to a selected temperature (273, 278, 283, 288, 293 K) at a rate of 10 K/min and kept in isothermal conditions until the end of crystallization, then heated to 393 K at a rate of 10 K/min. The results were analyzed with TRIOS software.

POM observations were performed for a sample between two glass slides without any aligning layer, under a Leica DM2700 P microscope with a Linkam temperature attachment. Textures were registered during cooling at a rate of 2 K/min in the 353–393 K range, and during cooling at a rate of 20 K/min and subsequent heating at a rate of 2 K/min in the 193–393 K range. The textures were analyzed numerically in the ImageJ program [27] using two methods. In the first method, textures were transformed into binary black-and-white images, and the fractal box count analysis [28,29] was applied for each texture, then the fractal dimension was plotted vs. temperature. In the second method, textures were split into red, green and blue components. The histogram of pixel luminance was made for each component, then the modal luminance of the blue component (the most sensitive to phase transitions) was plotted vs. temperature. Examples of numerical analysis are presented in the Supplementary Materials in Figures S2 and S3.

BDS measurements were performed for a sample of ca. 50 μm thickness between two gold electrodes with the Novocontrol Technologies spectrometer. The dielectric spectra were registered in the frequency range of 1– 10^7 Hz upon cooling and heating in the 173–383 K range. Additional measurements in the external bias field of 40 V were performed in the 363–383 K range during cooling to investigate the soft mode after suppression of the stronger Goldstone mode. In order to study isothermal cold crystallization, the sample was cooled directly from 383 K to 173 K, heated to a selected temperature (265, 268, 271, 273 K) and kept at this temperature until the end of crystallization.

3. Results and Discussion

3.1. Phase Sequence

The results of the DSC measurements (Figure 2, Table 1) show that 3F7FPhH6 is a glassformer undergoing the vitrification of the SmC_A^* phase, even for the smallest applied cooling rate, 2 K/min. The glass transition temperature, obtained as an inflection point in the DSC curve in the 225–250 K range equals $T_g = 233$ K for 2 K/min and increased with the increasing cooling rate to 234.5 K for 20 K/min. The spiky anomalies appearing below T_g are probably caused by small fractures in the vitrified material. After heating back up above the glass softening temperature, cold crystallization was observed for only the 2 K/min heating rate (Figure 2a). The small anomalies between 260 K and 275 K on heating are connected with the pre-transitional effect. The larger exothermic anomaly, with the onset temperature of 275.7 K, originates from cold crystallization. The following two endothermic anomalies with onset temperatures of 287.2 K and 301.2 K are explained as the melting of two crystal phases, denoted as Cr2 and Cr1, respectively. For higher heating rates (5–20 K/min, Figure 2b) the cold crystallization was not observed, and the sample remained in the SmC_A^* phase until the $\text{SmC}_A^* \rightarrow \text{SmC}^*$ transition. The transitions between the smectic phases took place close to the clearing temperature, and were revealed as small anomalies in the DSC curves, as presented in the insets in Figure 2a. The results from heating imply the presence of three smectic phases, which agrees with earlier results [5]. However, during cooling, an almost negligible additional anomaly was visible, merged with a larger anomaly connected with the $\text{Iso} \rightarrow \text{SmA}^*$ transition. It could be a sign of the presence of the fourth smectic phase, namely the SmC_α^* sub-phase, previously reported for the 3F5FPhF6 compound [30].

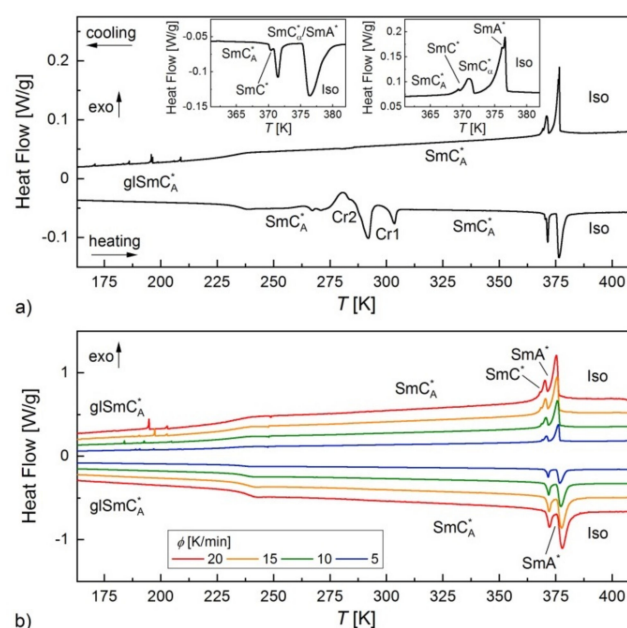


Figure 2. DSC curves of 3F7FPhH6 registered at the 2 K/min rate (a) and 5–20 K/min rates (b). The insets in (a) show the enlarged parts of the DSC curves for the 2 K/min rate close to the clearing temperature.

Table 1. Phase transition temperatures (onset temperature T_o and peak temperature T_p) and energy effects (enthalpy change ΔH and entropy change $\Delta S = \Delta H/T_p$) determined from the DSC results for the 2 K/min rate.

Transition	T_o (K)	T_p (K)	ΔH (kJ/mol)	ΔS (J/(mol·K))
Cooling				
Iso $\rightarrow$ SmA^*	377.0	376.8	9.3	24.8
$SmA^* \rightarrow (SmC_A^*) \rightarrow SmC^*$	371.9	(376.3) ¹ 371.1	2.1	5.5
$SmC^* \rightarrow SmC_A^*$	—	369.5	1.1	2.9
$SmC_A^* \rightarrow SmC_A^*$ glass	233	—	—	—
Heating				
SmC_A^* glass $\rightarrow$ SmC_A^*	233	—	—	—
$SmC_A^* \rightarrow Cr2$	275.7	280.4	3.4 ³	12.1 ³
$Cr2 \rightarrow (SmC_A^*) \rightarrow Cr1$ ²	287.2	292.1	10.9 ³	37.2 ³
$Cr1 \rightarrow SmC_A^*$	301.2	303.7	2.9 ³	9.6 ³
$SmC_A^* \rightarrow SmC^*$	370.1	370.6	1.3	3.5
$SmC^* \rightarrow (SmC_A^*) \rightarrow SmA^*$	370.9	371.6	2.3	6.2
$SmA^* \rightarrow Iso$	375.5	376.6	9.7	25.6

¹ For the SmA^*/SmC_A^* transition, only T_p value (in parentheses) upon cooling can be determined. ² Crystallization to the $Cr1$ phase starts directly after melting of the $Cr2$ phase. ³ Values likely underestimated due to overlapping of anomalies and incomplete crystallization.

The observation of cold crystallization by POM was carried out for a sample cooled down at a rate of 20 K/min to 193 K (SmC_A^* glass) and heated back up at a rate of 2 K/min. The fractal box count analysis makes it easier and more objective to compare the POM results with the DSC curve registered during heating at the 2 K/min rate (Figure 3). The glass softening of the SmC_A^* phase did not lead to any change in texture (Figure 3a,b), while the pre-transitional effect was noticeable as texture darkening (Figure 3c) and an increase of the fractal dimension above 253 K. Cold crystallization leads to the decrease of the fractal dimension above 275 K and the dark texture observed in the 278–293 K range (Figure 3d) is attributed to the $Cr2$ phase. The melting of the $Cr2$ was observed by POM at 294 K as an increase of the fractal dimension. The textures registered above 294 K are similar; however, the numerical analysis indicates a phase transition at ca. 306 K, interpreted as a melting

of the Cr1 phase. The textures registered in the 295–306 K range are therefore attributed to a co-existence of the SmC_A^* phase and developing Cr1 phase (Figure 3e), and textures observed above 306 K are attributed to the pure SmC_A^* phase (Figure 3f).

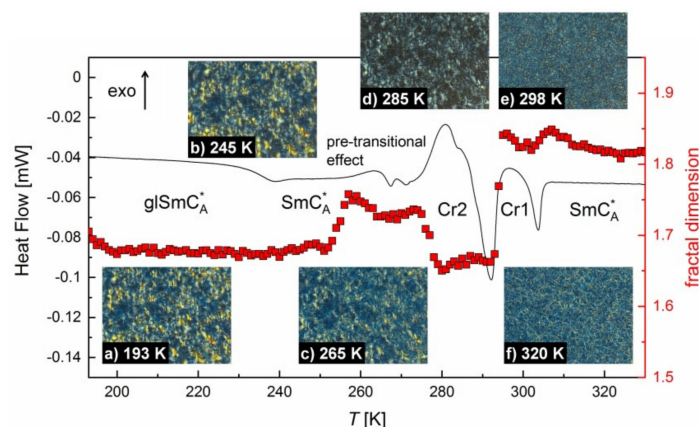


Figure 3. (a–f) POM textures of 3F7PhH6 collected during heating at the 2 K/min rate with the results of the fractal box count numerical analysis (squares) and DSC curve (line) registered with the same rate.

The polymorphism of the smectic phases was investigated by POM upon cooling and heating at the 2 K/min rate (Figure 4). In order to unambiguously detect all transitions between the smectic phases, two methods of numerical analysis were necessary: a fractal box count analysis and the determination of the modal luminance of red, green and blue components of each texture. For clarity, only the results for the blue component are plotted in Figure 4. The POM results confirm the presence of the SmC_α^* sub-phase upon cooling (Figure 4a). The $\text{Iso} \rightarrow \text{SmA}^*$ transition is visible as the discontinuity in the fractal dimension at 379 K. In the 373–375 K range, the fractal dimension is much lower than in the SmA^* phase, while the texture colour is almost the same. This implies a transition to the SmC_α^* phase, which is characterized by a small tilt angle and a very short helix pitch [31,32]. The next phase transition upon cooling occurred at 372.5 K and led to both the decrease of the fractal dimension and a change in texture color, indicating a more pronounced structural change. It is interpreted as a transition to the SmC^* phase, where the tilt angle is larger than in SmC_α^* [32]. The results of the numerical analysis indicate two further transitions at 365 K and 361.5 K. There are possible sub-phases between the SmC^* and SmC_A^* phases [31], however, the DSC results indicate a direct $\text{SmC}^* \rightarrow \text{SmC}_A^*$ transition (Figure 2). This is why we interpret the textures observed in the 361.5–365 K range as a co-existence of the SmC^* and SmC_A^* phases, which can occur over a relatively wide temperature range in thin samples, the fact which was confirmed experimentally, based on dielectric spectra, for other compounds [33,34]. A similar situation was observed during heating (Figure 4b). The $\text{SmC}_A^* \rightarrow \text{SmC}^*$ transition occurred with a coexistence region in the 366.5–369.5 K range. The change of texture color and increase of the fractal dimension at 374 K indicates either a $\text{SmC}^* \rightarrow \text{SmC}_\alpha^*$ or $\text{SmC}^* \rightarrow \text{SmA}^*$ transition. The $\text{SmC}_\alpha^* \rightarrow \text{SmA}^*$ transition temperature could not be determined; however, the width of the temperature range, between 374 K and 380 K ($\text{SmA}^* \rightarrow \text{Iso}$ transition), is comparable with the sum of temperature ranges of the SmA^* and SmC_α^* phases upon cooling (Figure 4c,d). It leads to a conclusion that the SmC_α^* sub-phase is also present on heating, and that the transition observed at 374 K should be interpreted as $\text{SmC}^* \rightarrow \text{SmC}_\alpha^*$.

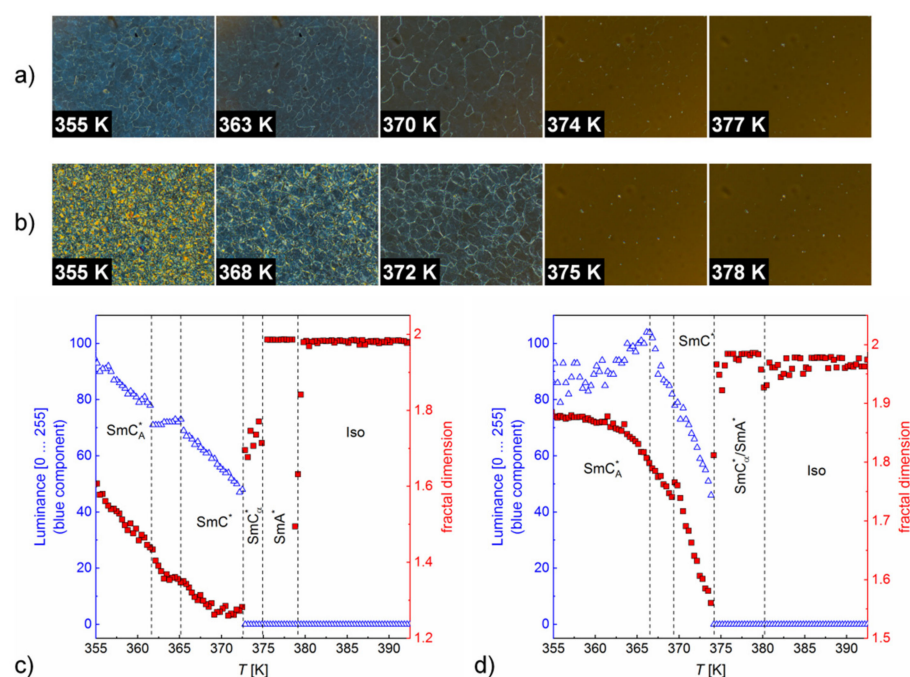


Figure 4. POM textures of 3F7FPhH6 collected during cooling (a) and heating (b) with the 2 K/min rate and the corresponding results of the numerical analysis for cooling (c) and heating (d).

3.2. Molecular Dynamics

The BDS spectra of 3F7FPhH6 registered without the bias field upon cooling and heating are gathered in Figures S4 and S5, respectively, of the Supplementary Materials. The absorption (imaginary) part ϵ'' of the complex permittivity is presented vs. frequency in Figure 5a,b for several temperatures. For the analysis of the dielectric relaxation processes of 3F7FPhH6, the Cole–Cole [35] and Havriliak–Negami [36] models were applied together with the contribution of the ionic conductivity to the absorption part [37], leading to the fitting formula:

$$\epsilon^*(f) = \epsilon_0 + \sum_j \frac{\Delta\epsilon_j}{(1 + (2\pi i\tau_j f)^{1-\alpha_j})^{\beta_j}} - \frac{iS}{f}, \quad (1)$$

where ϵ^* is the complex permittivity of the sample; the summation runs over relaxation processes in the sample; $\Delta\epsilon_j$ and τ_j are the dielectric strength and characteristic relaxation time of the j -th relaxation process; $\alpha_j \in \langle 0, 1 \rangle$ is a parameter describing the width of the distribution of the relaxation time; $\beta_j \in \langle 0, 1 \rangle$ is a parameter describing the asymmetry of this distribution (symmetric distribution for $\beta_j = 1$); and S is the fitting parameter proportional to the ionic conductivity. The dielectric strength of each process (except the γ -process), determined by fitting Equation (1), is shown in Figure 5c, and the Arrhenius plot of relaxation times is presented in Figure 5d.

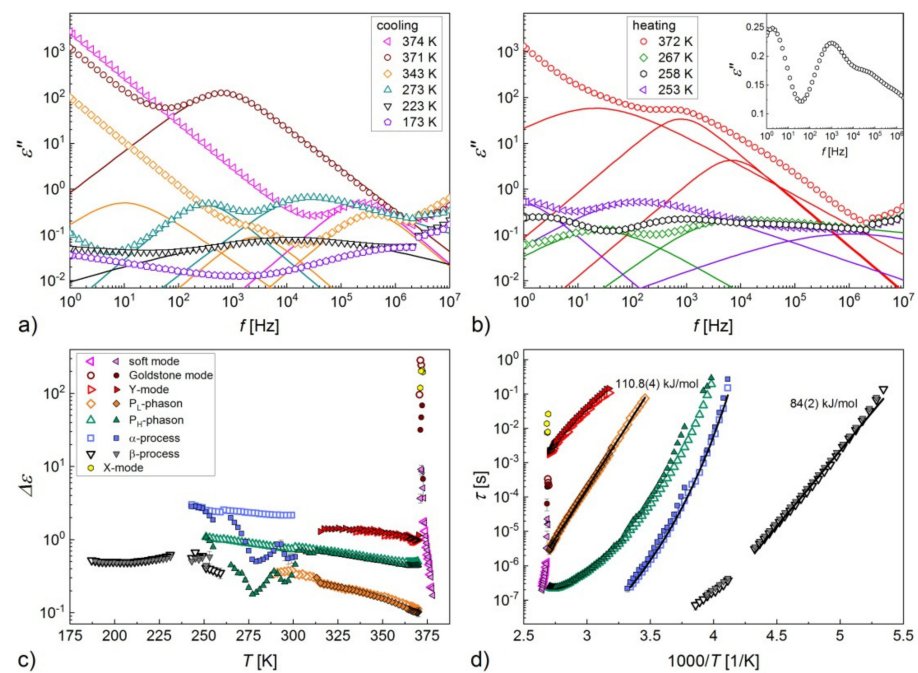


Figure 5. Absorption part of the dielectric spectra of 3F7FPhH6 upon cooling (a) and heating (b), dielectric strength values vs. temperature (c) and Arrhenius plot of relaxation times (d). Inset in (b) is an enlarged part of the results from 258 K. The lines in (a,b) show the fitting results of Equation (1), separately for each relaxation process and with omitted ionic conductivity contribution. The lines in (d) show the fitting results of the Arrhenius formula for the P_L process and β -process, and fitting results of the Vogel–Fulcher–Tammann equation (Equation (2)) for the α -process. Panels (c,d) have a common legend; open and solid symbols in these panels correspond to results obtained upon cooling and heating, respectively.

The first relaxation process upon cooling arose in the high frequency region of 10^5 – 10^6 Hz at 377 K, which corresponds to the $\text{Iso} \rightarrow \text{SmA}^*$ transition. This relaxation process is characterized by the Debye distribution ($\alpha = 0$, $\beta = 1$), the relaxation time increasing with decreasing temperature from $2.6 \cdot 10^{-7}$ s to $1.2 \cdot 10^{-6}$ s between 377 K and 373 K, and a small dielectric increment which increases, respectively, from 0.2 to 1.7 in the same temperature range. This process can, therefore, be identified as a soft mode, a collective fluctuation of the amplitude Θ of the complex order parameter $\Theta \exp(i\varphi)$ of the smectic phase, where Θ is the tilt angle and φ is the azimuthal angle around the tilt cone [37]. Below 373 K, another relaxation process, described by the Debye distribution, with a large dielectric strength reaching 280, appears around the 10^3 Hz frequency region. This process is identified as the Goldstone mode, a collective fluctuation of the azimuthal φ angle of the order parameter [37]. The $\text{SmC}^* \rightarrow \text{SmC}_A^*$ transition occurs at 370 K, when two additional relaxation processes appear in the frequency region between $5 \cdot 10^5$ Hz and 10^6 Hz. Three relaxation processes, with the symmetric distribution of relaxation times ($\beta = 1$), were observed in total, down to 55 K below the transition to the SmC_A^* phase, as shown in Figure 5a for 343 K. An unknown Y-process, with the lowest frequency, has a dielectric strength equal to 1–1.4 and the Cole–Cole distribution parameter $\alpha \approx 0.17$. Two other relaxation processes shown for 343 K can be identified as two phasons. The middle-frequency relaxation process ($f = 3 \cdot 10^3$ Hz, $\Delta\epsilon = 0.2$ at 343 K) is the P_L phason, the so-called antiferroelectric Goldstone mode, connected with in-phase fluctuations of the azimuthal angle φ in neighboring smectic layers. The high-frequency relaxation process ($f = 4 \cdot 10^5$ Hz, $\Delta\epsilon = 0.6$ at 343 K) is the P_H phason, i.e., the anti-phase fluctuations of the azimuthal angle φ in neighboring smectic layers [33,38,39]. Although the P_L process is a collective mode, its relaxation time shows the Arrhenius behavior (Figure 5d) with the activation energy $E_a = 110.8(4)$ kJ/mol. This is explained by the overlapping of P_L with the

molecular s-process (rotations around the axis of the highest moment of inertia) [33]. This assumption agrees with the occurrence of the larger Cole–Cole parameter (wider distribution of τ) for P_L ($\alpha = 0.1$ – 0.2) than for P_H ($\alpha = 0$). Below 300 K, the next high-frequency relaxation process with a dielectric strength of 2–3 was observed, as shown in Figure 5a for 273 K. This relaxation process is characterized by the asymmetric distribution of the relaxation time ($\alpha = 0.11$, $\beta = 0.38$ at 273 K), which is typical for the α -process, probably arising from the rotations of molecules around the axis of the smallest moment of inertia (l-process). The l-process is the molecular relaxation process; therefore, its relaxation time should follow the Arrhenius dependence on temperature. However, due to the glass transition in the SmC_A^* phase, the relaxation time shows a non-linear dependence in the Arrhenius plot (Figure 5d), as described by the Vogel–Fulcher–Tammann formula [40]:

$$\tau_\alpha = \tau_\infty \exp\left(\frac{B}{T - T_V}\right), \quad (2)$$

which transforms to the Arrhenius equation when the Vogel temperature $T_V = 0$. The fitting of the VFT formula to the relaxation time τ_α of the α -process determined upon cooling is presented in Figure 5d, with the fitted parameters $\tau_\infty = 3(1) \cdot 10^{-13}$ s, $B = 1565(55)$, $T_V = 184(2)$ K. The parameters of the VFT equation can be used to determine the fragility index m_f of a glassformer, which describes the deviation of $\tau_\alpha(T)$ dependence from the Arrhenius dependence [41]:

$$m_f = \left. \frac{d \log \tau_\alpha(T)}{d(T_g/T)} \right|_{T=T_g} = \frac{BT_g}{\ln 10 (T_g - T_V)^2}, \quad (3)$$

where the glass transition temperature T_g is defined as the temperature at which $\tau_\alpha = 100$ s [41]. For 3F7FPhH6, the T_g value determined from the parameters of the VFT formula is equal to 230.8(2) K, which agrees well with the DSC results. The fragility index of 3F7FPhH6, determined from Equation (3), is $m_f = 72(1)$. The strongest glassformers, with an Arrhenius-like behavior of the α -process and a weak tendency to crystallization, have a fragility index $m_f = 16$, while for the most fragile glassformers $m_f \approx 200$ [12,15,18,41,42], which means that 3F7FPhH6 is a glassformer with an intermediate fragility. In the high-frequency tail of the α -process, there is a secondary β -process, characterized by the dielectric strength of ca. 0.5, and a wide and symmetric distribution of the relaxation time ($\alpha = 0.6$ – 0.7 , $\beta = 1$). In the 233–241 K range, the parameters of the β -process are not determined because it is still overlapping with the α -process, which is, for the most part, out of the studied frequency range; therefore, the uncertainties of fitting would be considerable. The characteristic time τ_β of the β -process shows the Arrhenius dependence on temperature, with the activation energy $E_a = 84(2)$ kJ/mol (Figure 5d). For the flexible 3F7FPhH6 molecule, the β -process can be either the Johari–Goldstein process (movements of whole molecules) or the pseudo-JG process (movements of some parts of molecules) [43,44]. Recently, for the very similar 3F7HPhH7 compound with a longer $-C_rH_{2r+1}$ chain (see Figure 1a), the activation energy of the β -process has been reported to be equal to ca. 50 kJ/mol [18]. Based on such E_a value and DFT calculations, the β -process in the SmC_A^* glass of 3F7HPhH7 was interpreted as an intra-molecular rotation around the CC bond between the benzene ring and COO group [18]. For the 3F7FPhH6 compound, the activation energy of the β -process is much larger and DFT-B3LYP/def2TZVPP calculations of conformational energy performed for selected dihedral angles (see Figure S1) imply that this process cannot be ascribed to a single intra-molecular rotation. We suppose that, in the case of 3F7FPhH6, the β -process may originate from correlated rotations within the molecular core. The rotation of the benzene ring requires simultaneous changes of dihedral angles φ_3 (energy barrier 33.2 kJ/mol) and φ_4 (17.0 kJ/mol), leading to a total energy barrier of 50.2 kJ/mol. Meanwhile, the rotation of the biphenyl can occur, e.g., via change of dihedral angles φ_1 (28.5 kJ/mol) and φ_2 (3.5 kJ/mol), with a total energy barrier of 32.0 kJ/mol. With the assumption of correlated rotations of the benzene ring and biphenyl,

the total calculated energy barrier equals 82.4 kJ/mol, in agreement with the experimental activation energy of the β -process; therefore, such an explanation seems reasonable. The highest-frequency relaxation process observed for 3F7FPhH6 in the studied temperature range, denoted as the γ -process, appeared in the 10^6 – 10^7 Hz range close to 173 K, the lowest temperature achievable in the used spectrometer. This relaxation process was only partly visible in the measured frequency range, therefore a fitting of Equation (1) was not performed in this case. The very high frequency of the γ -process suggests that it originates from some conformational changes, e.g., within the $-C_3F_7$ chain [18,45], although the exact assignment to a particular intra-molecular rotation cannot be made because the activation energy of the γ -process in 3F7FPhH6 remains unknown.

On subsequent heating up to 253 K, the observed relaxation processes showed the same $\Delta\epsilon(T)$ and $\tau(T)$ dependences as upon cooling (Figure 5c,d). In the 255–265 K range, there is a splitting of the absorption peaks of the α -process (inset in Figure 5b), as similarly reported for 3F7HPhH7 [18]; the lower-frequency peak decreases and the higher-frequency peak increases with increasing temperature. The overlapping of two α -processes is too significant for a fitting of Equation (1). Upon cooling, only a single α -process was observed, and the splitting of this process occurred only on heating above the glass softening temperature; therefore, it can be explained as the rearrangements within the material (pre-translational effect) before the beginning of crystallization. In the 265–279 K range, the $\Delta\epsilon$ values of P_H and α -processes decreased quickly with the increasing temperature, indicating cold crystallization, although they did not decrease to zero, which means that crystallization was not complete. Above 279 K, the Cr2 phase started melting, which was shown as an increase of dielectric strength in both processes. After reaching maximum at 289–291 K, the $\Delta\epsilon$ values decreased, which is a sign of crystallization to the Cr1 phase. The melting of Cr1 started at 295 K, leading to the increase of $\Delta\epsilon$ of the P_H and α -processes. At 303 K, the $\Delta\epsilon$ of P_H is the same as that obtained upon cooling, while the α -process is out of the fitting range. In the SmC_A^* phase after the melting of Cr1, the relaxation processes show the same temperature dependences as observed upon cooling, while in the SmC^* phase, a strong X-process, not observed upon cooling, appears at low frequencies (Figure 5b). The unidentified Y-process and X-process both appear at small frequencies. One possible explanation is that they are related to the Maxwell–Wagner relaxation, although this process is more common for samples inside cells with aligning polymer layers [34,37,46]. In our case, the low-frequency processes may be caused by inhomogeneity in the distribution of ionic charge or by the distortion of the molecular alignment [47–49]. Since the Y-process appears only in the SmC_A^* phase and the X-process only in the SmC^* phase, the most probable explanation is relaxations arising from different molecular alignments close to the interface and in the middle of the sample. For the X-process, the relaxation related to the phase boundaries is also a possible explanation, since the temperature range of the SmC^* phase is narrow.

The soft mode in the SmC^* phase is difficult to investigate because it is hidden under the Goldstone mode with a larger dielectric strength. Therefore, the dielectric spectra close to the clearing temperature were registered in the external constant bias field of 40 V. As can be seen in Figure S6 of the Supplementary Materials, the bias field suppresses the Goldstone mode, which enables us to study the weaker soft mode in a wider temperature range. The real part of the complex permittivity at 10^4 Hz vs. the temperature obtained from the BDS measurement in the bias field is presented in Figure 6. The increase of ϵ' at 380.5 K corresponds to the $Iso \rightarrow SmA^*$ transition (shifted to higher temperature compared to the BDS results without the bias field). Two sharp maxima, that appeared on further cooling at 377 K and 375 K are interpreted as the signs of the $SmA^* \rightarrow SmC_\alpha^*$ and $SmC_\alpha^* \rightarrow SmC^*$ transitions, respectively. In the SmC^* phase, the permittivity decreases with a decreasing temperature down to the transition to the SmC_A^* phase at 372.5 K, below which ϵ' has a constant value. The temperature dependence of the frequency and inverse dielectric increment of the soft mode confirm the presence of the SmC_α^* sub-phase (inset in Figure 6). According to theoretical predictions, both the frequency and $\Delta\epsilon^{-1}$ of the soft mode decrease

with a decreasing temperature in the SmA^* phase and increase in the SmC^* phase, giving a V-shaped temperature dependence of these parameters [50,51]. For 3F7FPhH6, the decrease of f and $\Delta\epsilon^{-1}$ of the soft mode with a decreasing temperature is observed down to 377 K, but within the 375–377 K range both considered parameters are almost temperature independent. Below 375 K, the values of f and $\Delta\epsilon^{-1}$ apparently start increasing, although the fitting was not possible for temperatures lower than 374 K. The behaviour of the soft mode between 375 K and 377 K implies the presence of the SmC^* sub-phase, as similar observations were made for the SmC^* phase in the 3F5FPhF6 compound [30].

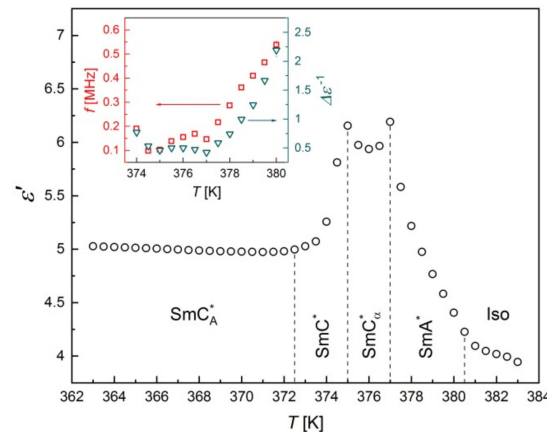


Figure 6. Dispersion part registered at 10^4 Hz upon cooling of the 3F7FPhH6 sample in a bias field of 40 V. The inset shows the frequency and inverse dielectric strength of the soft mode vs. temperature obtained by fitting Equation (1) to the spectra collected in the bias field.

3.3. Kinetics of Cold Crystallization

The kinetics of the cold crystallization of 3F7FPhH6 was studied for two samples: the sample within an aluminum pan, used in the DSC measurement (denoted further as the DSC sample), and the sample in the form of a thin film of ca. 50 μm thickness between two gold electrodes, used in the BDS measurement (referred to as the BDS sample). Figure 7a shows the DSC curves registered in isothermal conditions after heating the sample above the glass softening temperature. For each studied crystallization temperature T_{cr} from the 273–293 K range, an exothermal anomaly indicating cold crystallization, was observed. The crystallization degree $X(t)$ (the fraction of a crystal phase in the sample) was determined by the integration of the exothermal anomaly over time, from the initialization time t_0 to the time t_{end} when crystallization finished [52]:

$$X(t) = \frac{\int_{t_0}^{t_{end}} \Phi(t) dt}{\int_{t_0}^t \Phi(t) dt} = \frac{\int_{t_0}^{t_{end}} \Phi(t) dt}{\Delta H_{cr}}, \quad (4)$$

where $\Phi(t)$ is the heat flow and ΔH_{cr} is the enthalpy change of crystallization. The ΔH_{cr} value increases with the increasing T_{cr} , from 5.8 kJ/mol for 273 K to 14.9 kJ/mol for 283 K, then decreases slowly with further increasing of the crystallization temperature, down to 12.5 kJ/mol for 293 K (Table 2). The differences in ΔH_{cr} can be explained by an analysis of the DSC curves registered during heating the sample after the end of the cold crystallization (Figure 7b). For the cold crystallization in 273 K, the results from the subsequent heating revealed two endothermic anomalies with the onset temperatures 284.5 K and 299.2 K, arising from the melting of the Cr2 and Cr1 phases, respectively. This means that in 273 K, the sample crystallized to the mixture of Cr1 and Cr2. For higher T_{cr} (278–293 K), only an anomaly interpreted as the melting of Cr1 was observed, and its onset temperature shifted towards higher values (from 298.5 K to 302.6 K) with the increasing T_{cr} . Only after the cold crystallization in 283 K, was an additional small anomaly with the peak temperature of 311 K noticeable, which might originate from another, third crystal phase; however, a

more probable explanation is an inhomogeneity in the microstructure of the crystal, i.e., the presence of crystal domains with a smaller number of defects and, consequently, a higher melting temperature. The total enthalpy of melting ΔH_m follows the same dependence on T_{cr} as the enthalpy of crystallization, with the maximal value $\Delta H_m = 18.5$ kJ/mole for 283 K. The change of ΔH_m with T_{cr} is likely caused by the different microstructures of the crystals grown at different temperatures (e.g., the number of defects and the crystal shape). Note that the melting enthalpy of Cr1 given in Table 1 was strongly underestimated because of the incomplete crystallization to the Cr1 phase in non-isothermal conditions.

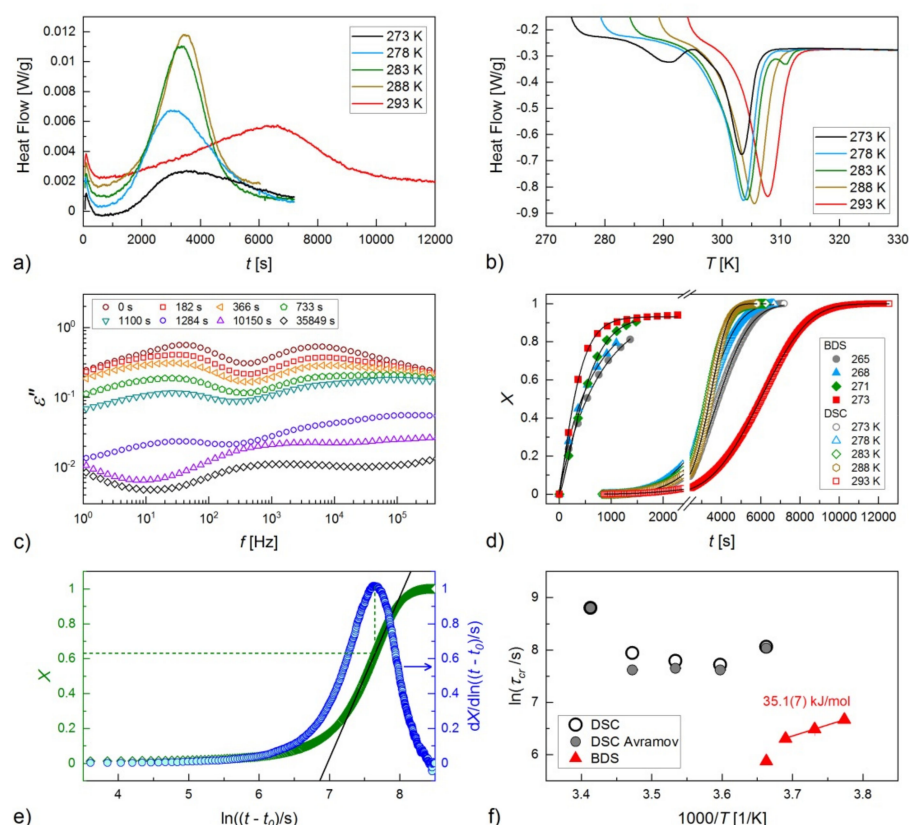


Figure 7. Isothermal cold crystallization of 3F7PhH6: DSC curves registered during cold crystallization (a) and during subsequent heating with the 10 K/min rate (b); absorption part of the BDS spectra during cold crystallization in 268 K (c); crystallization degree $X(t)$ with fitting results of Equation (6) (d); Avramov plot for isothermal cold crystallization in 283 K (e); and the Arrhenius plot of the characteristic crystallization time τ_{cr} (f).

Table 2. Crystallization enthalpy ΔH_{cr} and melting enthalpy ΔH_m together with onset T_o and peak T_p temperatures of anomalies related to the melting of a crystal phase after the isothermal cold crystallization of 3F7PhH6 in various T_{cr} temperatures.

T_{cr} (K)	ΔH_{cr} (kJ/mol)	T_o (K)	T_p (K)	ΔH_m (kJ/mol)
273	5.8	284.5, 299.2	291.0, 303.3	2.7, 12.6
278	12.3	298.5	303.7	17.6
283	14.9	298.4, –	304.2, 310.8	18.6, 0.9
288	13.8	299.8	305.5	17.7
293	12.6	302.6	307.7	15.7

The BDS method was used to investigate cold crystallization in the lower temperature range of 265–273 K. Crystallization was visible in the dielectric spectra as a decrease in

the dielectric strength of relaxation processes, as shown for $T_{cr} = 268$ K in Figure 7c. The crystallization degree (Figure 7d) was determined from the BDS spectra as [53]:

$$X(t) = \frac{\varepsilon''_{P_{Hmax}}(0) - \varepsilon''_{P_{Hmax}}(t)}{\varepsilon''_{P_{Hmax}}(0)}, \quad (5)$$

where $\varepsilon''_{P_{Hmax}}(t)$ is the maximal imaginary part ε'' of the dielectric permittivity in the frequency range of the P_H -process. Although for all the T_c values (273, 271, 268, 265 K) applied in the BDS measurements the cold crystallization began with an initialization time close to zero, a very weak relaxation process with a wide distribution of the relaxation time was visible in the spectra even after several hours. This relaxation process could be the remaining α -process, shifted towards lower frequencies during crystallization, as is sometimes observed [54], which would suggest incomplete crystallization. However, a weak relaxation process can also originate from the developed crystal phase [18].

The modified version of the Avrami model [55–57] was applied to describe the crystallization degree vs. time dependence:

$$X(t) = A \left(1 - \exp \left(- \left(\frac{t - t_0}{\tau_X} \right)^n \right) \right), \quad (6)$$

where the Avrami exponent n depends on the nucleation rate and the type of crystal growth (1-, 2-, 3-dimensional), τ_{cr} is the characteristic time of crystallization and t_0 is the initialization time of crystallization. The A parameter was introduced to properly fit Equation (6) to the $X(t)$ values obtained by BDS. In the classical Avrami model, $A = 1$. Equation (6) is often transformed to the form $\ln(1 - \ln(1 - X(t)))$ vs. $\ln(t - t_0)$, for which τ_{cr} and n can be determined by the linear fit. This requires a preliminary determination of t_0 , which can be accomplished by a method proposed by Avramov et al. [57]. This method is based on the fact that in the Avrami model, the $dX(t)/d\ln(t - t_0)$ derivative has a maximum at time $t = \tau_{cr}$, when $X(\tau_{cr}) \approx 0.63$, only for the proper choice of the initialization time t_0 . This relationship can be used to determine both the t_0 and τ_{cr} values. The Avrami exponent can be then obtained by fitting a line to the linear part of the $X(\ln(t - t_0))$ plot as $n = eb$, where e is the Euler constant and b is the line slope. DSC data were analyzed by both fitting the Equation (6) in the whole $X(t)$ range (Figure 7d, $A = 1$) and by using the Avramov method (Figure 7e). The results are compared in Table 3. For crystallization in 293 K, the initialization time was set to zero for each method, and the unphysical t_0 values were obtained (−1000 s from the fitting of Equation (6) and −1700 s by the Avramov method). While for 273 K, similar results were obtained by both methods; for 278–288 K there was a discrepancy, as the initialization time determined by the Avramov method was larger than that obtained from the fitting of Equation (6). The probable explanation is that the crystallization kinetics was different in the beginning and in the main part of the crystal growth. Then, the t_0 value of the main crystallization process can be larger than the actual time when the crystallization begins. Since we are more interested in the crystallization kinetics for the intermediate $X(t)$ values (0.3–0.8), in further discussion we will refer to the values determined by the Avramov method. For the BDS data, with a much smaller number of experimental points, the parameters of the Avrami model were obtained solely by fitting Equation (6) (Figure 7d). Since for each crystallization temperature the decrease of $\varepsilon''_{P_{Hmax}}(t)$ was already observed in the second registered spectrum, the initialization time was set as $t_0 = 0$. For $T_{cr} = 265$ K and 268 K, a good fitting could be obtained with $A = 1$ (Figure 7d). For $T_{cr} = 271$ K and 273 K, it was necessary to assume an incomplete crystallization ($A = 0.93$).

Table 3. Initialization time t_0 , characteristic time τ_{cr} and Avrami exponent n of the isothermal cold crystallization of 3F7FPhH6 investigated by BDS and DSC. For results obtained by fitting Equation (6), $A = 0.93$ for 271, 273 K and $A = 1$ for other temperatures.

T_{cr} (K)	t_0 (s)	τ_{cr} (s)	n
BDS, fitting results of Equation (6)			
265	0	785(8)	0.94(2)
268	0	658(1)	0.88(1)
271	0	549(12)	1.32(4)
273	0	357(5)	1.20(3)
DSC, fitting results of Equation (6)			
273	1291(2)	2991(2)	2.31(1)
278	1300(1)	2440(1)	2.15(1)
283	786(3)	2817(3)	3.58(1)
288	178(5)	3485(5)	4.89(1)
293	0	6642(1)	3.58(1)
DSC, Avramov method			
273	1209(23)	3080(23)	2.13(2)
278	1687(13)	2034(13)	1.65(2)
283	1483(19)	2103(19)	2.52(3)
288	1613(20)	2032(20)	2.65(4)
293	0	6652(4)	3.40(2)

Comparing the BDS and DSC results (Table 3, Figure 7f), it can be seen that cold crystallization started and occurred much faster in the BDS sample than in the DSC one. In the BDS sample, crystallization started immediately after heating to a given crystallization temperature ($t_0 = 0$). The easier crystallization in the BDS sample, which was thinner than the DSC sample, can be explained by a more significant contribution of nucleation on the cell/sample interface to overall nucleation in the sample [58]. It is confirmed by the $\tau_{cr}(T)$ dependency, as the decrease of τ_{cr} from 800 s to 350 s with increasing temperature means that the crystallization rate is controlled more by the diffusion (crystal growth) rate rather than by the nucleation rate [59]. The τ_{cr} values for $T_{cr} = 268$ –273 K follow the Arrhenius dependence with a rather low activation energy $E_a = 35.1(7)$ kJ/mol (the respective activation energy determined by BDS for the isothermal cold crystallization of 3F7HPhH7 is ca. 130 kJ/mol [18]). The characteristic crystallization time for $T_{cr} = 273$ K was smaller than expected from the Arrhenius dependence obtained for lower temperatures. The possible explanation is that in the 268–273 K range, the sample crystallizes only in the Cr2 phase, while in 273 K there is a co-crystallization of Cr2 and Cr1 phases, which leads to a change in crystallization kinetics. In the DSC sample, the initialization time in 273–278 K was $t_0 \approx 1400$ –1700 s, while for 293 K it decreased significantly. The τ_{cr} values also do not show a monotonous dependence on temperature. At 273 K, $\tau_{cr} \approx 3100$ s, in the 278–288 K range, the τ_{cr} value was almost constant and equal to 2000–2100 s, while in 293 K crystallization occurred considerably slower ($\tau_{cr} \approx 6700$ s) than in the lower studied temperatures, despite the smaller initialization time. The results for the DSC sample are unusual. The obtained $\tau_{cr}(T)$ dependency suggests that in the 273–288 K range the crystallization rate depends almost equally on the rates of nucleation and diffusion, while for 293 K the crystallization process is governed mostly by nucleation. However, t_0 has the smallest value for 293 K, which implies that nucleation rate is higher than for 273–288 K. The explanation may lay in the fact that the Cr2 phase starts melting at 285–287 K. The likely scenario is that in the 273–283 K range, the nuclei of Cr2 phase are initially formed. On the other hand, DSC results show that the sample was entirely or mostly in the Cr1 phase after completed crystallization (Figure 7b), which requires the formation of the nuclei of Cr1. If we assume that the presence of Cr2 nuclei hinders the formation of Cr1 nuclei, it can explain the larger t_0 values in the 273–283 K range. During heating to $T_{cr} = 293$ K,

Cr2 nuclei formed in lower temperatures are destroyed, but they leave defects which can further be the basis for the heterogeneous nucleation of the Cr1 phase, leading to a smaller t_0 than in lower temperatures. Due to relatively fast (10 K/min) heating, the number of developed Cr2 nuclei is presumably smaller than during isothermal crystallization in the 273–283 K range, so the number of Cr1 nuclei formed by heterogeneous nucleation is also small. Moreover, the homogeneous nucleation does not occur easily for $T_{cr} = 293$ K because of the proximity of the melting temperature of Cr1 (301 K), which leads to a small thermodynamic driving force of crystallization [58]. The results for $T_{cr} = 288$ K suggest that there were still some surviving Cr2 nuclei in the sample, even if it was slightly above the melting temperature of Cr2 determined by DSC, as the crystallization kinetics more resembles that observed in the 273–283 K range. The melting temperatures of Cr1 and Cr2 determined in this study indeed show that they vary with crystallization conditions (Tables 1 and 2).

The obtained Avrami exponents are smaller for the BDS sample ($n = 0.9$ – 1.3) than for the DSC sample ($n = 1.7$ – 3.4), which is caused by the smaller thickness of the former. The $n \approx 1$ value indicates a one-dimensional crystal growth with already formed nuclei [57], which agrees with assumption of a mostly heterogeneous nucleation in the BDS sample. In the DSC sample, for $T_{cr} = 273$ – 288 K the Avrami exponent equals $n = 1.7$ – 2.7 , which implies a one-dimensional ($n = 2$) or two-dimensional ($n = 3$) crystal growth with a constant nucleation rate [57]. For $T_{cr} = 293$ K the Avrami exponent is larger, $n = 3.4$, which can be interpreted as a three-dimensional crystal growth with non-zero nucleation rate [57]. This is in accordance with the previously discussed temperature dependence of τ_{cr} : nucleation occurs not only in the beginning of crystallization, but also simultaneously with the crystal growth, and reduced dimensionality of growing crystals at lower temperatures is likely caused by previously formed small domains of Cr2.

3.4. Comparison with the 3F7HPhF6 and 3F7HPhH7 Glassformers

The results regarding the glass transition of the SmC_A^* phase and isothermal cold crystallization obtained herein for 3F7FPhH6 have been collected in Table 4, together with the corresponding results for 3F7HPhF6 ($m = 7$, $X_1 = \text{H}$, $X_2 = \text{F}$, $r = 6$, see Figure 1a) [12,13] and 3F7HPhH7 ($m = 7$, $X_1 = \text{H}$, $X_2 = \text{H}$, $r = 7$) [16,18]. Each compound differs from 3F7FPhH6 by one detail of the molecular structure: the fluoro substitution of the molecular core (3F7HPhF6) or the $-\text{C}_r\text{H}_{2r+1}$ chain length (3F7HPhH7). For 3F7FPhH6 and 3F7HPhF6, crystallization was never observed upon cooling, while for 3F7HPhH7, melt crystallization occurred for a very slow cooling rate (1 K/min). Since the type of the sample container was shown to influence the crystal growth, only the DSC results regarding cold crystallization kinetics have been compared. The exception is 3F7HPhF6, where the results obtained by X-ray diffraction (XRD) were also included, as they were in accordance with the DSC results. The BDS results have been used to compare the glass transition temperatures and fragility parameters. Looking at the results for 3F7FPhH6 and 3F7HPhF6, it can be noted that for $r = 7$, fluoro substitution at the X_2 position decreases the glass transition temperature T_g and increases the cold crystallization rate. A comparison with 3F7HPhH7 implies that the increasing length of the $-\text{C}_r\text{H}_{2r+1}$ chain also leads to faster crystallization, but the T_g is higher than that for 3F7FPhH6. The fragility parameter has the lowest value for 3F7FPhH6, making it the strongest glassformer among the three discussed compounds. There is also a significant difference in the cold crystallization mechanism between 3F7FPhH6 and the previously studied 3F7HPhF6 and 3F7HPhH7 [13,16]. For both 3F7HPhF6 and 3F7HPhH7, cold crystallization is controlled mostly by the diffusion rate, as the characteristic crystallization time decreases with the increasing temperature, according to the Arrhenius equation. The activation energies determined by DSC (and XRD for 3F7HPhF6) are 79 kJ/mol [13] and 133 kJ/mol [16] for 3F7HPhF6 and 3F7HPhH7, respectively. For 3F7FPhH6, instead, the cold crystallization investigated by DSC does not show the Arrhenius dependence of $\tau_{cr}(T)$, and both nucleation and diffusion have an equal impact on the crystallization kinetics. As is explained in Section 3.3, such a situation for

3F7FPhH6 is caused by the presence of two crystal phases. For 3F7HPhF6 and 3F7HPhH7, only one crystal phase was reported, which explains the simple Arrhenius dependence of the characteristic crystallization time.

Table 4. Comparison of the glassforming properties and cold crystallization kinetics of 3F7FPhH6 presented in this paper and previously reported for the 3F7X₁PhX₂r compounds with almost identical molecular formulas.

Compound	3F7FPhH6	3F7HPhF6	3F7HPhH7
DSC results			
Vitrification of the SmC _A [*] phase	Always upon cooling ¹	Always upon cooling ¹ [11]	For cooling rate ≥2 K/min [15]
Investigated T_{cr} (K)	273–293	233–250 [12]	261–264 [15]
τ_{cr} (s)	2200–6650	100–2200 ² [12]	350–750 [15]
BDS results			
T_g (K)	231	223 [11]	259, 239 [17]
m_f	72	102 [11]	150, 136 [17]

¹ No crystallization even for slow cooling during BDS or XRD measurement. ² Also including XRD results.

The hindrance of cold crystallization by the presence of different crystal phases seems even more probable when one looks at the behavior of the 3F5HPhF6 compound [14] from the same homologous series as 3F7HPhF6. The DSC results for these homologues [12,14] show that for 3F5HPhF6, cold crystallization occurs much slower than for 3F7HPhF6 and, most importantly, in 3F5HPhF6 there are two crystal phases confirmed by the XRD measurement [14]. Although the detailed investigations of the cold crystallization kinetics for 3F5HPhF6 have not yet been published, there is a high possibility that the slowing down of crystallization is connected with a polymorphism of the crystal phases, as is suspected for 3F7FPhH6.

Finally, the 3F5HPhH6 compound ($m = 5$, $X_1 = H$, $X_2 = H$, $r = 6$) [60], from the same series as 3F7FPhH6 but with a shorter -C_mH_{2m}- chain and slightly higher fragility $m_f = 89$, shows a much faster cold crystallization despite possessing two crystal phases. However, in 3F5HPhH6 there is a rather direct Cr2 → Cr1 transition, without the previous melting of the Cr2 phase as was observed here for 3F7FPhH6. This is why, for 3F5HPhH6, the presence of two crystal phases does not have a hindering effect on cold crystallization.

4. Conclusions

The phase transitions of the chiral 3F7FPhH6 compound were investigated in detail by complementary methods. Next to the reported earlier SmA^{*}, SmC^{*} and SmC_A^{*} liquid crystal phases, an additional SmC_α^{*} sub-phase was observed in the DSC and POM results between the SmA^{*} and SmC^{*} phases; its presence was also confirmed by the temperature behavior of the soft mode in the BDS spectra. 3F7FPhH6 undergoes a glass transition of the SmC_A^{*} phase, even for the lowest applied cooling rate (2 K/min). Analysis of the non-Arrhenius behavior of the characteristic time of the α-process in the supercooled SmC_A^{*} phase allows for the obtainment of the fragility parameter $m_f = 72$. 3F7FPhH6 is, therefore, a stronger glassformer with a weaker tendency to cold crystallization than the previously investigated 3F7HPhF6 and 3F7HPhH7, which have fragility parameters above 100. Upon heating, and close to the onset of cold crystallization, the splitting of the α-process was noticeable in the BDS spectra of 3F7FPhH6, as it was for 3F7HPhH7. The splitting is explained as a pre-transitional effect, as it is not observed upon cooling. Next to the α-process, the secondary β-process and γ-process are observed. Both are interpreted as intra-molecular motions. The β-process, according to the results of the DFT/B3LYP-TZVPP calculations, is attributed to the correlated rotations of the benzene ring and biphenyl within the molecular core, while the faster γ-process may be connected with conformational changes of flexible chains. An investigation of the isothermal cold

crystallization of 3F7FPhH6 showed that crystallization occurs slower than in 3F7HPhF6 and 3F7HPhH7. Moreover, the characteristic crystallization time of 3F7FPhH6 did not show a simple Arrhenius dependence (diffusion-controlled process), as reported for the two mentioned compounds. The complicated dependence of the initialization time and crystallization time on temperature is explained by the presence of two crystal phases, the low-temperature Cr2 and high-temperature Cr1, which can co-nucleate below the melting temperature of Cr2. A comparison of the crystallization kinetics determined for two types of samples, the bulk DSC sample and the thin BDS sample, proves that different boundary conditions can lead to crucial differences in the crystallization rate. This is why, while comparing crystallization kinetics for various liquid crystalline substances, it is advised to compare results obtained by the same method if possible.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11121487/s1>, Figure S1: Relative conformational energy calculated with PM7 and DFT-B3LYP/def2TZVPP methods for selected torsional angles within the isolated 3F7HPhH6 molecule, Figure S2: Textures of 3F7FPhH6 registered during heating from 173 K with 2 K/min rate analyzed with the fractal box count method, Figure S3: Textures of 3F7FPhH6 registered upon cooling with 2 K/min rate with histograms of luminance of red, green and blue components, Figure S4: Dielectric spectra of 3F7FPhH6 registered upon cooling without the bias field, Figure S5: Dielectric spectra of 3F7FPhH6 registered on heating without the bias field, Figure S6: Dielectric spectra of 3F7FPhH6 registered upon cooling in the 40 V bias field.

Author Contributions: Conceptualization: A.D. (Aleksandra Deptuch); methodology: A.D. (Aleksandra Deptuch) and W.Z.; Investigation: A.D. (Aleksandra Deptuch), M.J.-D., E.J.-G. and A.D. (Anna Drzewicz); Resources: M.U.; Formal analysis: A.D. (Aleksandra Deptuch); Writing—original draft preparation: A.D. (Aleksandra Deptuch); Writing—review and editing: all authors; Visualization: A.D. (Aleksandra Deptuch). All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Institute of Nuclear Physics Polish Academy of Sciences, Kraków, Poland.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: DFT calculations were carried out on the Prometheus cluster from the Academic Computer Centre, ‘Cyfronet’, AGH (PL-Grid infrastructure, grant plgmolcryst).

Conflicts of Interest: The authors declare no conflict of interest.

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