Molecular Orientation and Dynamics in Ferroelectric Diblock Copolymers Monitored by FT-IR Spectroscopy

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ABSTRACT: In ferroelectric liquid crystalline block copolymers the properties of ferroelectric liquid crystals (LC) are combined with those of diblock copolymers: hence, one observes in these materials a microphase separation between the amorphous polymer (polystyrene [PS]) and the ferroelectric liquid crystal segment. The latter group can be switched by applying an external electric field ($<10^4$ V cm^{-1}). FT-IR spectroscopy (time-resolved) was employed to study structure and dynamics in these systems. From analysis of the dichroism of the FT-IR spectra, it was concluded that the components in the PS microphase are oriented randomly while the liquid crystalline groups form an ordered phase. Time-resolved measurements of the switching of the LC block were performed during the application of an external electric field. It may be shown that switching is of an electroclinic type and that the tilt angle and the mesogenic motion increase with temperature, especially if the PS block is heated above T_g. The orientation of the LC block after heating to the isotropic phase is completely restored due to the memory effect of the polymer microstructure.

Introduction

Block copolymers have attracted attention for many years since they have been recognized as materials that combine the properties of two completely different polymers without macroscopic phase separation. Polymers containing liquid crystalline (LC) and amorphous blocks are currently under intensive investigation.[1−3] Due to microphase separation, the LC block is confined by an amorphous microphase that may dramatically influence the properties of the LC state. A study of the influence of the amorphous component on orientation and structure of the LC component is one of the main goals for such systems. Until recently, these studies have been limited to block copolymers containing nematic LC components.[4] To probe the effect of polymer microstructure on ferroelectric liquid crystals (FLC) (e.g., fast electrooptical response), new block copolymers containing smectic C* liquid crystal components have been synthesized.[5,6] FLCs show bistable electrooptical switching in the Sm C* phase if their helical superstructure is suppressed in a surface stabilized cell geometry. It was assumed that confining of the Sm C* phase in lamellar layers of block copolymers would also break the helix.[7] Electrooptical studies of these systems showed that the ferroelectric block copolymers possess both ferroelectric and electroclinic switching depending on molecular composition and sample preparation technique.[5] To understand the mechanism of molecular orientation in such systems, a detailed analysis of segmental motion must be performed. IR spectroscopy is a very informative technique for this purpose since the reorientational motion of different chemical groups can easily be monitored with this method. To elucidate the influence of microphase confinement on orientation and the mobility of different molecular segments in ferroelectric liquid crystalline block copolymer (FLCBC), we present in this paper the results of our studies by FT-IR spectroscopy.

Table 1. Composition of the Diblock Copolymers and Their Thermal Properties

sample	M_{PS}	M_{FLC}	T_{gPS} [°C][a]	T_{gLC} [°C][a]	phase behavior[a]
B46/54	46000	54000	95	25	SmC* 117 °C SmA 130 °C I
B8/13	8000	13000	72	33	SmC* 103 °C SmA 122 °C I

[a] Determined by DSC in ref 5.

Experimental Section

The chemical structure of the FLC block copolymers investigated in this report is shown in Figure 1. The polymer chain consists of two blocks: polystyrene (PS) and a side-chain ferroelectric liquid crystalline polymer (LC). The two polymers (B8/13 and B46/54) with different lengths of PS and FLC blocks were investigated. The molecular weights of the blocks in these polymers and their mesophase sequences are given in Table 1. The synthesis of the investigated polymers has been described elsewhere.[5] Orientation of polymers was achieved by shearing the polymer melt between two indium tin oxide (ITO)-coated CaF_2 plates at 10 °C below the clearing point. A gap of 2 μm between the ITO electrodes was maintained by PET spacers. The CaF_2 windows are transparent to both visible and infrared (up to 1000 cm^{-1}) regions. This provided the possibility to study the switching phenomena in both visible and infrared light. The IR spectra (at a spectral resolution of 4 cm^{-1}) were recorded with an IR microscope attached to a BioRad 6000 FT-IR spectrometer. The experimental geometry is shown in Figure 2. The measured spot was 100 × 100 μm^2. To follow the segmental motion, time-resolved IR spectra were recorded at a rate of 25 spectra per second during reorientation of the polymer segments under an electric

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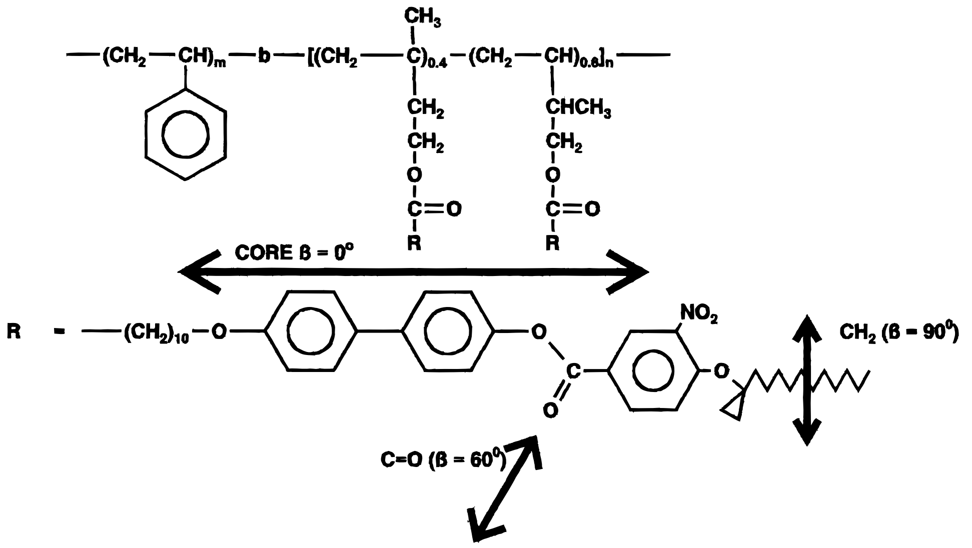

Figure 1. Molecular structure of the block copolymers. The thick double-arrowed lines indicate the direction of the transition moment of the IR bands for the corresponding molecular moieties.

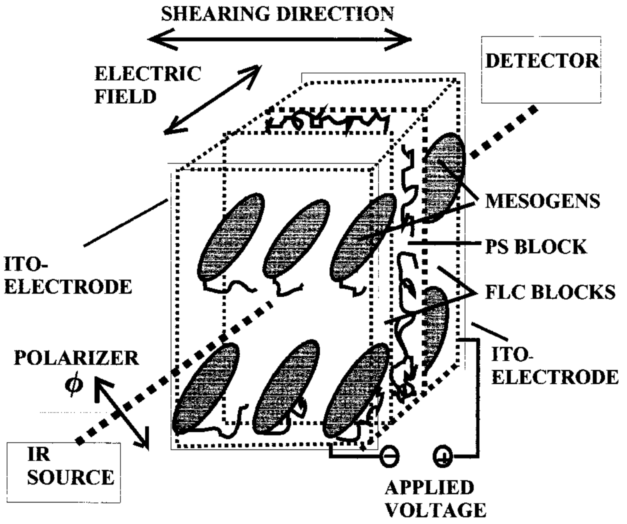

Figure 2. Principal scheme of the experimental setup. The polarizer angle ϕ is indicated.

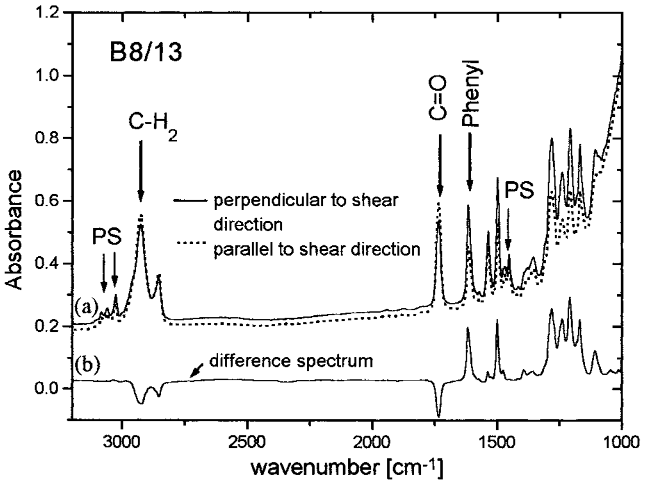

Figure 3. (a) Polarized static spectra of the block copolymer B8/13 at 25 °C recorded with polarization perpendicular (solid line, $A_\perp$) and parallel (dotted line, $A_\|$) to the shearing direction. (b) Polarized difference spectrum $A_\perp - A_\|$ for block copolymer B8/13.

field. Details of the measurement setup can be found in ref 8.

Results and Discussion

Band Assignment. The information about arrangement of molecular segments can be derived from polarized IR spectra if the IR absorption bands can be unequivocally assigned to vibrations in the corresponding moiety and if the angle β, which is formed by the transition moment of that vibration and the segmental axis, is known. Figure 3a shows the absorption spectra recorded with polarization perpendicular (solid line, $A_\perp$) and parallel (dotted line, $A_\|$) to the shearing direction. For determination of the orientation of the FLC component we used the 1613 and 1495 cm^{-1} bands (ν(C–C)$_{ar}$, benzoic ring of the mesogens, $\beta \approx 0°$) and the 1737 cm^{-1} band (ν(C=O), $\beta \approx 60°$). The bands due to different carbonyls (the carbonyl in the mesogen and that close to the backbone) are heavily overlapped and cannot be distinguished. The bands with a maximum absorption at 2927 and 2854 cm^{-1} are related to symmetric and asymmetric stretching vibrations of CH$_2$ groups ($\beta \approx 70-90°$).

Orientation of Molecular Segments. Figure 3b shows the difference spectra obtained by subtraction of absorption spectra recorded with polarization perpendicular ($A_\perp$) and parallel to the shearing direction. As can be seen from this figure, the 1613, 1495, and 1280 cm^{-1} bands show perpendicular dichroism ($A_\perp > A_\|$) whereas 2927, 2854, and 1737 cm^{-1} bands show parallel dichroism ($A_\perp < A_\|$). If it is taken into account that the transition moments for 1613 and 1495 cm^{-1} bands are nearly parallel to the long axis of the mesogen and the transition moment for 1737 cm^{-1} is inclined at 60° to the axis of the mesogen, it is possible to conclude from the dichroism of these bands that the mesogens orient preferably perpendicular to the shearing direction.

All bands due to polystyrene chains show no dichroism, and for this reason they do not appear in the difference spectrum. This observation means that the segments in polystyrene domains are randomly oriented. For this reason the observed dichroism of the 2927 and 2854 cm^{-1} bands can be related to the orientation of the CH$_2$ groups in the FLC part of the

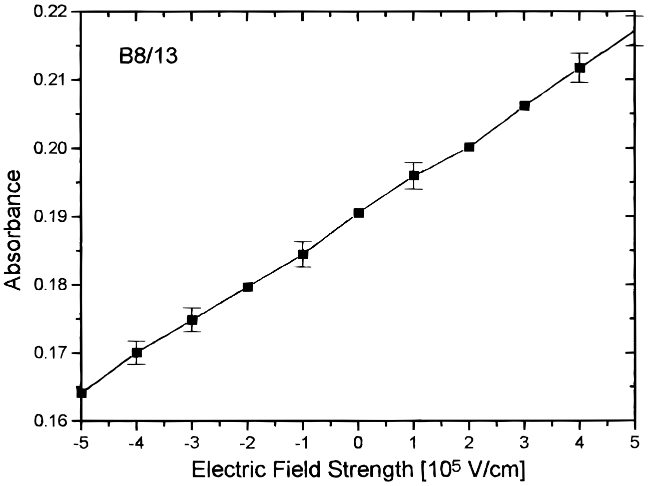

Figure 4. Absorbance changes of the phenyl band (1613 cm^{-1}) versus the applied external electric field at 90 °C for block copolymer B8/13. IR polarizer angle is fixed at 45°.

block copolymer (mainly the tail and the spacer which links the mesogen to the backbone).

Switching Behavior in an Electric Field. Electrooptical studies in visible light carried out on B8/13 and B46/54 samples provide evidence that these block copolymers show electroclinic-like switching behavior over all temperature ranges. We explain the switching behavior as follows: The block copolymer B46/54 should possess a lamellar structure, because of similar volume fraction of LC and amorphous block. The block copolymer B8/13 should possess a cylindrical PS structure because of a lower volume fraction of the amorphous block. A freshly prepared sample has a random orientation of the LC and PS domains. After shearing, the lamellae (or cylinders) align in the plane of the glass plates, resulting in an orientation of the smectic layers perpendicular to the shearing direction. The oriented lamellae (or cylinders) force the mesogens to align parallel to the interface. This indicates that the block microdomain structure may stabilize the FLC. This kind of switching is also revealed by the IR absorbance spectra. This is demonstrated in Figure 4, which shows intensity changes of the 1613 cm^{-1} band versus applied dc voltage at 90 °C. The linear dependence of the intensity on voltage reflects the tilt angle of the mesogenic groups changing proportionally to electric field. To obtain the induced tilt angles for different molecular moieties, we recorded the IR spectra of B8/13 for different polarizations of the IR beam (from 0° to 180° in steps of 10°) at temperatures of 110 and 90 °C. The polar plot of absorption of the 2927 ($\nu_{as}(CH_2)$), 1737 (ν(C=O)), and 1613 cm^{-1} ($\nu(C-C)_{ar}$) bands at voltages −120, 0, and +120 V are presented in Figure 5a, b, and c, respectively (110 °C). The 0° polarization in these plots corresponds to polarization parallel to the shearing direction. As can be seen from Figure 5b (0 V), all selected bands attain maxima or minima at 0 or 90°. This behavior corresponds to a symmetrical distribution function of different molecular moieties and the absence of rotational bias of the carbonyl group.[9,10] The shift of the absorption maxima and minima (relative to their position at 0 V) of 11° for 1613, 7° for 1737, and 6° for 2927 cm^{-1} bands indicates movement of segments under applied field. Since the transition moment of the 1613 cm^{-1} band is nearly parallel to the long axis of the mesogen, the shift of 11° for this band is directly connected to the induced tilt angle for the mesogen.[11] The shift of the 2927 cm^{-1} band can be related to an induced tilt angle of the oligo(methylene) segments in the FLC part of the block copolymer.[12,13] The low value of the tilt angles for oligo(methylene) has also been detected in IR studies of ferroelectric LC polymers and dimers.[8,12] The low value of the apparent tilt angle for the 1737 cm^{-1} band deals with biased rotation of the carbonyl about the mesogenic long axis.[10,12] The rotational bias appears only under electric field as is usually observed for Sm A phases. The possible orientation of carbonyls about the mesogenic axis has been discussed in detail in refs 10 and 12. Although the investigated block copolymers show electroclinic-like switching behavior (like a ferroelectric LC in SmA phase), the temperature dependence of the induced tilt angle for block copolymers is opposite to that for a ferroelectric in the SmA phase. It was observed that the induced tilt angles rapidly decrease with decreasing temperature. We obtain values of 8°, 5°, and 5° for the 1613, 1737, and 2927 cm^{-1} bands, respectively, at 90 °C (at 120 V). Since the precision of our measurements is ±1°, the absolute tilt angles for different molecular segments at low temperatures become unreliable. To follow the molecular reorientation in a wide temperature range, we measured the IR spectra of the block copolymers under a dc voltage of +120 and −120 V with IR polarization directions fixed at 45° with respect to the shear direction. This allowed us to detect very small changes in the amplitude of molecular reorientation through observation of the difference in absorption,

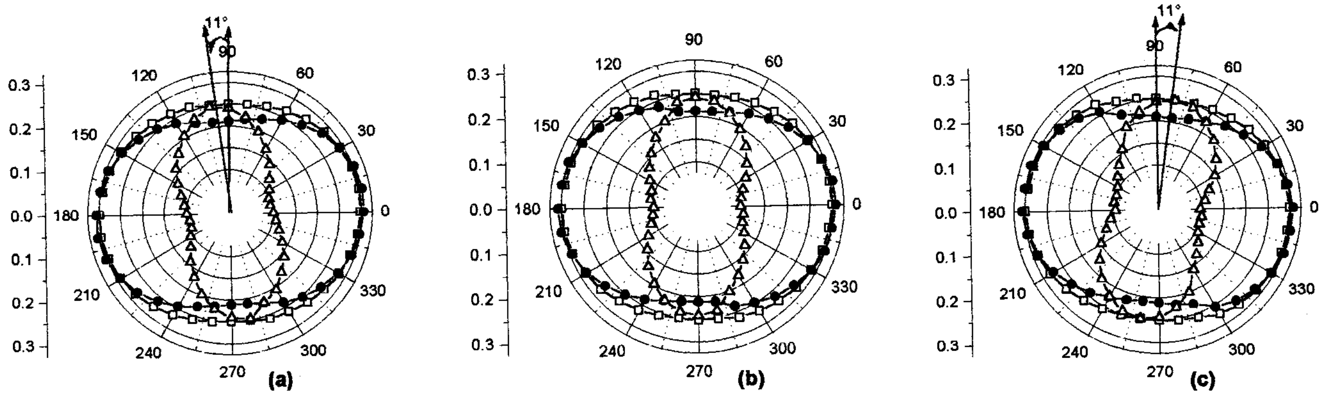

Figure 5. Polar plot of absorbance versus polarizer angle ϕ for the CH_2 stretching vibration at 2927 cm^{-1} (□); the C=O stretching vibration at 1737 cm^{-1} (●), and the phenyl stretching band at 1613 cm^{-1} (△) for block copolymer B8/13 at 110 K at voltages (a) −120, (b) 0, and (c) +120 V. Polarizer angle $\phi = 0°$ corresponds to a polarization vector parallel to the shearing direction.

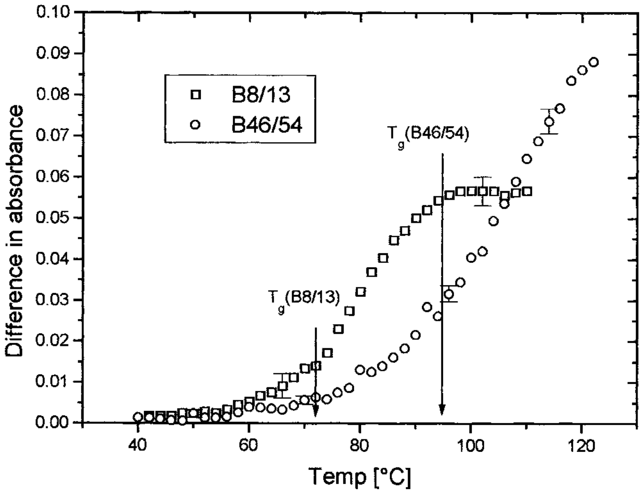

Figure 6. Difference in absorbance [$\Delta A_{\pm 120} = A_{+120} - A_{-120}$] for the 1613 cm^{-1} versus temperature with polarizer angle fixed at 45° for block copolymers B8/13 (□) and B46/54 (○).

$\Delta A_{\pm 120} = A_{+120} - A_{-120}$, for corresponding bands. The temperature dependence of the $\Delta A_{\pm 120}$ for the 1613 cm^{-1} band is presented in Figure 6 for B8/13 and B46/54. As can be seen from this figure, the response to an electric field is small at low temperatures but grows rapidly at higher temperatures. The $\Delta A_{\pm 120}$ for B8/13 and B46/54 becomes constant at temperatures above 100 and 120 °C, respectively, up to temperatures corresponding to phase transition to the isotropic phase. This indicates that the amplitude of induced orientation of the ferroelectric segments changes drastically at higher temperatures. According to the DSC data,[5] the temperatures 345 and 368 K correspond to the temperatures of the glass transition of the PS block in the corresponding block copolymers (Table 1). The observed effect of increasing amplitude of molecular motion (or tilt angle) with temperature is an unusual phenomenon for ferroelectric liquid crystals. This effect can be explained by the increase of the degree of freedom of the molecular segments presumably due to softening of the PS block above T_g.

Segmental Mobility of the FLCBC in an Electric Field. Since response time decreases with increasing temperature and increasing field strength, time-resolved experiments were carried out at a temperature of 90 °C and the highest available field strength of 6 × 10^5 V cm^{-1}. The IR polarization direction corresponded to a value of 50°. The field polarity was reversed at time t = 5 s. The relative intensity versus time of the four bands corresponding to mesogenic units (1613 cm^{-1}), the carbonyl group (1737 cm^{-1}), and the spacer (2927 cm^{-1}) are presented in Figure 7 for the block copolymer B8/13. The intensity of the 1613 cm^{-1} band decreases, whereas those for the 1737 and 2927 cm^{-1} bands increase when the polarity of the electric field is inverted. This is in agreement with the static model described in detail in refs 10 and 12. The reorientation starts immediately after the inversion of the field polarity and takes 5 s under the given experimental conditions. It can be derived from these data that all molecular segments in the FLC part of the diblock block copolymers take part in the reorientational process.

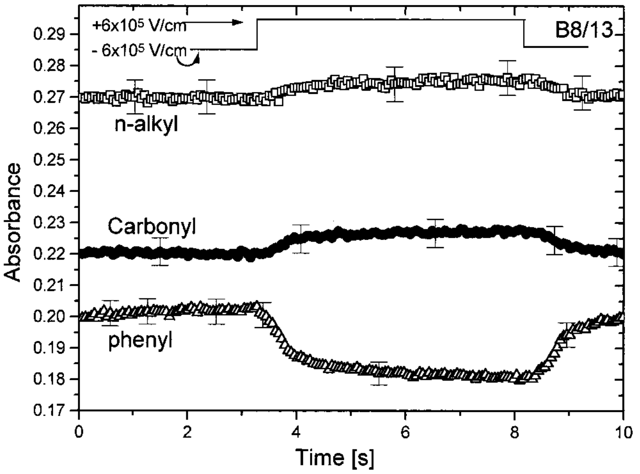

Figure 7. Time dependence of absorbance under electric field (±120 V [solid line]) for the CH$_2$ stretching vibration (□), the phenyl band (△), and the carbonyl (●) band with polarizer angle fixed at 45° at 90 °C for block copolymer B8/13. Also indicated is the applied electric field (solid line).

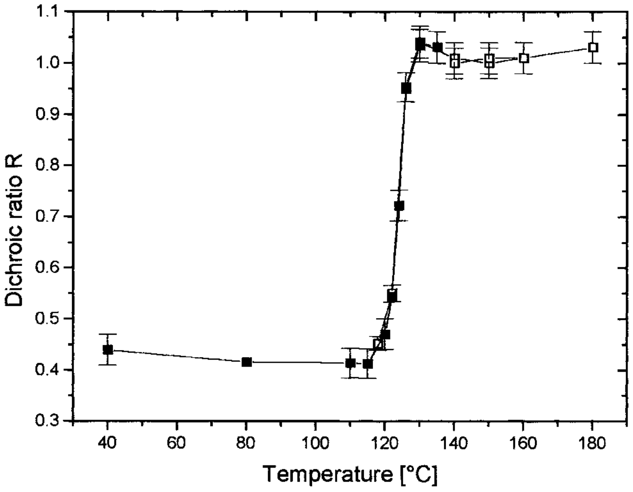

Figure 8. Temperature dependence of the dichroic ratio $R = (A_{\parallel}/A_{\perp})$ for the phenyl band (1613 cm^{-1}) for block copolymer B8/13 during heating (■) and cooling (□).

Memory Effect. The changes of the dichroic ratio $R = A_{\parallel}/A_{\perp}$ for the 1613 cm^{-1} band of the B8/13 block copolymer are plotted in Figure 8. This ratio reveals the ordering of the mesogens. The dichroic ratio does not change when the temperature increases up to temperatures that correspond to the transition into the isotropic phase. The value $R = 1$ corresponds to complete disordering of the mesogens in the isotropic phase. However, when the sample is cooled, the dichroic ratio is completely reproduced. It is restored even when the sample is kept for 30 min at 180 °C. We can explain this enormous memory effect as follows: during the shearing process the FLC and PS blocks are oriented, and this orientation of the blocks is maintained even if the molecular segments inside the FLC block become disordered. When the sample is cooled from the isotropic state (this isotropic state is related to the isotropic orientation of molecular segments inside FLC block only), the surface of the PS domain acts as orientational support for the mesogens. This explanation is supported by recent observations that the X-ray reflections due to domains are maintained even in the isotropic phase.[7]

Conclusions

FT-IR spectroscopy has enabled the elucidation the orientation of molecular-segment orientation in ferroelectric block copolymers. It was proven that the PS segments in diblock copolymers are in a disordered state and do not take part in reorientations under an electric field. Investigated samples show only electroclinic-like switching behavior over the whole temperature range examined. The mesogenic tilt angle increases with temperature, and the amplitude of the segmental orientation under applied electric field increases rapidly at temperatures higher than the T_g of PS. This is presumably due to softening of the PS blocks with increasing temperature.

The initial orientation of the FLC segments is completely restored during heating to the isotropic phase followed by cooling. This is explained by disorientation of the FLC segments inside the FLC block in the isotropic phase while maintaining the relative orientation of PS−FLC block microstructure.

Analysis of FT-IR time-resolved data reveals that all molecular segments of the LC part of the diblock copolymer take part in reorientation under electric field with reorientation rates in the range of seconds.

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