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# Side-Chain LC Block Copolymers with Well Defined Structures Prepared by Living Anionic Polymerization. 3: Effect of the Composition on the Microdomin Structure and the Phase Behavior of the LC Segment

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# Side-Chain LC Block Copolymers with Well Defined Structures Prepared by Living Anionic Polymerization. 3: Effect of the Composition on the Microdomin Structure and the Phase Behavior of the LC Segment

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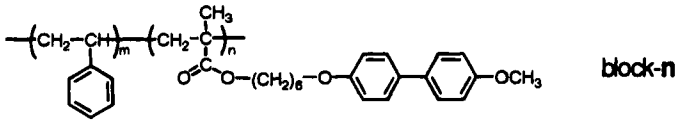
We have synthesized the AB type diblock copolymer with polystyrene and poly(6-[4-(4′-methoxyphenyl)phenoxy]hexyl methacryrate) by sequential anionic living polymerization. The copolymers were prepared with quantitative yields, possessing the predictable $M_n$ values, compositions and narrow molecular weight distributions. The thermotropic phase behavior and structures were examined for six copolymers with the weight fraction of LC segments from 24wt% to 45wt%. All copolymers exhibit the crystal-SmA and the SmA-isotropic phase transitions. Microphase separations were examined as a function of the weight fraction of two segments and in a relation with the micro structure of LC segment.

*Keywords:* side chain liquid crystal polymer; block copolymer; smectic phase; micro phase separation; methoxy biphenyl

## INTRODUCTION

Liquid crystal (LC) polymers with mesogenic groups in the side chains (SCLCP) have been extensively studied. More recently, the research interests have focussed on a role of the main-chain backbone on liquid crystal structures and properties. Previously, we prepared the block copolymers (PS-*b*-poly(**1**)) composed of the polystyrene and LC poly(**1**) segments by sequential anionic living polymerization[1].




All the block copolymers with various molecular weights but with the similar compositions of segments around 50wt% exhibit the lamellar type of segregation. The LC segment in the lamellar microdomain forms crystal, SmA and isotropic phases. The layered structures of crystal and SmA are formed with a preferential orientation of side-chain mesogens lying parallel to the microdomain interface. The lamellar thickness is dependent on the SmA temperature (Figure 1). With increasing temperature, it decreases from the lamellar thickness of the crystal phase to that of isotropic phase and no jump can be seen on the crystal-SmA and SmA-isotropic transitions. The overall change is completely reversible on heating and cooling cycles, indicating that it proceeds at

a thermodynamic equilibrium. The reduction is about 20-25%, which can be caused by the conformational change in the main chain of LC segment from the extended form in the crystalline phase to the random coil in the isotropic phase. Such a conformational change is considered to arise as a result of the counterbalance between entropic gain of the main chain conformation and energetic cost of the side chain mesogenic layer structure.

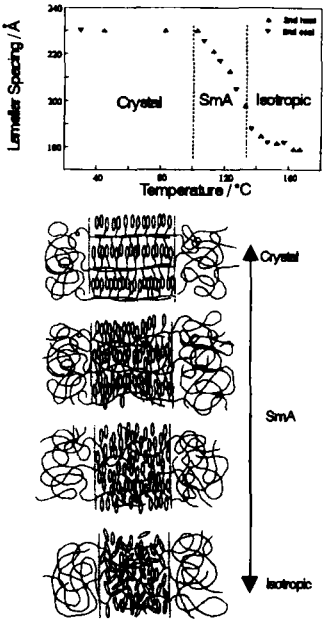



**Figure 1** Temperature dependence of the lamellar spacing for the PS-*b*-poly(**1**) and schematic illustration of the conformational changes of the main chain at the SmA temperature region.

Block copolymers composed of incompatible segments form the microdomains which include lamellae, cylinders, spheres and bicontinuous morphologies depending on the relative volume fractions of the two blocks[2]. Fisher and coworkers[3] reported a morphology diagram for LC-coil block copolymers (PS-*b*-PChEMA) synthesized by polymer analogous reaction. In their morphology diagram, PS spheres, PS cylinders, lamellae and LC spheres were observed, however no LC cylinders appeared. The LC phase in the spherical microdomain only showed a nematic phase rather than the smectic phase that appears in other morphologies. This suggested that a thermodynamically stable smectic layered structure could not be formed in a cylindrical and spherical microdomains. Recently, we reported that the smectic temperature region are broadened in the LC cylindrical microdomain for the LC-

coil block copolymer composed with PS and poly(6-[4-(4'-cyanophenyl)phenoxy]hexyl methacryrate) [4]. Ober *et. al.* [5] also reported the same phenomena. Interestingly, our observation and Ober's are in contrast to Fisher's. It needs more experiments and discussions for the interrelations between morphologies and phase transitions of LC-coil block copolymers. In this paper, we prepared PS-*b*-poly(**1**) which had the various compositions of segments and examine the structural aspects.

## EXPERIMENTAL

The AB block copolymers were prepared by sequential anionic living polymerization. The molecular weight of poly(**1**) segment in this study was around 20000 with the composition from 24wt% to 45wt%. The composition of each segment was finally determined by $^1$H NMR. $M_n$ and $M_w/M_n$ values were estimated from SEC profile based on the standard polystyrene calibration and $^1$H NMR.

Differential scanning calorimetric (DSC) measurements were carried out with

**TABLE 1. BLOCK COPOLYMERIZATION OF STYRENE WITH (1) [a]**

| | $M_n$ | | $M_w/M_n$[c] | poly(1) |
|---|---|---|---|---|
| | PS segment | poly(1) segment[b] | | |
| block-1 | 26000 | 21000 | 1.03 | 45wt% |
| block-2 | 34000 | 21000 | 1.05 | 41wt% |
| block-3 | 34000 | 18000 | 1.03 | 35wt% |
| block-4 | 36000 | 17000 | 1.04 | 32wt% |
| block-5 | 40000 | 17000 | 1.04 | 30wt% |
| block-6 | 51000 | 16000 | 1.04 | 24wt% |

[a] Block copolymerization was carried out by sequential addition of styrene at first and then (**1**) in THF at -78°C with sec-BuLi as an initiator. Yields of polymers were quantitative in all runs. [b] $M_n$ of poly(1) segment was determined by $^1$H NMR. [c] $M_w/M_n$ was determined from SEC profile using calibration of PS standard.

TABLE 2. DSC DATA OF POLYSTYRENE-*BLOCK*-POLY(1)[a]

| | Transition temperature / °C (Corresponding enthalpy changes / kcal•mol$^{-1}$[b]) | | | |
|---|---|---|---|---|
| | Heating | | Cooling | |
| | $T_1(H_1)$ | $T_2(H_2)$ | $T_1(H_1)$ | $T_2(H_2)$ |
| block-1 | 108.2 (1.03) | 132.6 (0.52) | 102.8 (0.99) | 133.4 (0.52) |
| block-2 | 105.6 (0.84) | 126.9 (0.40) | 99.8 (0.81) | 125.5 (0.39) |
| block-3 | 104.8 (0.74) | 133.2 (0.38) | 100.3 (0.71) | 132.5 (0.33) |
| block-4 | 103.0 (0.74) | 124.9 (0.27) | 98.2 (0.74) | 124.4 (0.30) |
| block-5 | 103.4 (0.68) | 128.5 (0.35) | 98.9 (0.74) | 127.8 (0.35) |
| block-6 | 105.9 (0.62) | 132.9 (0.37) | 101.4 (0.74) | 131.6 (0.26) |

[a]Determined by DSC measurement at 2nd heating and cooling (2°C/min.).
[b]Estimated per mole of poly(1) segment.

a Perkin-Elmer DSC Model II at scanning rate of 2°C min$^{-1}$.

X-Ray measurements were performed by using a Rigaku Denki X-ray generator with Ni-filtered Cu-Kα radiation. Reflection spacings were calibrated by using a silicon standard. Temperatures of the sample were regulated within 1°C by using a Mettler FP-82 hot stage.

The transmission electron microscopic (TEM) observation to clarify the morphology of block copolymers was performed by Hitachi H-500 transmission electron microscope with 100kV of accelerating voltage. For this observation, the block copolymer was cut into ultrathin sections (700-1000Å) by ultramicrotome with a glass knife. The sectioned specimens were stained with the vapor of ruthenium tetraoxide ($RuO_4$) for 10 min before observation.

## RESULTS AND DISCUSSION

The transition temperatures and enthalpies measured by DSC are summarized in Table II. All the copolymers exhibit the two transitions, similarly as the homopolymers of poly(1) and block copolymers composed of segments around 50wt%[11]. The phase sequence, crystal-SmA-isotropic, is same for all the materials and the transiton temperatures are also similar.

We expected that the block copolymers in the isotropic phase form the microphase separated structure with lamellar, cylindrical and spherical microdomains depending on the volume fraction of the two segments similarly as coil-coil block copolymers. Figure 2(a), 2(b) and 2(c) show the TEM photographs for ultrathin section cut out of the block copolymers which is annealed in the isotropic phase at 150°C overnight and quenched to room temperature. The LC poly(**1**) microdomains appear dark due to the preferential

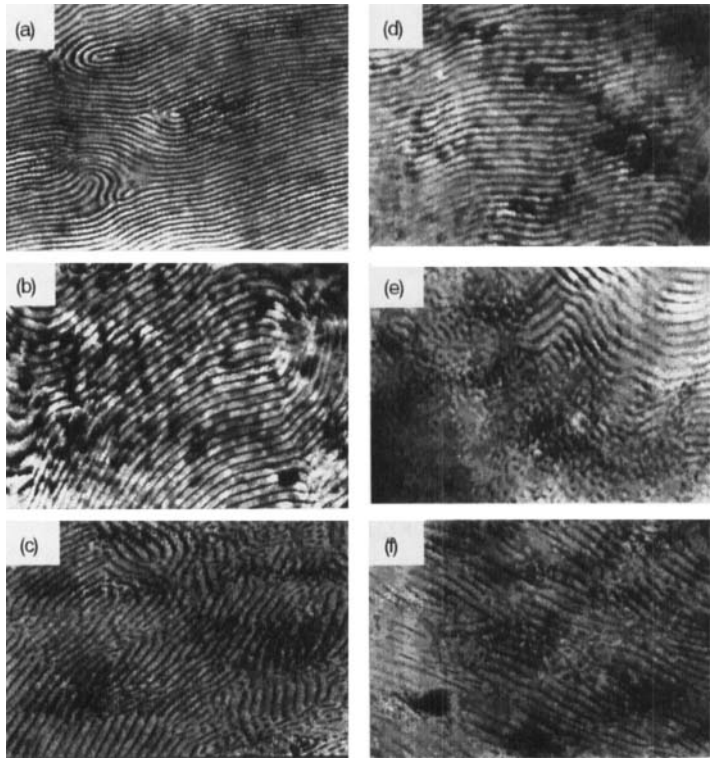



**Figure 2.** Transmission electron microscopic photographs for the ultrathin section cut out the block copolymers stained by $RuO_4$. Dark area is the LC poly(**1**) microdomain. (a)block-2, (b)block-4, (c)block-6, quenched from the isotropic phase, respectively. (d)block-2, (e)block-4, (f)block-6, annealed at the smectic temperature of 115°C and quenched to room temperature., respectively.

staining by $RuO_4$. The lamellar type morphology is observed for block-1 ~ 5 containing the LC poly(1) segment from 45wt% to 30wt%, while the cylindrical type of microseparated structure is formed from block-6 with the weight fractions 24wt% of the LC poly(1) segment. The result is thus similar to that observed for conventional coil-coil block copolymers.

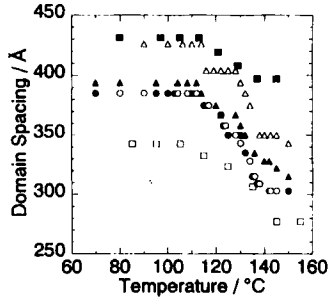



**Figure 3.** Temperature dependence of the microdomain spacing observed for (□)block-1, (●)block-2, (○)block-3, (▲)block-4, (△)block-5, (■)block-6, respectively.

According to the Leibler's theory for the AB block copolymer[6], the phase diagram is determined by the fraction of A segment in a chain and $\chi N$ (where $N$ is the polymerization index and $\chi$ is the Flory parameter characterizing the effective interaction of segments AB, $\chi \sim T^{-1}$). As the weight fraction of A segment deviates from 50wt%, decreasing temperature causes the morphological reorganization to the higher ordered structure, for example, from the spheres to the cylinders and from the cylinders to the lamellae. These order-order transition of the morphology are also experimentally observed[7]. Sänger *et al.* observed the reversible order-order transition in the coil-LC-coil triblock copolymer with the PS blocks (12 vol%) from PS spheres above the clearing temperature to the PS cylinders in the nematic phase[9]. Thus, we can expect the morphological reorganization due to the phase transition in the present diblock copolymer.

Figure 3 shows the domain spacing dependence on temperature changes for block copolymers by small angle X-ray scattering (SAXS) measurements on

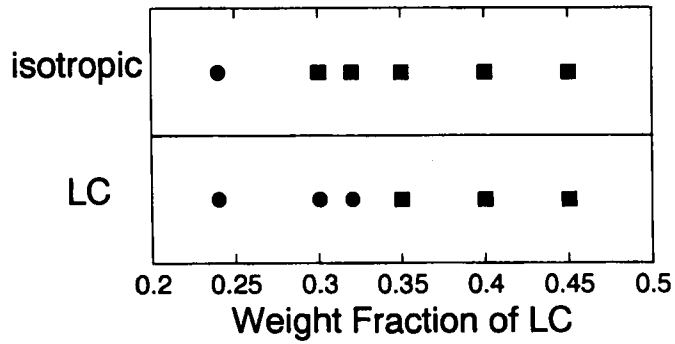



**Figure 4.** Morpholigy diagram of PS-*b*-poly(1). (●) for cylindrical type micorophase seperated structure, (■) for lamellar type micorophase seperated structure, respectively.

cooling (reversibly on heating). The spacings decrease remarkably through the SmA temperature region from the size of the isotropic phase to that of the crystalline phase for all copolymers. In the previous work[1] treating the block copolymers with the equal weight fractions of 50%, the reduction of spacing was 20~25% of original spacing, which was explained to be caused by conformational change in the main chain of LC poly (1) segment from the extended form to the random coil (see Figure 1). In this study, block-**1**~block-**5** show the similar extent of reduction. On the other hand, the reduction is only 35Å for block-**6** which is 8% of the original spacing. This small reduction may be due to the cylindrical morphology.

The most distinct feature here is that the extraordinary morphological changes can be observed from lamellae to cylinders by decreasing of temperature. Figure 2(d), 2(e) and 2(f) show the TEM photographs for ultrathin section cut out of the block copolymers which were annealed at the smectic temperature of 115°C and quenched to room temperature. The lamellar morphology is observed for block-**1**, block-**2** and block-**3** and the cylindrical morphology for block-**4**, block-**5** and block-**6** (see Figure 4). Obviously, the lamellar morphology is altered to the cylindrical one on the isotropic to smectic phase transition, indicating that the cylindrical microdomain may be more comfortable for the

smectic structure of the LC segments than the lamellar microdomain. However, we can not give a clear reason for this. Analysis on the mechanism of transformation is now in progress.

## CONCLUSIONS

We have synthesized the AB type block copolymers with polystyrene as A segment and side-chain LC polymer as B segment by sequential living polymerization. In these copolymers, the moleular weight of LC segment is maintained around 20000 and the composition of LC segment is varied from 24wt% to 45wt%. The well defined microphase separation was observed for all the copolymers and LC segment in microdomain exhibits crystal, SmA and isotropic phases. In the isotropic melt, the lamellar type microphase separated structure is formed for the block copolymers with the side-chain LC segment from 30wt% to 45wt%, while the cylindrical microphase separation was observed for the block copolymer with the side-chain LC segment 24wt%. In the smectic phase, on the other hand, the lamellar domain of the block copolymers containing the side-chain LC segment 30wt% and 32wt% is altered to the cylindrical domain, suggesting that the cylindrical domain gives the more comfortable space for the smectic association of the present side-chain LC polymer.

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