Phase Behavior of a Weakly Interacting Block Copolymer by Temperature-Dependent FTIR Spectroscopy

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Received October 19, 2005

ABSTRACT: The phase transitions of polystyrene-block-poly(n-pentyl methacrylate) (PS–PnPMA) have been investigated by temperature-dependent infrared spectroscopy with two-dimensional correlation spectroscopy. PS–PnPMA was shown to exhibit a closed-loop type of phase behavior, where, upon heating, a disorder-to-order transition (LDOT) was found at lower temperature and an upper order-to-disorder transition (UODT) was observed at higher temperature. Sudden changes in the absorbance (A) and maxima in the slope dA/dT were observed at the transition temperatures. In the disordered state below the LDOT, the intensity of the conformational band at 1255 cm$^{-1}$ was greater than that at 1274 cm$^{-1}$, whereas the reverse was found in the disordered state above the UODT. This suggests that the conformation of the C–C–O group in the PnPMA chain (and thus the directional enthalpic gain) is different in the two disordered states and, therefore, that the driving force to induce the disordered state at lower temperatures is different from that at higher temperatures.

1. Introduction

Block copolymers have been extensively investigated because of their self-assembly into nanometer-sized morphologies. Various microdomains of lamella, cylinder, sphere, and gyroid structures are found. At temperatures higher than the order–disorder transition (ODT) temperature, the microdomains disappear, and the two blocks are mixed. Numerous experimental and theoretical studies have been performed to determine or predict the ODTs of block copolymers. Recently, we showed by small-angle X-ray scattering (SAXS), rheometry, and depolarized light scattering that polystyrene-block-poly(n-pentyl methacrylate) (PS–PnPMA) exhibits closed-loop phase behavior bounded by the lower disorder-to-order transition (LDOT) and the upper order-to-disorder transition (UODT). The phase behavior of weakly interacting polymer systems with lower critical solution transitions (or LDOTs) has been theoretically investigated by numerous research groups. Dudowicz and Freed developed the lattice cluster theory considering monomer structure, nonrandom mixing, and compressibility that predicted a closed-loop behavior for block copolymers. Recently, Cho showed that the LDOT and UODT of PS–PnPMA could be predicted theoretically once the weak interaction, free-volume, and fluctuation effects were incorporated into the random-phase approximation.

However, the origin of the closed loop has not been fully elucidated. One possible explanation is as follows: Even though PS–PnPMA does not have any strong segmental interactions, such as hydrogen bonding, a weak interaction might exist at temperatures lower than the LDOT. Here, the conformations of specific chemical groups could be very important as this might give rise to slight enthalpic gains that could compensate for a loss in entropy. On the other hand, a main driving force to induce a disordered state at higher temperatures might be the gain in the combinatorial entropy rather than the gain in the directional enthalpic energy. If so, the conformations of specific chemical groups would change with temperature. This information can be obtained spectroscopically, but not from scattering or rheometry. Maeda et al. measured the upper and lower critical solution temperatures of poly[3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate]-block-poly(N,N-diethylacrylamide) copolymer (PDMAEPS–PdEA) in water using Fourier transform infrared (FTIR) spectroscopy and turbidity measurements. Because PDMAEPS–PdEA can form hydrogen bonds with water, the absorption spectra changed in a distinctive manner with temperature. Huang et al. have also employed spectroscopy to study the miscibility of polymer blends with either hydrogen bonding or weak interactions. However, the phase transitions of block copolymers with weak segmental interactions have never been studied by FTIR spectroscopy.

Here, we determine the phase transition temperatures of PS–PnPMA by temperature-dependent FTIR spectroscopy. Even though there are no strong segmental interactions in PS–PnPMA, it is still possible to assess changes in the absorption
spectrum for a weakly interacting system undergoing transitions. We determine the LDOT and UODT from temperature-dependent FTIR spectra with two-dimensional correlation spectroscopy (2DCOS). Furthermore, we demonstrate that the conformation of the C–C–O group in the disordered state at temperatures below the LDOT is qualitatively different from that in the disordered state observed at temperatures above the UODT.

2. Experimental Section

PS–PnPMA was synthesized by the sequential, anionic polymerization of styrene and n-pentyl methacrylate in tetrahydrofuran (THF) at −78 °C under purified argon using sec-BuLi as an initiator. The number- and weight-average molecular weights ($M_n$ and $M_w$, respectively) of PS–PnPMA were determined (49 000 and 49 900, respectively) by size-exclusion chromatography coupled using a multi-angle laser light scattering detector. The volume fraction of the PS block was 0.5. PS–PnPMA showed two transition temperatures, 140 and 224 °C, as determined by SAXS, rheometry, and depolarized light scattering.

FTIR spectra were measured at a spectral resolution of 4 cm$^{-1}$ with a Bomem DA8 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The Seagull attachment (Harrick Scientific Corporation), which includes a heating block attachment, was used in this study. A powder consisting of PS–PnPMA and KBr was prepared using a freezer mill. Before making the powder, PS–PnPMA was annealed at 120 °C for 2 days to obtain the fully disordered state. All diffuse-reflectance FTIR spectra were measured by co-adding 256 scans from 100 to 250 °C at an interval of 5 °C after the sample had been equilibrated for 30 min at the measurement temperature.

3. Results and Discussion

Figure 1 shows the FTIR absorption (A) spectra of PS–PnPMA measured during heating from 100 to 250 °C. Prominent infrared bands are observed at 1300–1400, 1200–1300, and 1050–1150 cm$^{-1}$, which are assigned to the C–H deformation mode, the C–C–O stretching mode, and the C–O stretching mode, respectively. Interestingly, the intensity of the C–C–O mode at 1255 cm$^{-1}$ was greater than that at 1274 cm$^{-1}$ at lower temperatures, whereas the opposite was observed at higher temperatures (see the inset in Figure 1). This indicates that the conformation of the PnPMA block is different in the two temperature regions. On the other hand, for PnPMA homopolymer ($M_n = 8030$, polydispersity = 1.02), the absorption at 1255 cm$^{-1}$ was always larger than that at 1274 cm$^{-1}$ at the entire temperature ranges as Figure 2. Therefore, we can conclude that the orientation of the C–C–O moiety was affected by the presence of PS chains and that the orientation of this moiety at lower temperatures is different from that at higher temperatures, even though the chains are in the disordered state.

Figure 3 gives the 2D map of dA(v, T)/dT as a function of wavenumber and temperature (T). It can be seen in Figure 3 that the highest value of dA/dT occurs at 142 °C for all bands. Another maximum is observed at 212 °C, although this is much smaller than that observed at lower temperature. The small change at higher temperature is attributed to thermal fluctuations (or increased combinatorial entropy) of the whole chain. Because the infrared absorption by a bond is proportional to the square of the vibrational transition moment, increased absorption indicates an alignment of the bonds in all chains toward a specific direction. Thus, the chain conformations changed at both 142 and 212 °C. Because the values of LDOT and UODT determined by SAXS, rheometry, and depolarized light scattering are 140 and 224 °C, respectively, the 2D map can allow us to determine these two transition temperatures. It is noted, however, that PnPMA homopolymer itself does not exhibit any peak showing the abrupt absorption change in dA/dT in the 2D map at the entire temperatures (130–250 °C) (data not shown). Thus, the peak in the 2D map for PS–PnPMA given in Figure 3 is due not to PnPMA homopolymer itself but to the transition
temperatures of PS–PnPMA. Furthermore, the LDOTs of PS–block-poly(ethyl methacrylate), PS–block-poly(n-propyl methacrylate), and PS–block-poly(n-butyl methacrylate) determined from the maxima in $\frac{d\alpha}{dT}$ in the 2D maps were identical to those determined by SALS and rheometry. Figure 4 gives the 2D map of PS–block-poly(2-vinyl pyridine) copolymer ($M_n = 19,300$, polydispersity = 1.06, and volume fraction of PS block = 0.51). The highest value of $\frac{d\alpha}{dT}$ was observed at $-183^\circ C$ for all bands, and this temperature is consistent with the ODT temperature ($190^\circ C$) determined by SALS, rheometry, and depolarized light scattering. These results indicate that the transition temperatures of the block copolymers can be measured by temperature-dependent FTIR spectroscopy.

On the basis of results given in Figure 1, we can conclude that the orientation of the C–C–O moiety at lower temperatures is distinctly different from that at higher temperatures, even though the chains are in the disordered state. A difference in the orientation of the C–C–O moiety should be accompanied by a difference in the directional enthalpy. Here, we consider that the weak interactions in PS–PnPMA arise mainly from interactions between the dipole in the phenyl ring and the induced dipole. Hsu and co-workers$^{20}$ showed that the absorption peak positions corresponding to the C=C group and C–O groups for PS and poly(vinyl methyl ether) (PVME) blend in the homogeneous state are different from those observed in the phase-separated state, which suggests that there are weak interactions (dipole and induced dipole) between the phenyl rings of PS and the ether group of PVME. The presence of an induced-dipole in the PnPMA block can be anticipated from the hindered chain motions of the $n$-pentyl group existing in the nanophase domains. Hsieh et al.$^{21}$ reported that the hindered chain motion of the rigid cyclohexyl group in poly(cyclohexyl acrylate) (PCHA) is a main source of induced dipole and dipole interactions in a PS/PCHA blend. This suggests that the weak interactions that determine the magnitude of the directional enthalpic gain in PS–PnPMA are different in the disordered states observed at $T < T_{\text{LDOT}}$ and $T > T_{\text{UODT}}$.

To demonstrate the different characteristics of the two disordered states more clearly, we employed two-dimensional correlation spectroscopy (2DCOS), which is now a well-established technique for interpreting spectral data sets obtained during the observation of spectra with an external perturbation.$^{23,24}$ The intensity of the 2D correlation spectrum, $X(\nu_1,\nu_2)$, is expressed by the dynamic spectrum of a system $[\tilde{y}(\nu,t)]$ as follows$^{23,24}$

$$X(\nu_1,\nu_2) = \langle \tilde{y}(\nu_1,t) \tilde{y}(\nu_2,t) \rangle$$

Here, $y(\nu,t)$ is the perturbation-induced variation of a spectral intensity measured at a spectral variable along the external perturbation $t$ (e.g., temperature in this study) between $T_{\text{max}}$ and $T_{\text{min}}$, and $\tilde{y}(\nu)$ is the reference spectrum chosen as the spectrum $[\tilde{y}(\nu,t = 250^\circ C)]$ measured at the highest temperature employed in the FTIR experiment. To simplify the mathematical manipulation, $X(\nu_1,\nu_2)$ is treated as a complex number function consisting of two orthogonal (i.e., real and imaginary) components, known as the synchronous ($\Phi$) and asynchronous ($\Psi$) 2D correlation intensities, respectively$^{23,24}$

$$X(\nu_1,\nu_2) = \Phi(\nu_1,\nu_2) + i\Psi(\nu_1,\nu_2) =$$

$$\frac{1}{\pi(T_{\text{max}} - T_{\text{min}})} \int_0^{\infty} \tilde{y}(\nu,\omega) \tilde{y}^*(\nu_2,\omega) \text{d}\omega$$

in which $\tilde{Y}$ and $\tilde{Y}^*$ are the Fourier transform and the conjugate of the Fourier transform of $\tilde{y}(\nu,t)$, respectively. The intensity of peaks located at the diagonal positions in synchronous 2D spectrum represents the overall susceptibility of the corresponding spectral region to change in spectral intensity as an external perturbation is applied to the system. Cross-peaks located at the off-diagonal positions of a synchronous 2D spectrum represent simultaneous or coincidental changes of spectral intensities observed at two different spectral variables ($\nu_1$ and $\nu_2$).

Figure 5a–c shows synchronous 2D correlation spectra for the disordered state at lower temperature, the ordered state, and the disordered state at higher temperature, respectively. Band assignments of FTIR spectra for PS–PnPMA in the region of $1100–1800\text{ cm}^{-1}$ are summarized in Table 1. As shown in Figure 5, the synchronous 2D correlation spectrum of the ordered state is completely different from those in the two disordered states. Namely, in the ordered state, all positive synchronous cross-peaks were observed, indicating intensities of all bands are increasing together with temperature. However, synchronous correlation spectra in the disordered states have positive and negative cross-peaks, suggesting that the one spectral intensity of two wavenumbers is increasing while the other is decreasing. We further notice that, in addition to the band at $1382\text{ cm}^{-1}$, a new band at $1391\text{ cm}^{-1}$, not observed in the two disordered states, was observed in the ordered state. This band corresponds to the C–H deformation band in the PnPMA block. Because the vibrational coupling of these modes

Table 1. Band Assignments in the Region of 1100–1800 cm$^{-1}$

<table>
<thead>
<tr>
<th>peak (cm$^{-1}$)</th>
<th>assignment</th>
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</thead>
<tbody>
<tr>
<td>1140</td>
<td>C–O stretching</td>
</tr>
<tr>
<td>1224</td>
<td>C–O stretching</td>
</tr>
<tr>
<td>1258</td>
<td>C–O stretching</td>
</tr>
<tr>
<td>1382</td>
<td>C–H deformation</td>
</tr>
<tr>
<td>1391</td>
<td>C–H deformation</td>
</tr>
<tr>
<td>1406</td>
<td>phenyl ring stretching</td>
</tr>
<tr>
<td>1452</td>
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<td>phenyl ring stretching</td>
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<tr>
<td>1602</td>
<td>C=C stretching</td>
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<tr>
<td>1731</td>
<td>C=O stretching</td>
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is sensitive to the local environment, dipole pairs due to the chains locating far away from each other do not give significant contribution to the splitting,25 which is the case of the disordered state. Thus, FTIR spectroscopy can determine the ordered (or disordered) state at a given temperature.

On the other hand, the overall features of the synchronous spectra of the two disordered states at \( T > T_{UODT} \) and \( T < T_{LDOT} \), as shown in Figure 5 a and c, respectively, are similar. However, there appear to be distinct differences in two disordered states in the cross-correlations of the bands at 1456 and 1496 cm\(^{-1}\) (both peaks from the phenyl group in PS) with that at 1270 cm\(^{-1}\) (C–C–O group in PnPMA). A strong positive correlation is seen for the lower-temperature disordered state (Figure 5a), but this correlation is much reduced for the higher-temperature disordered state. This indicates that the conformations of PS–PnPMA, and thus the directional interactions between PS and the side group of PnPMA, in the two disordered states are different.
4. Conclusion

We have shown that temperature-dependent FTIR spectroscopy in conjunction with 2DCOS analysis provides a new method for determining the transition temperatures of PS–PnPMA. Furthermore, information on the conformational changes of specific chemical bonds near the transition can be assessed that cannot be obtained by SAXS (or SANS), rheometry, or depolarized light scattering. We showed that the nature of the disordered state depends on temperature, implying that the degree of weak segmental interactions arising from the dipole and induced-dipole interactions changes with temperature. Consequently, the driving forces for ordering (or disordering) transitions are different in the two temperature regimes. Finally, information on the conformational changes of specific chemical bonds near the transition can be assessed that cannot be obtained by SAXS (or SANS), rheometry, or depolarized light scattering. We showed that the nature of the disordered state depends on temperature, implying that the degree of weak segmental interactions arising from the dipole and induced-dipole interactions changes with temperature. Consequently, the driving forces for ordering (or disordering) transitions are different in the two temperature regimes. Finally, from synchronous 2DCOS, the splitting of bands around 1350–1400 cm$^{-1}$ (assigned to C–H deformation modes) were detected in the ordered state, whereas this behavior was not observed at the disordered state.

Acknowledgment. We thank J. Dudowicz, K. F. Freed, S. L. Hsu, and J. Cho for stimulating discussions. This work was supported by the Creative Research Initiative Program of KOSEF, the NSF-supported Materials Research Science and Engineering Laboratory, and the Department of Energy Office of Basic Energy Science.

References and Notes

(3) Leibler, L. Macromolecules 1980, 13, 1602.