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Mutual Interactions in Main-Chain/ Side-Group Liquid Crystalline Block Copolymers

Giancarlo Galli and Emo Chiellini*

Dipartimento di Chimica e Chimica Industriale,
Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

Michele Laus

Dipartimento di Chimica Industriale e dei Materiali,
Università di Bologna, Viale Risorgimento 4,
40136 Bologna, Italy

Dino Ferri, Dietmar Wolff, and Jürgen Springer*

Institut für Technische Chemie,
Technische Universität Berlin, Strasse des 17. Juni 135,
D-10623 Berlin, Germany

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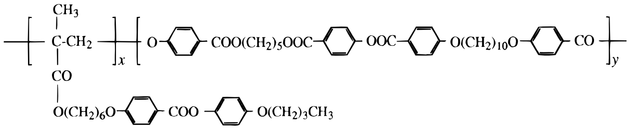
Introduction. Liquid crystalline (LC) block copolymers that are constituted by one LC polymer block and one non-LC, either amorphous or crystalline, polymer block are a newly developed class of anisotropic materials.[1] Owing to the incompatibility of the polymer components, they can phase separate at a nanoscale level and originate different types of morphologies.[2−8] These include familiar spherical, cylindrical, and lamellar ordered morphologies with various phase transitions taking place between them,[6] but new, unconventional morphologies have also been described.[7] More recently, LC block copolymers, such as **A**−**E** herewith described, have been introduced.[9−12] In these systems mesogenic units are incorporated at the same time into the main chain (MC) of one block component and as the side group (SG) substituents of the other block component. It is anticipated that the LC character of each block should enhance their incompatibility and drive a separation into phases in which both the different molecular orders can mutually affect each other.



General structure of block copolymer samples **A-E**

We have previously shown[13] that indeed various mesophases are formed by each individual phase-separated MC and SG block and that they coexist over well-defined ranges of temperature. They respond differently to orienting (magnetic or mechanical) fields, thereby adopting different orientations. The present work was aimed at addressing the question of an influence of the MC and SG mesophases of copolymer samples **A**−**E** on each other and their reciprocal organization in the phase-separated systems.

Experimental Section. Differential scanning calorimetry (DSC) analysis was performed with a scanning rate of 10 K/min using a Perkin-Elmer DSC 7 apparatus. X-ray diffraction was carried out in a custom-made temperature-controlled vacuum chamber with a flat film camera (sample to film distance, 84 mm). Nickel-filtered Cu Kα radiation ($\lambda = 0.154$ nm) was collimated by a glass capillary. The samples were oriented inside the chamber by slowly cooling (0.4 K/h) from the isotropic state at 430 K under an applied magnetic field (2.4 T). Azimuthal intensity scans were performed by digitalizing the X-ray patterns. Pixels were then selected in a thin (0.05 mm) circular ring with a radius corresponding to the distance of the intensity maximum of the layer reflection from the beam stop.

Table 1. Phase Transition Temperatures[a] of LC Block Copolymer Samples A−E

	MC block				SG block	
copolymer	M_n[b]	wt %[c]	T_{I-N} (K)	T_{N-S} (K)	T_{I-N} (K)	T_{N-S} (K)
A	3400	65	417	394	382	348
B	3400	41	420	401	385	362
C	3400	33	422	402	386	365
D	3400	21	423	403	387	371
E	12000	29	425	408	383	366

[a] I = isotropic, N = nematic, S = smectic (by DSC, on cooling at 10 K/min). [b] By SEC, with universal polyester calibration. [c] By ^{1}H NMR.

Results and Discussion. The AB-type diblock copolymers **A**−**E** were prepared by sequential polycondensation and free-radical polymerization, as reported elsewhere.[10] According to this procedure, copolymers **A**−**D** have MC blocks of the same molar mass (M_n = 3400 g/mol), while the M_n of the SG blocks varies regularly (Table 1). The MC block of copolymer **E** has a higher molar mass (M_n = 12 000 g/mol).

The MC and SG blocks are phase separated and each block exhibits its individual smectic and nematic mesophases.[13] The phase transition temperatures were taken from the DSC cooling curves on account of the better resolution of the transition exotherms (Table 1). Supercoolings of 2−10 K were detected with respect to the heating curves. The trends of the isotropic−nematic and nematic−smectic phase transition temperatures (T_{I-N}, T_{N-S}) of the SG block as a function of its degree of polymerization (DP_n) for **A**−**D** are shown in Figure 1. Both T_{I-N} and T_{N-S} increase with DP_n for low DP_n values and then level off with further increasing molar mass, as is usually found in SG homopolymers.[14] The estimated plateau value (375 K) of T_{N-S} for the copolymers coincides with that of a much higher molar mass SG homopolymer ($DP_n = 200$). Rather surprisingly, the T_{I-N} of the homopolymer is 20 K lower than the corresponding plateau value (387 K) of the SG blocks. The thermal stability of the nematic mesophase of the SG block is enhanced by the surrounding smectic mesophase of the MC block, which suggests that an interplay occurs between the morphology and the mesophase of the copolymers.

Qualitatively, all magnetically oriented copolymer samples exhibited very similar diffraction behaviors. As a typical example, Figure 2 illustrates the small-angle X-ray patterns for **E** at different temperatures, at which the smectic mesophase (layer periodicity 2.0 nm) of the

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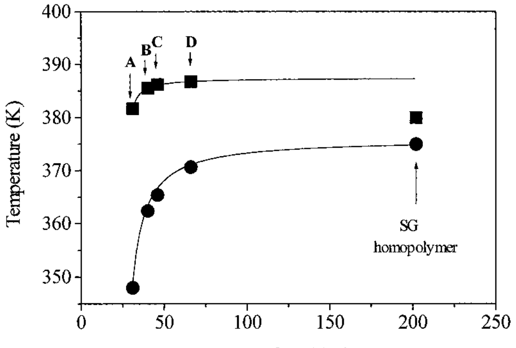

Figure 1. DP_n dependence of the isotropic–nematic (■) and nematic–smectic (●) transition temperatures of the SG block of copolymer samples **A**–**D** and an SG homopolymer sample.

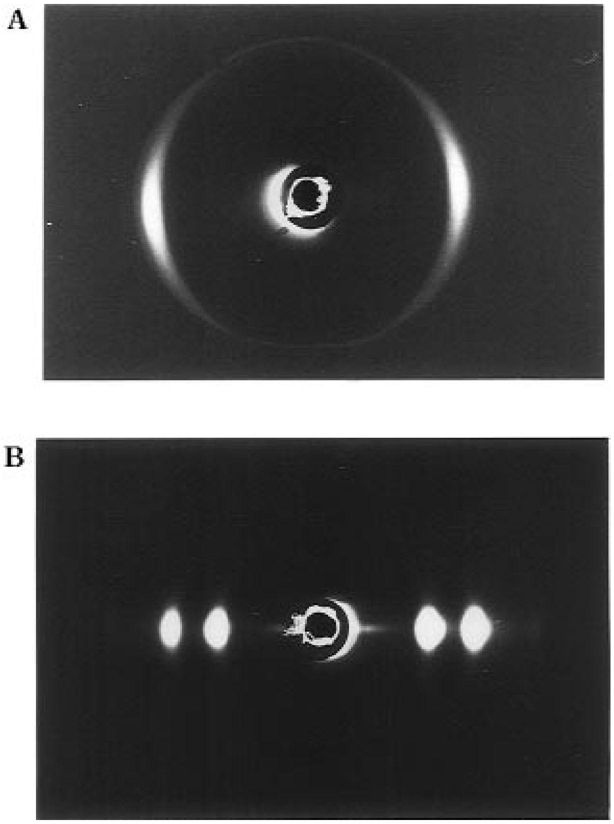

Figure 2. Small-angle X-ray patterns of oriented copolymer sample **E** (horizontal magnetic field) at (A) 392 K (MC smectic and SG isotropic) and (B) 363 K (MC and SG smectic).

MC blocks coexists with the isotropic phase (Figure 2A) or with the smectic mesophase (layer periodicity 2.9 nm) (Figure 2B) of the SG blocks. The smectic layer reflections lie on the meridian, which shows that the smectic planes of both the MC and SG phases are aligned orthogonal to the field direction, independent of the copolymer composition. The azimuthal spread of the X-ray peaks can be used to measure the orientation distribution function of LC polymers.[15] In the present copolymers the azimuthal intensity profile $I(\phi)$ (diffraction angle 2θ = constant) of the MC smectic layer reflections provides information on the orientational distribution of the MC smectic planes with respect to the magnetic field direction, narrow profiles implying a high degree of orientation. In each copolymer, $I(\phi)$ narrows with decreasing temperature (Figure 3), due to unequal influences of the ordered nematic and smectic mesophases of the SG blocks on the smectic mesophase of the MC blocks. The full width at half-maximum $\Delta\phi$ of the intensity profiles exhibits two sharp drops in correspondence with the isotropic–nematic and nematic–smectic transitions of the SG blocks (Figure 4). It was verified that the adopted experimental conditions permitted us to attain the best alignment, which did not improve with longer times and could be reversibly obtained in successive cooling/heating cycles. At high temperatures (region I), the MC smectic domains experience an isotropic environment constituted by the isotropic SG block domains. The disordered state of the SG blocks contrasts with the ordered arrangement of the MC smectic blocks, and this unfavorable boundary condition hinders the orientation of the MC smectic layers, as reflected in a broad azimuthal intensity profile ($\langle\Delta\phi\rangle = 26.3°$). When the SG blocks are in the nematic state (region II), the MC smectic domains interact with a more ordered environment, which favors an improved orientation of the MC smectic planes orthogonal to the magnetic field direction. Consistently, $\langle\Delta\phi\rangle$ is approximately halved to 14.4°. Finally, when both the MC and SG blocks present a same layered LC mesophase (region III), the MC blocks experience optimal boundary conditions and achieve the greatest degree of orientation ($\langle\Delta\phi\rangle = 10.4°$). However, the $\langle\Delta\phi\rangle$ values of **A**–**D** are systematically lower than those of **E**, as exemplified for **C** in Figure 4. This is especially evident at high temperatures (region I), when the SG blocks are in the isotropic state, where in fact $\langle\Delta\phi\rangle$ of **E** is more than twice the one of **C** ($\langle\Delta\phi\rangle = 12.5°$). Nevertheless, when the SG and MC blocks are both in the smectic mesophase (region III) a $\langle\Delta\phi\rangle = 8.8°$ was evaluated for **C** very similar to that of **E**.

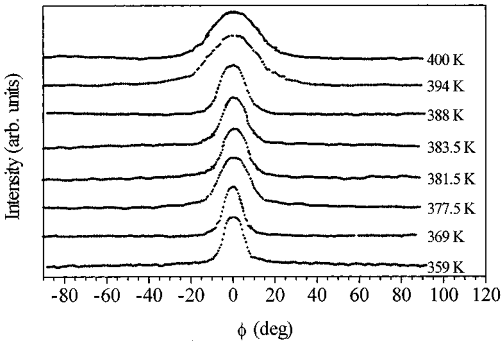

Figure 3. Azimuthal intensity profiles I(ϕ) of the MC smectic layer reflections of copolymer sample **E** at different temperatures.

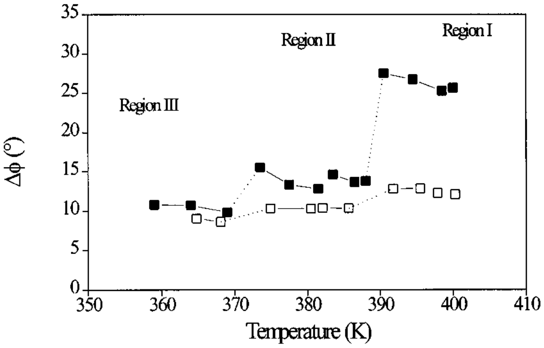

Figure 4. Temperature dependence of the full width at half-maximum $\Delta\phi$ (±0.5°) of the azimuthal intensity profiles I(ϕ) of the MC smectic layer reflections of copolymer samples **E** (■) and **C** (□).

In a previous work,[13] we observed that the MC homopolymer did not orient under a magnetic field of the same strength, probably because of the high melt viscosity. In contrast, the present findings suggest that in the block copolymers, the ordering of the SG block in the smectic mesophase results in boundary conditions suitable for the achievement of a significant orientation by the MC block. This is better evidenced for copolymer **E** in which the MC block is longer than the one in the other copolymer samples. In conclusion, the different LC blocks can mutually influence each other. The anisotropic environment created by the SG blocks makes it possible for the MC domains to reorganize and align preferentially with their planes orthogonal to the magnetic field direction. It is interesting to speculate that the microphase-separated domains in the copolymers can be more easily aligned than the polydomain mesophase of the MC homopolymer, as in the latter an equilibrium defect structure has to be broken down prior to alignment.

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