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Mesogen Orientation within Smectic C* Side Chain Liquid Crystalline Diblock Copolymers

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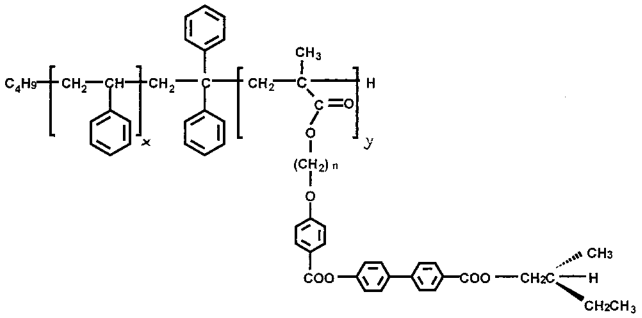
Introduction. Chiral smectic C* liquid crystals are of considerable importance to a number of industrial electrooptical and display applications due to their unique ferroelectric properties. By incorporation of side chain smectic C* mesogens into a block copolymer, materials containing isolated domains of ferroelectric liquid crystals tens of nanometers in size can be produced.[1−5] Such materials are of interest for many reasons, including the self-stabilization of the liquid crystal by the block copolymer interface, increased dimensional stability, and the ability to manipulate final properties using processing.

A variety of means exist for the orientation of block copolymers, including mechanical shear in the melt, thermal annealing of thin films on a selective surface, and fiber-drawing. Many of these orientation studies have recently been reviewed.[6] Lamellar and cylindrical domains in block copolymers have been macroscopically aligned into a parallel, a perpendicular, or a transient transverse orientation by controlling frequency and strain in oscillatory shear.[7−11] The solvent roll-casting technique has been successfully applied to a number of block copolymer systems[12,13] to obtain perpendicular orientations or "single crystal" oriented block copolymers. In liquid crystalline block copolymers, the degree of orientation and the relative arrangement of the side chain liquid crystals with respect to the block copolymer domains may be studied in such well-oriented samples. These factors are critical to the mode of operation of the ferroelectric liquid crystals within the domains when exposed to an applied electrical field.

In principle, the helical Sc* phase is mechanically unwound within the block domains due to the confinement of the liquid crystal within the block copolymer domain. During the orientation process, lamellar or cylindrical blocks are aligned unidirectionally, resulting in an ordered mesophase within a larger supramolecular order; the orientation process is expected to result in large monodomains of liquid crystal. This uniform mesogenic order can display highly anisotropic properties, in particular electrooptical properties, and consequently presents significant potential for electrooptical applications; electrooptical properties of these block copolymers will be reported separately. Previous investigations of lamellar liquid crystalline block copolymers, including those with smectic A and smectic C mesophases, suggest that the preferred orientation of the smectic layers of the LC phase is perpendicular to the orientation of the block copolymer lamellae; a recent review summarizes results from several research groups on this topic.[14] Orientation of the morphology parallel to the smectic layers was found only in cases with oriented elliptical[4] (oriented spherical) and cylindrical domains.[14] For the first time, we report the reverse orientation in anionically polymerized smectic C* polystyrene−polymethacrylate-based polymers in which the LC smectic layers are parallel to the direction of the block copolymer lamellae.

Results and Discussion. The structure of the block copolymers described are shown as follows:



Synthesis by direct living anionic polymerization is fully described in a previous publication.[1]

In this paper, we present our initial findings for the oriented morphology of the PS-DBPB59 ($n = 10$) block copolymer. Investigations on the orientation of other LC block copolymer systems are currently underway. On the basis of results from GPC,[3] the copolymer PS-DBPB59 presented in this paper has a polystyrene block with $M_n = 11\,700$, a polymethacrylate side chain liquid crystal block with $M_n = 17\,300$, and a nominal composition of 40.8 wt % polystyrene. The molecular weight polydispersity is very narrow, with $Mw/Mn = 1.06$. The thermal transitions as determined from differential scanning calorimetry following various processing conditions are given in Table 1.

Unoriented films were simple-cast from 5 wt % solution in toluene by slowly evaporating solvent for several hours. The thin film was then extensively dried in a vacuum oven for an additional 2 days to remove solvent residue. The dry film was annealed at 110 °C overnight. Oriented samples of PS-DBPB59 were prepared by roll-casting from 25 wt % solution in toluene. During the roll-casting process, a block copolymer solution is processed between rotating cylinders, while at the same time the solvent is evaporated at a controlled rate. As the solvent evaporates, the polymer concentration increases, and the block copolymer microphase-segregates into a globally oriented microstructure. Detailed information on the experimental aspects of roll-casting are available in several references.[12,13]

The ordering of both roll-cast and simple-cast block copolymer samples was examined. Small-angle X-ray scattering was conducted using a Rigaku RU−H3R rotating anode generator producing Cu Kα radiation ($\lambda = 1.54$ Å) at 40 kV and 30 mA. Data were collected using a two-dimensional GADDS/HI−STAR area detector manufactured by Siemens, containing an array of 512 × 512 wires. All experiments were conducted in an evacuated flight path at a sample to detector distance of 63.8 cm. which enabled the resolution of *d* spacings in the range 20−450 Å. SAXS analysis of a simple-cast film of PS-DBPB59 results in the 2D SAXS diffractogram shown in Figure 1a. The phase segregated structure was verified by SAXS, as shown, and with

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Table 1. Summary of High M_w Liquid Crystalline Block Copolymers (ND = Not Determined)

polymer	10^{-3} M_n PS block	10^{-3} M_n LC block	M_w/M_n	% LC content	LC behaviors (°C)/(J/mol)	morphology
simple-cast PS-DBPB59	11.7	17.3	1.06	59.2	G_{LC} 13, G_{PS} 76, S_C ND, S_A 160, I	lamellar
roll-cast PS-DBPB59					G_{LC}, 16 G_{PS} 70.1, S_C* 127, S_A 160, Ch 168, I	oriented lamellar
PS-DBPB59 fiber					G_{LC} 15, G_{PS} 86, S_C* 165, S_A 178, I	ND

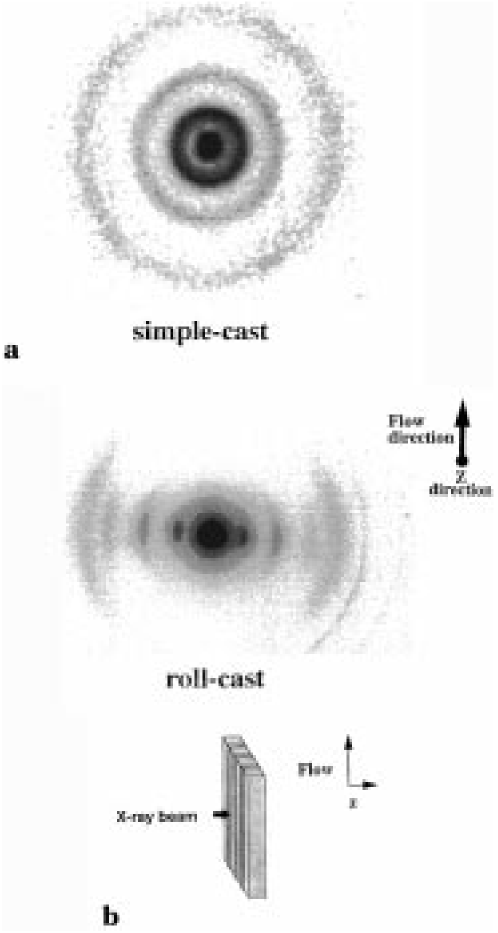

Figure 1. 2D SAXS patterns of (a) simple cast PS-DBPB59 block copolymer film and (b) of roll-cast block copolymer film.

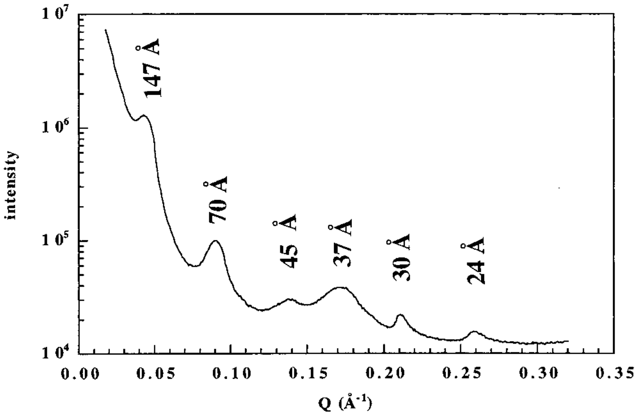

Figure 2. 1D line profile of PS-DBPB59 block copolymer film taken from 2D SAXS profile of the roll-cast film in Figure 1b). The inset shows a WAXD diffractogram of a PSDBPB59 sample at low angles, illustrating the presence of two peaks in the 32−39 Å range representing (left) a fourth-order lamellar reflection and (right) a reflection due to smectic layer spacing.

electron microscopy and DSC. The SAXS profile of the simple-cast film shows three broad, continuous rings of scattering due to the presence of block copolymer lamellar morphology and smectic C* liquid crystalline order. A first-, second-. and a third-order reflection of the block copolymer lamellae appear at positions corresponding to 140, 70, and 45 Å respectively, for which the first-order peak indicates a *d* spacing of 140 Å. The third reflection is a superposition of the third-order reflection from the lamellar block copolymer and the liquid crystal smectic ordering. Studies of the homopolymer using WAXD indicate smectic layer spacings of 43 Å, and WAXD results of the block copolymer PS-DBPB59 indicate *d* spacings of the liquid crystal layer ranging from 32 to 38 Å as a function of temperature.[3] Electron micrographs indicate lamellar domains with approximate *d* spacings of 120−150 Å, consistent with the SAXS findings; the lamellar regions appear to contain 50% polystyrene by volume.

The 2-D SAXS pattern of the roll-cast sample in Figure 1b was obtained on a dry roll-cast film of PS-DBPB59 specimen without any subsequent thermal annealing. The X-ray beam was perpendicular to the surface of the roll-cast film and the direction of the flow field, and the arcs seen in the profile indicate the preferential orientation of the block copolymer microdomains. Since SAXS measurements were conducted with the X-ray beam normal to the surface of the roll-cast film, the peaks in Figure 1b indicate that the lamellae are aligned in the perpendicular orientation of the lamellar domains with respect to the plane of the film. The process flow or shear direction is shown in Figure 1b. These results are consistent with other lamellar block copolymer samples prepared using the same roll-casting method. The azimuthal broadening of the reflections that correspond to the block copolymer domains is due to the presence of many small grains with numerous helicoid surface twist boundaries, which have been observed in unannealed roll-cast films of lamellar morphology.[15] TEM micrographs of the block copolymer were taken from cross sections perpendicular to the flow direction which confirmed that there is preferred orientation of the lamellae perpendicular to the plane of the film, and along the flow direction.

A line profile is given in Figure 2. The *d* spacing of the first-order peak at 147 Å represents the spacing of the lamellar block copolymer repeat. The difference in the *d* spacing of the roll-cast and simple-cast films is relatively small and may be due to error, particularly for the less ordered simple-cast film with more diffuse peaks, or due to slight morphological differences derived from processing such as different solvent removal rates. The corresponding scattering vectors calculated from the remaining five peaks appear as the second-, third-, fourth-, fifth-, and sixth-order reflections relative to the position of the first-order scattering peak. These findings are consistent with lamellar block copolymer domains, as observed in TEM. The fourth peak, corresponding to a *d* spacing of 37 Å, is unusually large when compared to the intensities of the other reflections; this peak is close to the position of a fourth-order reflection, but its magnitude indicates that this peak is a convolu-

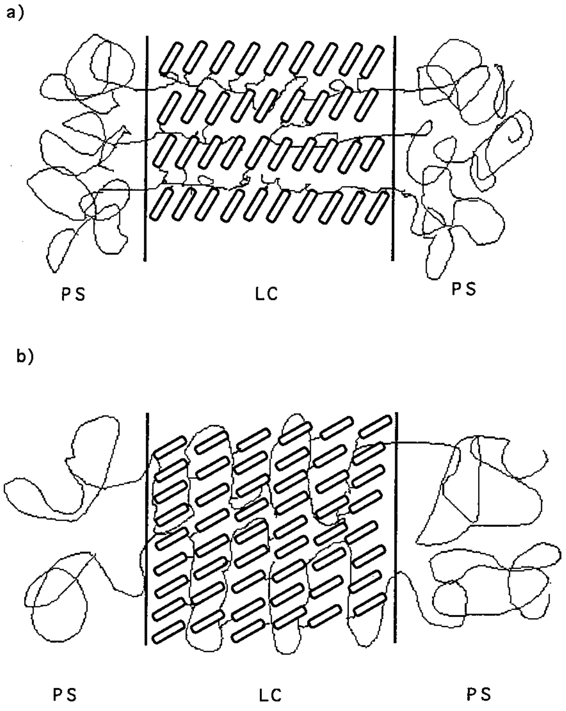

Figure 3. Schematic of arrangement of LC smectic layers in block copolymer lamellae: (a) perpendicular arrangement of smectic layers in lamellae; (b) parallel arrangement of smectic layers, as seen for PS-DBPB59 sample.

tion of the scattering signal from both the liquid crystalline smectic layers and the fourth-order reflection due to microphase segregated lamellar structure. This observation has been verified by WAXD patterns of simple cast films of the same polymer,[16] which indicate a weak reflection at small angles corresponding to smectic liquid crystalline order at 32 Å, as well as a second peak appearing at slightly lower angles, with a *d* spacing of 39 Å, due to phase segregated lamellar domains.

Thus, it appears that the smectic layers of the liquid crystal in this diblock copolymer lie parallel to the direction of the block copolymer lamellae. This finding is counter to the observations of other researchers who have studied smectic side chain liquid crystalline block copolymers.[5,17–20] In these cases, the block copolymer lamellae were arranged in the direction of shear, with the smectic layers arranged normal to the lamellae. It is reasoned that the perpendicular arrangement of the smectic layers is conducive to narrow block copolymer interfaces and that a parallel arrangement would result in much thicker interfaces. It is also argued that it would be difficult to realize a smectic phase with only four to five layers, as would be required for a parallel arrangement in a 15–20 nm thick block copolymer domain. Each of the previous reports describes block copolymers which exhibit the normal arrangement of layers shown in the schematic in Figure 3a. The diblock copolymer described here represents the first reported deviation from this observation, with a parallel orientation as shown in Figure 3b.

This observation brings up several issues. From TEM and SAXS data, the morphology shown here is lamellar. Some defects were observed in certain high-temperature annealed solution cast films of the block copolymer, which suggest the presence of a transient hexagonal perforated lamellar[21,22] (HPL) or mixed layer[23] (ML) system, such as those observed in amorphous block copolymers at volume fractions between 60 and 68%. However ML defects were not detected in shear oriented films. SAXS data of the simple- and roll-cast films discussed here also confirms that there is no hexagonal layer arrangement. This observation suggests that there may be an unstable transitional morphology exhibited in PS-DBPB59 between the lamellar phase and a polystyrene cylindrical phase; during the film formation via solvent evaporation, this morphology may directly influence the arrangement of the smectic layers.

Another factor which may be important to the relative arrangement of the mesogens is the flexibility of the polymer backbone. The PS-DBPB block copolymer discussed here exhibits a glass transition temperature at 16 °C, below the apparent glass transitions of the LC blocks in many other reported systems. The increased flexibility of the polymer backbone may make it feasible for the polymer main chain to backfold along the direction of the interface to allow the formation of smectic layers, as shown in the inset of Figure 3b. This type of arrangement would allow the formation of thin layers of smectic C* mesogens while minimizing the amount of polystyrene phase mixing present in the block copolymer. Such an arrangement would not be possible with stiffer polymer systems with higher glass transitions. However, for such an arrangement to be stable there must be a thermodynamic driving force which favors parallel orientation. Space-filling arguments might be considered, in which the smectic layers orient parallel to the block copolymer interface if the thickness of the lamellae is an integral number of the liquid crystal layer thickness.

It is possible that the nature of the block copolymer interface is important for mesogen orientation, and the interfacial free energies between the mesogen, the LC block main chain, and the polystyrene block are minimized when the smectic layers are parallel to the polystyrene layers. In this case, one may consider the fact that a decyl spacer is used to attach the mesogen to the polymer main chain in these block copolymers. Most of the previous systems studied have hexyl or shorter spacers.[17–20] The higher degree of decoupling of the mesogen from the polymer main chain should enable mesogen arrangements which are more independent of main chain orientation.

Previous studies on the interaction between morphological order and liquid crystalline order within the domains suggest that for lamellar block copolymers, the morphological structure is oriented or aligned by mechanical treatment, rather than the layers of the smectic LC phase.[14] We have observed that the roll-cast film of PS-DBPB59 shows clear macroscopic anisotropy corresponding to LC orientation under the polarized optical microscope. Thermal analysis results of the oriented and simple-cast films are shown in Table 1. DSC thermograms of roll-cast specimens show very similar thermal behavior to that of simple-cast films with respect to the glass transitions of both blocks. It is worth noting that the diblock copolymer exhibits a well phase segregated structure, although some phase mixing is present in the polystyrene phase. The LC block actually has a glass transition temperature very close to that of the homopolymer,which suggests only a minimal presence of polystyrene phase mixed in the LC domains. DSC results also suggest that a better organized LC phase exists in the roll-cast sample than that in the unannealed simple-cast film; the isotropic transition, T_i, of the roll-cast film was slightly higher than that of the simple cast polymer, and the DSC thermograms of mechanically sheared specimens also gave sharper endothermic transitions for LC phases and higher transition enthalpies. Fibers, which would tend to be even more oriented than the roll-cast films, indicate even larger transition temperatures.

In lower molecular weight samples of PS-DBPB block copolymer with a high liquid crystalline content (63 wt %), large focal conic superstructures were observed using TEM as well as optical microscopy. It was observed that the focal conic structures incorporate the alternating lamellar block copolymers; this arrangement would require that the smectic layers of the liquid crystal and the block copolymer lamellae orient parallel to each other. Thus if the ordering found in the high molecular weight analogue can be extrapolated to the lower molecular weight systems, our findings are conducive to the appearance of LC superstructure order in these polymer samples.

The unexpected observation of parallel alignment of smectic layers in a lamellar diblock copolymer suggests that there are a number of factors which may be important in determining the relationship between morphology and liquid crystalline order. Previous studies have suggested that smectic layers are formed in these systems via extension of the main chain normal to the block copolymer domains. The findings discussed here imply that the arrangement of the smectic layers and the polymer main chain may potentially be dependent on a number of issues, including main chain flexibility and interfacial effects, as well as the morphological pathway that the polymer experiences during processing. Thermal analysis and the well-defined SAXS peaks exhibited in oriented materials, as well as TEM, suggest that these systems have fairly well-defined domains with narrow interfaces. The relative arrangement of LC in block copolymer domains is expected to affect the electrooptical properties of the resulting films. Parallel arrangements, for example, would give smectic layers more greatly influenced by the presence of the block copolymer interface, thus enhancing stability of the phase. Such systems may be interesting for semipermanent information storage or memory devices based on the heating of the polymer above its T_g. If the layers can be oriented in a liquid crystal cell such that the block copolymer lamellae are arranged end-on, faster electrooptical switching might be achieved. Studies of the electrooptical properties of these films, as well as examinations of the effects of LC volume fraction, polymer main chain flexibility, and mesogen spacer length, are ongoing.

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