Macromolecules **2003,** *36,* 8913−8918 **8913**

Phase Behavior of Polystyrene-*block*-poly(*n*-butyl methacrylate) Copolymers with Various End-Functional Groups

Unyong Jeong, Du Yeol Ryu, and Jin Kon Kim*

Department of Chemical Engineering and Polymer Research institute, Electric and Computer Engineering Division, Pohang University of Science and Technology, Kyungbuk 790-784, Korea

Received May 27, 2003
Revised Manuscript Received October 21, 2003

Introduction. The addition of end-functional groups to polymer chains can change surface properties and interfacial tension in polymer blends. Also, polymers or block copolymers with functional end groups have potential applications to drug delivery, lubrication, and reactive compatibilization.[1−3] Despite the potential importance, few research groups[4−8] have studied the effects of end groups on the phase behavior of polymer blends. Qian et al.[6] showed that the chemical structure and the amount of end-functional groups considerably affect the coexistence curve (or binodal temperatures) for polymer blends having low molecular weights. This is attributed to the change in the effective Flory interaction parameters (χ). However, for polymer blends with high molecular weight, the end-functional groups do not much change the phase behavior.

Koberstein and co-workers[7] investigated the upper critical solution transition temperature (UCST) for blends with lower molecular weights (~1000) of poly(isoprene) (PI) and poly(dimethysiloxane) having two different end-functional groups (PDMS-X, where X is NH_2 or COOH). They found that UCST decreased considerably with the addition of an NH_2 end-functional group; thus, the miscibility window was greatly expanded. The decrease of the UCST by the addition of NH_2 end-functional group was successfully predicted by the binary interaction approach,[9] where PDMS-X can be treated as a copolymer of DMS and X. Because of the large repulsive interaction between NH_2 and PDMS ($\chi_{NH_2-DMS} > \chi_{I-DMS} > \chi_{NH_2-I}$), PDMS-X can be more miscible with PI compared with PDMS without functional group.

The effect of the end groups on phase behavior of block copolymers has been investigated.[10−13] Floudas et al.[10] reported that the zwitterion can increase or decrease the ordered-to-disordered transition temperature (T_{ODT}) of polystyrene-*block*-polyisoprene copolymer (SI) depending upon the position of the zwitterion in the chain. Bates and co-workers[11,12] studied the effect of the block sequence on the T_{ODT} for polystyrene-*block*-polyisoprene-*block*-poly(ethylene oxide) (SIO) and ISO triblock copolymers (ABC and BAC triblock copolymers). At lower amounts of PEO, they found that the T_{ODT} of SIO decreased with increasing amount of PEO, whereas the T_{ODT} of ISO increased. This different behavior was easily explained by the relative magnitudes of three interaction parameters. When the miscibility between C and A blocks is better than that between C and B blocks, the ODT of ABC decreases compared with that of AB. They also explained this behavior using the incompressible random phase approximation (RPA) for ABC triblock copolymer.[14] However, according to their prediction and experimental results, when the amount of ethylene oxide is very small (such as one repeat group of EO is added), the T_{ODT} would not change. This suggests that the phase behavior or T_{ODT} of block copolymers would not change, when the total molecular weight of the block copolymer is much larger than the end-functional group (or one monomer group).

On the other hand, Schacht and Koberstein[8] showed that when the fluorosilane end group ($Si(CH_3)_2(CH_2)_2(CF_2)_5CH_3$) is attached to PS, the lower critical solution transition temperature (LCST) of high molecular weights ($M_{w,PS} = 31\,732$ and $M_{w,PVME} = 99\,000$) of PS/poly(vinyl methyl ether) blend increases by ~10 °C. Thus, the phase behavior of block copolymers with lower disordered-to-ordered transition (LDOT) might be significantly affected by the addition of an end-functional group. PS-*block*-poly(*n*-butyl methacrylate) copolymer (PS−PnBMA) exhibited the combined ODT and LDOT occurring at lower and higher temperatures, respectively, even though ODT was not easily detected experimentally due to the proximity to the glass transition of PS block.[15−17] It is known that the effect of molecular weight on LDOT is much larger than that on ODT.

In this study, we investigated, via small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM), polarized optical microscopy (POM), and rheology, the effect of the end-functional group (X), which is equivalent to one monomer group, on the ODT and LDOT of weakly interacting PS−PnBMA. We found that the addition of only one end-functional group to PS−PnBMA changed dramatically the LDOT. Furthermore, the ODT was also changed although the change was smaller compared with that of LDOT.

Experimental Section. A symmetric PS−PnBMA was prepared by successive addition of styrene (S) and *n*-butyl methacrylate (nBMA) monomers at −78 °C in tetrahydrofuran under argon environment by using *sec*-BuLi as an initiator.[18] Prior to the addition of nBMA monomer, PS anion precursor was extracted with a microsyringe and terminated with degassed methanol to determine the molecular weight of PS block. After dropwise addition of nBMA, the reaction was maintained for 4 h at −78 °C for complete reaction. Then, the PS−PnBMA anion was split into two batches. One was terminated with degassed methanol to yield proton-terminated PS−PnBMA (SBM66; compound **1** as shown in Scheme 1). The molecular weight of PS precursor was measured by size exclusion chromatography with a multiangle laser light scattering detector using PS standards, and the PS weight fraction in SBM66 was determined by ^1H nuclear magnetic resonance spectroscopy (NMR). The total weight-average molecular weight and polydispersity of SBM66 are 66 000 and 1.03, respectively, and the PS weight fraction is 0.5.

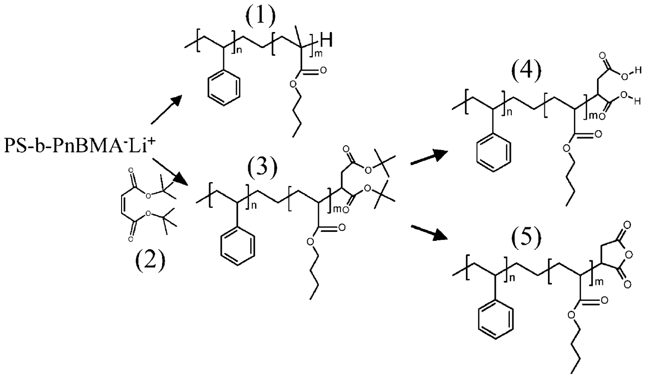
Five equivalent amounts of di-*tert*-butyl maleate (compound **2** synthesized by the method given in refs 19 and 20) to PS−PnBMA anion were added to the other batch, and the reaction remained for 2 h and terminated with degassed methanol. Because of the steric hindrance, only one functional group of di-*tert*-butyl male-

---

* To whom correspondence should be addressed: FAX +82-54-279-8288; e-mail jkkim@postech.ac.kr.

10.1021/ma034714g CCC: $25.00

Scheme 1



ate was attached to the PS−PnBMA anions;[20] thus, di-*tert*-butyl ester terminated SBM66 (SBM66-diE; compound **3**). The end-functionality of diE on SBM66 chains was 0.98 determined by ^{1}H NMR, and the polydispersity of SBM66-diE was 1.03, which is the same as SBM66. Diacid-terminated SBM66 (SBM66-diCOOH; compound **4**) was prepared by hydrolyzing SBM66-diE at 100 °C for 8 h in the presence of *p*-toluenesulfonic acid as a catalyst in 1,4-dioxane.[21] Then, SBM66-diCOOH was precipitated into heptane, filtered, and washed several times in order to remove any trace of the catalyst. The same hydrolysis reaction was carried out for neat SBM66 (compound **1**), and it was found that no hydrolysis of PnBMA chains was observed, which was confirmed by the identical ^{1}H NMR results before and after the reaction.

Finally, SBM66-diE was transformed into maleic anhydride-terminated SBM66 (SBM66-MAH; compound **5**) by reacting SBM66-diE at high temperatures (2 h at 200 °C and 1 h at 220 °C) under high vacuum. From SEC and thermogravitational analysis, neither PS nor PnBMA degraded at 240 °C for 3 h under nitrogen. Furthermore, ^{1}H NMR spectra of neat SBM66 annealed at 250 °C for 90 min under nitrogen were essentially the same as that without annealing at high temperature, indicating no chemical transformation of PnBMA chain into MAH (or acid) during the transformation of diE to MAH. The conversion from diE to MAH was almost unity confirmed by ^{1}H NMR. Furthermore, SBM66-MAH was reacted with three equivalent amounts of aliphatic amine-terminated PS (PS−NH$_2$) having number-average molecular weights of 1900 and 11 000 at 60 °C in THF.[21,22] When unreacted PS−NH$_2$ was completely extracted out using cyclohexane, which was confirmed by SEC, we did not observe any peak in SEC corresponding to the molecular weight of SBM66-MAH. Also, from ^{1}H NMR, the increased weight fraction of PS in the product was proportional to the added PS−NH$_2$, suggesting that all of SBM66-MAH employed in this study has only a single MAH functional unit.

With an Advanced Rheometrics Expansion System (ARES) with parallel plates of 25 mm diameter, a temperature sweep experiment was performed under isochronal conditions at a rate of 0.5 °C/min. Before the experiment, the thermal history of the samples was completely removed by annealing at homogeneous state of 120 °C for 10 h. The strain amplitude (γ_0) and the angular frequency (ω) were 0.05 and 0.1 rad/s, respectively, which lies in linear viscoelasticity.

Small-angle X-ray scattering (SAXS) profiles ($I(q)$ vs $q(= 4\pi \sin \theta/\lambda)$; here, q is the scattering vector and 2θ is the scattering angle) were conducted at the 4C1 beamline at the Pohang Light Source (PLS), Korea.[23] A one-dimensional position-sensitive detector (Diode-Array PSD; Princeton Instruments Inc.; model ST-120) with the distance of each diode of 25 μm was used. The sample thickness was 1.2 mm, and sample-to-detector distance was 2.4 m. The exposure time was 2 min. All the samples were first annealed at 120 °C for 10 h to remove any thermal history. Then the samples were cooled to 90 °C at a rate of 0.3 °C/min and further cooled to 50 °C at a rate of 0.1 °C/min. After the cooling experiment, the samples were heated to 120 °C and annealed for 5 h to ensure complete disordering. Then the SAXS profiles were obtained upon heating at a rate of 0.5 °C/min.

The microdomain structures of the block copolymers were investigated with a transmission electron microscope (TEM; JEOL 1200EX) operating at 120 kV. Three samples were first annealed at 120 °C for 10 h. Then, one specimen was heated to 240 °C at a rate of 0.5 °C/min and annealed for 3 h. The other sample was cooled to 60 °C at a rate of 0.1 °C/min and annealed for 24 h. Then, all samples were quenched to room temperature. Cryogenic ultrasectioning was performed with an RMC (MT-700) microtomer with a diamond knife at −100 °C. Finally, the specimens were stained with ruthenium tetroxide (RuO$_4$) for 20 min at room temperature, which selectively stained the PS microdomains.

A polarized optical microscope (POM; Zeiss Co.) with CCD camera was used to find whether a sample at a given temperature was in an ordered state. When a specimen is in an anisotropic ordered state (such as LAM microdomains), it shows distinct birefringence in the POM image, whereas no birefringence can be observed in disordered isotropic sample. Although the absence of birefringence is also observed for ordered structures with spherical microdomains (or cubic phases),[24,25] this possibility is completely excluded for all PS-*b*-PnBMA-X employed in this study because of symmetric compositions of the block copolymers. The sample for POM was prepared by solution-casting (5 wt % in toluene) onto a cover glass and annealed at 120 °C for 2 h under a nitrogen environment to remove residual solvent and stress during preparation. POM images at higher temperatures were obtained at a rate of 0.1 °C/min, whereas those at temperature below 120 °C were taken after a step decrease of 2.5 °C followed by 24 h annealing at each temperature.

The temperature dependence of volume expansion for PS−PnBMA-X was measured with a spectroscopic ellipsometer (J.A. Woollam Co.; M-2000V) upon heating from 70 to 200 °C at a rate of 0.5 °C/min. Thin films of PS−PnBMA-X with thickness of 600−700 nm were spun-coated onto silicone wafer and annealed at 120 °C for 3 h under vacuum and cooled to 70 °C.

Results and Discussion. Temporal change in the storage modulus (G') is a useful means to measure ODT and LDOT of a block copolymer.[26−29] Figure 1a shows the temporal change in G' for SBM66, SBM66-diE, SBM66-diCOOH, and SBM66-MAH. All the samples exhibit an abrupt increase in G' at a critical temperature, which is referred to as LDOT. The values of LDOT for SBM66, SBM66-diE, SBM66-diCOOH, and SBM66-MAH are 187, 175, 168, and 155 °C, respectively. It is rather unusual to find that only addition of one end-functional unit to SBM decreased LDOT by ∼32 °C.

Even though the transformation of diE into MAH is known to occur only at temperature above ∼200 °C,[21,22]

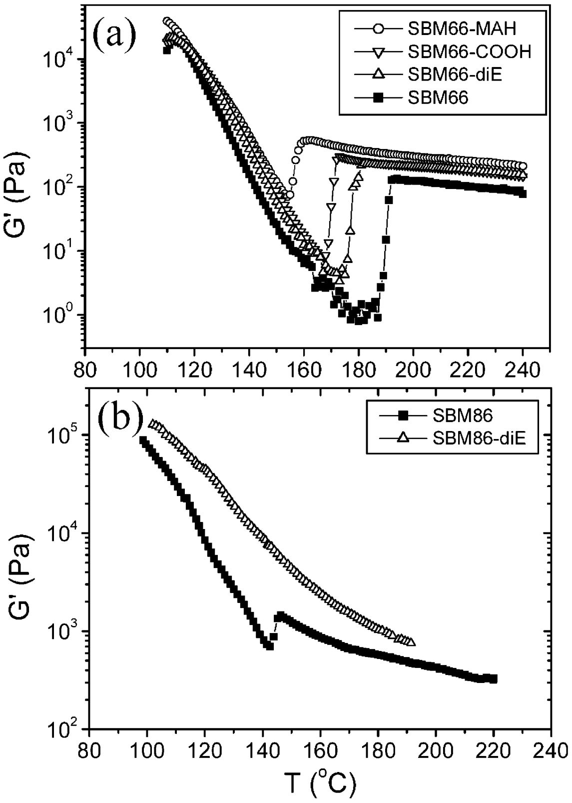


Figure 1. (a) Temporal change of G' upon heating at a rate of 0.5 °C/min for SBM66 (■), SBM66-diE (△), SBM66-COOH (▽), and SBM66-MAH (○). (b) Temporal change of G' upon heating at a rate of 0.5 °C/min for SBM86 (■) and SBM86-diE (△). The abrupt changes indicate a transition from a disordered to an ordered state.

the possibility of reaction at lower temperatures cannot be completely excluded. Thus, we performed an annealing test of SBM66-diE at 180 °C for 90 min under nitrogen. We found that ^{1}H NMR spectra of SBM66-diE before and after the annealing test were identical, indicating that the transformation to SBM66-MAH does not happen at 180 °C. To check again that the decrease of the LDOT of SBM66-diE was due to the existence of a diE end group, and not due to the transformation to MAH during a heating experiment, we synthesized a higher molecular weight of SBM86, with total molecular weight of 86 000 and the weight fraction of PS block of 0.48, and SBM86-diE. Figure 1b shows temporal changes of G' of SBM86 and SBM86-diE. The LDOT of SBM86 was 146 °C, at which no transformation of diE to MAH is guaranteed. We found that SBM86-diE did not show any sharp transition to MAH in the experimental range. Nonetheless, since G' of SBM86-diE is larger than that of SBM86 at a given temperature, it proves that LDOT of SBM86-diE should be lower than that of SBM86. This indicates that the decrease in LDOT for SBM86-diE did not result from the transformation reaction into MAH or possible existence of MAH.

Figure 2 shows SAXS profiles for SBM66 and SBM66-MAH. Those for SBM66-diE and SBM66-COOH are very similar to Figure 2, except the different values of the transition temperatures. For SBM66, any SAXS peak was not observed up to ~190 °C during heating from 120 °C. A small but distinct peak appeared at 192 °C, and then the SAXS intensity increased with increasing temperature. The values of LDOT for SBM66 and SBM66-MAH were determined from plots of $1/I(q_{\max})$ vs $1/T$, as shown in Figure 2c, ~192 and ~160 °C, respectively. Here $q_{\max}$ is a scattering vector where the $I(q)$ becomes a maximum. These values are consistent with rheological results given in Figure 1a, although there is a ~5 °C difference between the two methods.

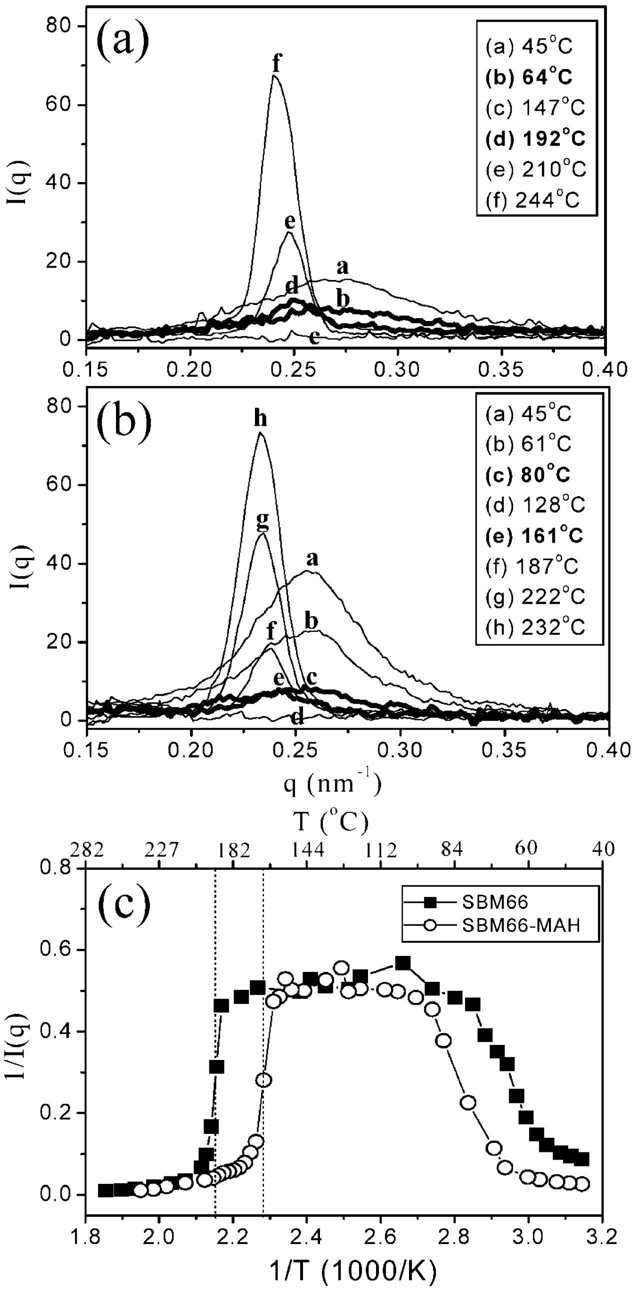


Figure 2. SAXS profiles at various temperatures for SBM66 (a) and SBM66-MAH (b). All the samples were first annealed at 120 °C for 10 h and cooled to 90 °C at a rate of 0.3 °C/min and further cooled to 50 °C at a rate of 0.1 °C/min. The samples were heated to 120 °C and annealed for 5 h and finally heated to 240 °C at a rate of 0.5 °C/min. (c) Plots of $1/I(q_{\max})$ vs $1/T$ for SBM66 (■) and SBM66-MAH (○), from which LDOT was determined from sharp changes in $1/I$ (shown by the dotted lines).

On the other hand, during cooling from 120 °C for SBM66, $1/I(q_{\max})$ first decreased at ~73 °C and approached to a steady value at ~55 °C. Thus, the transition is rather broad compared with LDOT. Similarly, a broad transition was observed between ~87 and ~68 °C for SBM66-MAH. We consider that this transition is ODT, which is consistent with a previous study by Russell and co-workers.[15] Even though the ODT for SBM-66 and SBM66-MAH is lower than the glass transition temperature of the PS block, this is still higher than T_g (~50 °C measured by DSC) of homogeneous mixtures of PS and PnBMA blocks.

From the results in Figure 2, only the addition of an MAH end-functional group to SBM66 decreased the LDOT by ~32 °C and increased the UODT up to ~14 °C. Thus, the miscibility window of SBM66 decreased, and the segregation power between PS and PnBMA block at a given temperature increased. The enhanced segregation power with the addition of the MAH is augmented by the fact that lattice spacing ($D = 2\pi/q_{\max}$) of SBM66-MAH (26.9 nm) above LDOT was slightly larger than that of SBM66 (26.1 nm). It is also seen in Figure 2a,b that D of microdomains occurring above LDOT is larger than that below ODT. This is because D depends on volume expansion and the segregation power. At temperatures near and above the LDOT, both the volume and segregation power increase together with increasing T. However, at temperatures near and below the ODT, with decreasing T, the volume decreases, whereas the segregation power increases. Since volume expansion and segregation power near and below ODT are in the opposite directions, D at temperatures lower than ODT is smaller than that at temperatures higher than LDOT.

It might be argued, however, that the peak in SAXS profiles at a temperature lower than ODT might be due to enhanced electron intensity near the T_g of the PS block (~100 °C) even when only concentration (or composition) fluctuation exists. The observation that a quenched sample from 120 °C to room temperature did not exhibit any SAXS peak indicates that the SAXS peaks observed during the slow cooling did not result from enhanced concentration fluctuation by T_g effect. We performed a temperature sweep experiment of G' to determine ODT, but no sharp increase of G' near the ODT was observed. This is attributed to the fact that the change of G' due to the formation of ODT was not sufficient to be detected by torque transducer because the G' near the ODT was already too high.

To verify that SAXS peaks observed at lower temperatures in Figure 2 resulted from the long-range lattice ordering, we used polarized optical microscopy (POM). Figure 3 shows POM images of SBM66-MAH annealed at four different temperatures: (a) 165, (b) 90, (c) 73, and (d) 60 °C. As shown in Figure 3a, birefringence was very clearly shown at 165 °C, indicating the sample is in an ordered state. But, between 80 and 160 °C, no birefringence was discernible, indicating the sample is disordered (or isotropic). Finally, when the sample was annealed at 73 °C for 2 days after a slow decreasing temperature, birefringence again appeared, although the intensity was very weak. When the sample was annealed at 60 °C for 2 days, the intensity increased, indicating that anisotropic property (thus segregation power) at this temperature was larger than at 73 °C. On the basis of POM results, we determined the ODT of SBM66-MAH at 73 ± 2.5 °C. This value is lower than ODT determined from the onset temperature for the transition (~87 °C) measured by SAXS. This is because the synchrotron SAXS results might be more powerful than POM to detect ODT. Therefore, we conclude that SBM66-MAH exhibits both LDOT and ODT. Both SBM66-diE and SBM66-diCOOH showed very weak birefringence below 68 ± 5 °C when the same cooling condition was used. Unfortunately, SBM66 did not show birefringence at any temperature down to ~52 °C, even though a broad and weak intensity was observed in SAXS.

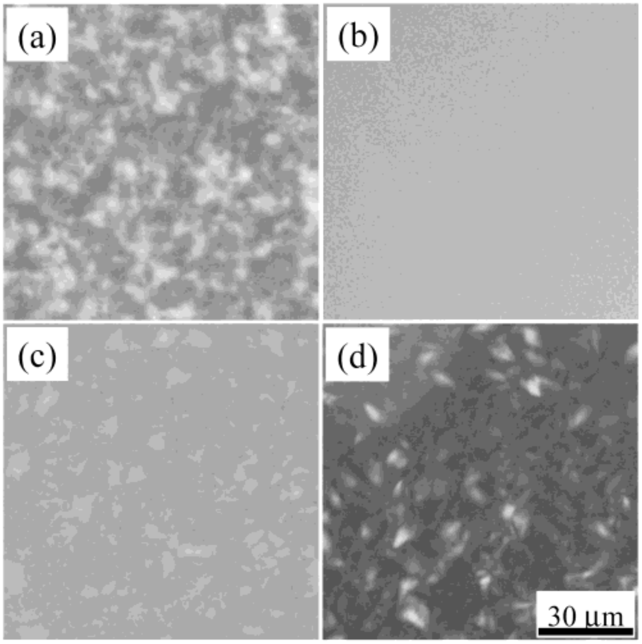


Figure 3. POM images for SBM66-MAH annealed at four different temperatures: (a) 165, (b) 90, (c) 73, and (d) 60 °C.

Since the SAXS intensity of all block copolymers employed in this study was very small due to small electron density between PS and PnBMA blocks, we could not observe any higher order peaks. Thus, to investigate the expected morphology of LAM microdomains, we performed TEM for SBM66-MAH at three different temperatures (240 °C (above LDOT), 120 °C (between ODT and LDOT), and 60 °C (below ODT)). The sample annealed at 240 °C clearly showed LAM microdomains with D of ~28 nm (Figure 4a), consistent with SAXS results ($D = 2\pi/q_{\max}$). The sample annealed at 120 °C (Figure 4b) exhibited a disordered state (or disordered fluctuation morphology). When the specimen was annealed at 60 °C, LAM microdomains were formed (Figure 4c), although the LAM ordering is poor compared with Figure 4a. The poor ordering of LAM microdomains is because of the reduced mobility since the annealing was done near the glass transition temperature. We found similar TEM images for other SBM66-X. For weakly interacting polymer systems such as SBM, the origin of the LCST (or LDOT) might be due to the free volume effect arising from the difference in compressibilities of the two components (or the equation-of-state variables).[30] However, it is hardly expectable that a small end group can alter the behavior of the thermal expansion coefficient (α) or free volume. We observed that α in the disordered state of neat SBM measured by ellipsometer was essentially the same that of PS−PnBMA-X regardless of end-functional groups. This indicates that the origin of the difference in LDOT is not likely due to the change of free volume difference resulting from the attached end-functional group.

Therefore, the reason that the LDOT and ODT of PS−PnBMA changed very much with only the addition of an end-functional group might be due to the change in the effective interaction parameter (χ_{eff}) with end groups. Even though only one end group is added, SBM-X can

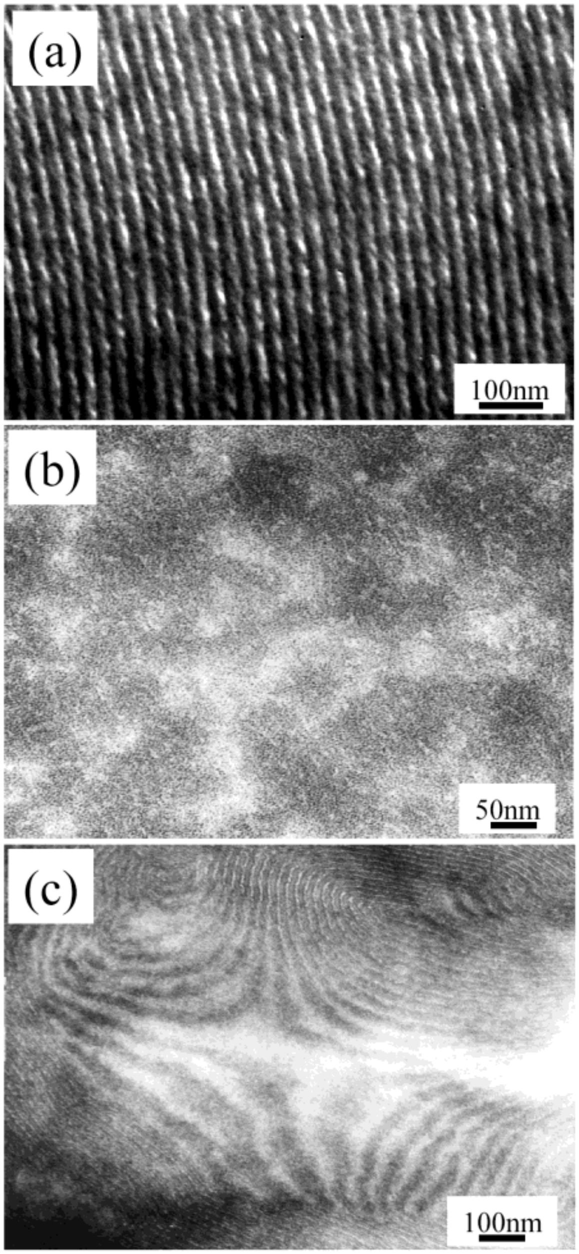


Figure 4. TEM images of SBM66-MAH annealed at three temperatures: (a) 240, (b) 120, and (c) 60 °C.

be considered as ABC triblock copolymer. According to recent results of ABC triblock copolymer by Bates and co-workers,[11,12] the ODT of ABC increased when $\chi_{AC} > \chi_{BC}$. For instance, for a small addition of PEO block to IS block copolymer, ODT of ISO is larger than that of IS. This is due to the fact that in a homogeneous state chain A should coexist with chain C, which causes a large enthalpy penalty. However, according to their experimental results[11] as well as RPA theory,[31−33] the change of ODT for ISO was very small (<∼3 °C) when the amount of PEO was less than ∼1 wt %.

The weight percents of diE, diCOOH, and MAH in SBM66-X are 0.35, 0.18, and 0.15 wt %, respectively. The interaction parameter (χ) for PS/PnBMA pair was reported as $\chi_{S/nBMA} = 0.0243 - 4.56/T$, in which T is the absolute temperature.[17] However, $\chi_{X/S}$ and $\chi_{X/nBMA}$ are not available in the literature. In this situation, the solubility parameter (δ) approach can be good estimates for χ, especially for weakly interacting polymer pairs. According to Hoy's group contribution,[34] the δ values of PS, PnBMA, and diE are estimated to be 19.3, 18.9, and 18.6 (MPa)$^{1/2}$, respectively. Since the reduced miscibility (namely, decreased LDOT and increased ODT) for SBM66-X can be expected since $\chi_{X/S} > \chi_{X/nBMA}$,[11,12] the solubility parameter approach is consistent with experimental result when $\chi_{ij} \sim (\delta_i - \delta_j)^2$.

However, diCOOH and MAH end-functional groups have specific interactions, so the solubility analysis itself might not be good for estimating χ. Paul and coworkers[35] estimated the interaction energy (B) between MAH and S, $B_{S/MAH}$ (14.9 cal/cm^3), and $B_{nBMA/MAH}$ (13.4 cal/cm^3). These values correspond to $\chi_{S/MAH}$ of 2.46 and $\chi_{nBMA/MAH}$ of 2.21, respectively, since $\chi = Bv_{ref}/(RT)$. Here, v_{ref} is the reference volume (100 cm^3/mol was taken) and R is the gas constant. This approach gives that $\chi_{S/MAH} > \chi_{nBMA/MAH} \gg \chi_{S/nBMA}$ (0.01). We therefore expect a large decrease in the miscibility for SBM66-MAH compared with SBM66, which is consistent with experiment.

We could not find $\chi_{diCOOH/nBMA}$ and $\chi_{diCOOH/S}$ in the literature, but Bendejacq et al.[36] reported that χ between poly(acrylic acid) (PAA) and PS should be larger than 0.3. Even though the chemical structure of diCOOH is maleic acid ($HO_2CCH{=}CHCO_2H$) instead of acrylic acid, we assume that χ_{diCOOH}/S would be similar to $\chi_{AA/S}$, which indicates $\chi_{diCOOH/S} < \chi_{S/MAH}$. Also, we assume $\chi_{diCOOH/S} > \chi_{diCOOH/nBMA} \gg \chi_{S/nBMA}$ because of the tendency of hydrogen bonding of carboxylic acids with nBMA.

The above approach, although it contains many assumptions, clearly demonstrates that the extent of the decrease in LDOT and the increase in ODT (thus, the reduced miscibility) is the greatest for SBM66-MAH, then SBM66-diCOOH, and the least for SBM66-diE.

Then, one may ask a question why only one end-functional group (or a very small amount) causes a large change of LDOT and ODT. We speculated that this kind of behavior is possible when the χ_{AB} is much smaller compared with χ_{XA} or χ_{XB}. This situation can be met for weakly interacting block copolymers or polymer blends. According to the RPA theory, the phase behavior depends on χN, where N is the number of segments. Thus, to achieve a given value of χN, a very small amount (or one end-functional group) is needed for χ_{XA} (or χ_{XB}) $\gg \chi_{AB}$. For the SIO case, $\chi_{IO}/\chi_{SI} \sim 3$;[14] thus, a very small amount of PEO (less than 1 wt %) does not change ODT of SIO or ISO. Moreover, very recently Choi and Han[37] investigated the effect of difunctional carboxylic acids (−COOH) on the ODT of SIS having molecular weight of 3.4×10^4 and the weight fraction of PS block of 0.44. They found that the ODT of SIS−COOH was marginally increased (∼2 °C) compared with that of neat SIS, whereas ODT of SIS with −COONa increased significantly due to strong ionic association. On the other hand, the experimental result[8] that only addition to the fluorosilane (F) end group on PS (the amount of the end group having 0.9 wt %) increased LCST of PS/PVME blend up to ∼10 °C can be explained for χ_{F-S} (or χ_{F-VME}) $\gg \chi_{S-VME}$. This speculation deserves to be tested more rigorously.

Finally, we observed that with addition of end-functional group the decrease in LDOT is more than twice the increase of ODT. This is due to a complex balance between enthalpy and entropy which varies with temperature. Since PS−PnBMA exhibited both LDOT and ODT, χ_{S-BMA} would decrease and then increase, with increasing temperature. Thus, the reported expression of $\chi_{S-nBMA} = 0.0243-4.56/T$[17] holds only at higher temperatures, not for the entire temperatures covering the low-temperature region near ODT. The exact expression of χ, which can be obtained from small-angle neutron scattering using deuterated PS−PnBMA, will be a future research subject. We speculate that the temperature dependence of χ_{S-nBMA} at high-temperature regions might be larger than that at the lower-temperature region to explain the experimental result that the decrease in LDOT is more than twice the increase of ODT when an end-functional group is added.

In summary, it has been shown that the LDOT and ODT of weakly interacting PS−PnBMA changed significantly with only the addition of one end-functional group. With the addition of MAH or COOH end-functional groups, the LDOT decreased, but the ODT increased, which suggests reduced miscibility. The change of LDOT and ODT with the addition of an end-functional group can be explained by relative magnitudes of three interaction parameters: χ_{S-X}, χ_{nBMA-X}, and χ_{S-nBMA}.

Acknowledgment. This work was supported by the POSTECH Research Fund (2003) and by the National RND Project for Nano Science and Technology (M1-0214-00-0230). Small-angle X-ray scattering was performed at PLS beamline supported by POSCO and KOSEF.

References and Notes

(1) Jalbert, C. J.; Koberstein, J. T.; Yilgor, I.; Gallagher, P.; Krukonis, V. *Macromolecules* **1993**, *26*, 3069.
(2) Fleischer, C. A.; Morales, A. R.; Koberstein, J. T. *Macromolecules* **1994**, *27*, 379.
(3) Elman, J. F.; Johs, B. D.; Long, T. E.; Koberstein, J. T. *Macromolecules* **1994**, *27*, 5341.
(4) Callaghan, T. A.; Paul, D. R. *Macromolecules* **1993**, *26*, 2439.
(5) Kuo, C. M.; Clarson, S. J. *Eur. Polym. J.* **1993**, *29*, 661.
(6) Qian, C.; Grigoras, S.; Kennan, L. *Macromolecules* **1996**, *29*, 1260.
(7) Lee, M. H.; Fleischer, C. A.; Morales, A. R.; Koberstein, J. T.; Koningsveld, R. *Polymer* **2001**, *42*, 9163.
(8) Schacht, P. A.; Koberstein, J. T. *Polymer* **2002**, *43*, 6527.
(9) ten Brinke, G.; Karasz, F.; Macknight, W. J. *Macromolecules* **1983**, *16*, 1827.
(10) Floudas, G.; Pispas, S.; Hadjichristidis, N.; Pakula, T. *Macromol. Chem. Phys.* **2001**, *202*, 1488.
(11) Bailey, T. S.; Pham, H. D.; Bates, F. S. *Macromolecules* **2001**, *34*, 6994.
(12) Bailey, T. S.; Hardy, C. M.; Epps, T. H.; Bates, F. S. *Macromolecules* **2002**, *35*, 7007.
(13) Lee, K. M.; Han, C. D. *Macromolecules* **2002**, *35*, 760.
(14) Cochran, E. W.; Morse, D. C.; Bates, F. S. *Macromolecules* **2003**, *36*, 782.
(15) Russell, T. P.; Karis, T. E.; Gallot, Y.; Mayes, A. M. *Nature (London)* **1994**, *368*, 729.
(16) Ruzette, A. V. G.; Baerjee, P.; Mayes, A. M.; Pollard, M.; Russell, T. P.; Jerome, R.; Slawecki, T.; Hjelm, R.; Thiyagarajan, P. *Macromolecules* **1998**, *31*, 8509.
(17) Weidisch, R.; Stamm, M.; Schubert, D. W.; Arnold, M.; Budde, H.; Horing, S. *Macromolecules* **1999**, *32*, 3405.
(18) Ryu, D. Y.; Jeong, U.; Lee, D. H.; Kim, J.; Youn, H. W.; Kim, J. K. *Macromolecules* **2003**, *36*, 2894.
(19) McCloskey, A. L.; Fonken, G. S.; Kluiber, R. W.; Johnson, W. S. In *Organic Syntheses;* Rabjohn, N., Ed.; John Wiley and Sons: New York, 1963; Collect. Vol. 4, p 261.
(20) Cernohous, J. J.; Macosko, C. W.; Hoye, T. R. *Macromolecules* **1997**, *30*, 5213.
(21) Hautekeer, J. P.; Varshney, S. K.; Fayt, R.; Jacobs, C.; Jerome, R.; Teyssie, P. *Macromolecules* **1990**, *23*, 3893.
(22) Guegan, P.; Cernohous, J. J.; Khandpur, A. K.; Hoye, T. R.; Macosko, C. W. *Macromolecules* **1996**, *29*, 4605.
(23) Bolze, J.; Kim, J.; Huang, J.; Rah, S.; Youn, H. S.; Lee, B.; Shin, T. J.; Ree, M. *Macromol. Res.* **2002**, *10*, 2.
(24) Kimishima, K.; Koga, T.; Hashimoto, T. *Macromolecules* 2**000**, *33*, 968.
(25) Lee, H. H.; Jeong, W. Y.; Kim, J. K.; Ihn, K. J.; Kornfield, J. A.; Wang, Z.-G.; Qi, S. *Macromolecules* **2002**, *35*, 785.
(26) Bates, F. S.; Rosadale, J. H.; Fredrickson, G. H. *J. Chem. Phys.* **1990**, *92*, 6255.
(27) Han, C. D.; Kim, J.; Kim, J. K. *Macromolecules* **1989**, *22*, 383. Han, C. D.; Baek, D. M.; Kim, J. K. *Macromolecules* **1990**, *23*, 561.
(28) Han, C. D.; Baek, D. M.; Kim, J. K.; Ogawa, T.; Hashimoto, T. *Macromolecules* **1995**, *28,* 5043.
(29) Ryu, D. Y.; Jeong, U.; Kim, J. K.; Russell, T. P. *Nature Mater.* **2002**, *1*, 114.
(30) Sanchez, I. C.; Panayiotou, C. G. In *Models for Thermodynamic and Phase Equilibria Calculation*; Sandler, S. I., Ed.; Marcel Dekker: New York, 1994; Chapter 3.
(31) Ijichi, Y.; Hashimoto, T. *Polym. Commun.* **1988**, *29*, 135.
(32) Kim, J. K.; Kimishima, K.; Hashimoto, T. *Macromolecules* **1993**, *26*, 125.
(33) Kim, J. K. *Polymer* **1995**, *36*, 1243.
(34) Hoy, K. L. *J. Paint Technol.* **1970**, *42*, 76.
(35) Brannock, G. R.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym Phys***. 1991**, *29*, 413.
(36) Bendejacq, D.; Ponsinet, V.; Joanicot, M.; Loo, Y.-L.; Register, R. A. *Macromolecules* **2002**, *35*, 6645.
(37) Choi, S.; Han, C. D. *Macromolecules* **2003**, *36*, 6220.

MA034714G