Inclusion Compound Formed between a Poly(ε-caprolactone)-Polybutadiene Diblock Copolymer and Urea

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Introduction. It is well-known[1,2] that certain small molecules such as urea, perhydrotriphenylene (PHTP), and thiourea can form complexes with homopolymers such as polyethylene (PE), poly(ethylene oxide) (PEO), and polyesters. This provides an opportunity to study the conformations and the mobilities of polymer chains which are isolated from neighboring chains and are forced to occupy narrow cylindrical, crystalline channels. DSC, FTIR, and solid-state NMR spectroscopy are often applied in the characterization[3] of these polymer inclusion compounds (ICs).

Molecular modeling of aliphatic polyesters and polyamides was carried out.[4] It was suggested that poly(ε-caprolactone) (PEC) may be capable of forming an IC with urea. It was also suggested that PEC chains in either all-trans or certain kink conformers are slim enough to fit in the narrow IC channel (5.5 Å). Subsequently, PEC-U-IC was prepared[5] and characterized[6] using DSC, X-ray, FTIR, and solid-state NMR spectroscopy. It has been determined that the all-trans extended conformation of pure crystalline PEC is also adopted by the PEC chains in the narrow urea channels of the IC.

However, to date there were no reports on the complex formation between block copolymers and small molecules such as urea. In this paper we are extending our investigation to block copolymers, consisting of one block that can form an IC with urea while the remaining block does not. The IC formation of one block of a diblock copolymer with urea should give a different morphology compared with the morphology observed in the pure diblock copolymer samples. This provides an opportunity to better understand the phase-separated morphology of crystalline-amorphous diblock copolymers.

We have formed an inclusion compound between poly(ε-caprolactone)-polybutadiene diblock copolymer (PEC-PB) and urea. The diblock copolymer contains 47 wt % of PEC and 53 wt % of polybutadiene. The polybutadiene contains 51% trans-1,4, 37% cis-1,4, and 12% 1,2 units. We expect that only the PEC block can form an IC with urea. Preliminary studies were carried out on this diblock copolymer IC using differential scanning calorimetry and FTIR spectroscopy.

Experimental Section. Complex Formation. PEC-PB diblock copolymer with MW = 11 400 was formed as previously described.[7] IC was formed, by mixing a solution of PEC-PB in toluene (0.5 g/50 mL) with 50 mL of urea in a methanol solution (1.5 g/50 mL) while continuously warming and stirring. The combined solution was cooled to room temperature. A white precipitate was obtained over a 3-day period and was filtered and dried.

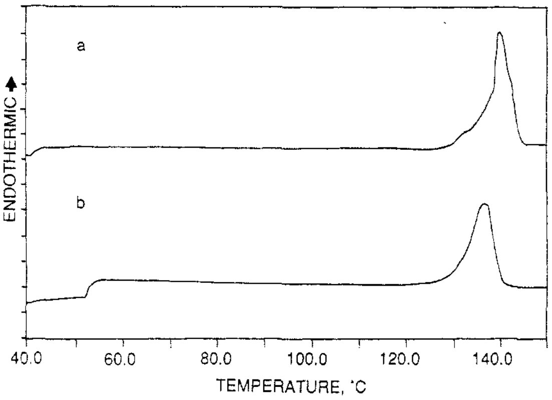

Figure 1. DSC analysis of the PEC-PB-U-IC: (a) first heating (10 °C/min); (b) second heating (10 °C/min).

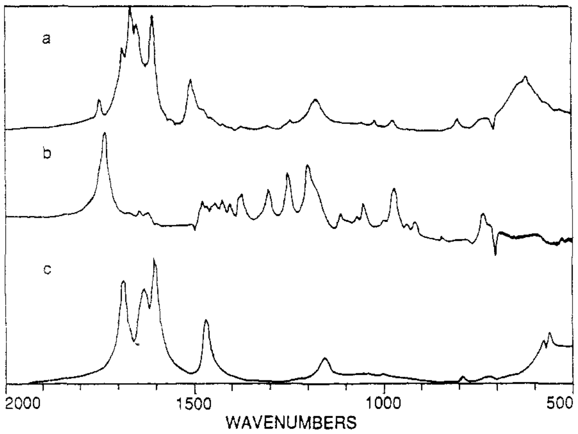

Figure 2. Fourier transform infrared spectrum in the region between 2000 and 500 cm^{-1} recorded at room temperature for (a) PEC-PB-U-IC, (b) PEC-PB, and (c) tetragonal urea.

DSC Measurements. To obtain melting temperatures and heats of fusion, differential scanning calorimetry was carried out on 3-10-mg samples with a Perkin-Elmer DSC-7 thermal analyzer. A heating rate of 10 °C/min was employed, and an indium standard was used for calibration.

FTIR Spectroscopy. FTIR spectra were recorded on powdered samples pressed into KBr pellets on a Nicolet 510P FTIR spectrometer at frequencies from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}.

Results and Discussion. The DSC thermogram of PEC-PB-U-IC recorded at a heating rate of 10 °C/min between 25 and 150 °C is presented in Figure 1. It shows a large endotherm at 140 °C, the melting temperature of the IC, and a shoulder at 137 °C, the melting temperature of uncomplexed free urea. From partial area calculations, one can estimate that 22% of the total sample is uncomplexed urea. It can be clearly seen that the melting temperature of the IC is higher than the melting temperature of both the free diblock copolymer (58 °C) and urea (137 °C). The melting temperature of this IC is 140 °C, with an enthalpy for 100% PEC-PB-U-IC calculated as 52.5 cal/g. This is very close to the enthalpy of PEC-U-IC (54 cal/g) obtained previously.[5] No transition was seen in the temperature range from 25 to 100 °C, indicating that there is no free uncomplexed diblock copolymer in the sample. In the second heating, only the melting of pure urea is apparent.

Figure 2 shows the Fourier transform infrared spectra of PB-PEC-U-IC, bulk diblock copolymer, and urea. The comparison of infrared spectra shows that new bands appear in the IC spectrum which are not present in either of the spectra taken for pure bulk diblock copolymer or tetragonal urea. The infrared spectrum of tetragonal urea

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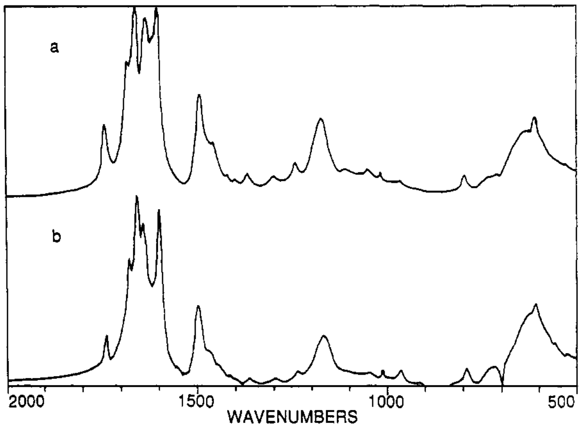

Figure 3. Comparison of FTIR spectra recorded for (a) PEC-U-IC and (b) PEC-PB-U-IC.

was studied and bands were assigned.[8] Major differences between the IC and tetragonal urea spectra are apparent in the 1400 to 1800 cm^{-1} region. The band at 1682 cm^{-1} due to the C=O stretching vibration is shifted to 1655 cm^{-1} and the band at 1467 cm^{-1} due to the N-C-N symmetric stretching is shifted to 1498 cm^{-1} in the IC, providing additional evidence for the formation of IC.

In Figure 3 the IR spectra recorded for PEC-U-IC and PEC-PB-U-IC are compared. The most notable difference between these two IC spectra was seen in the C=O stretching and N-C-N symmetric stretching vibrations. In the case of PEC-U-IC, bands due to tetragonal urea at 1682 and 1467 cm^{-1} are shifted to 1658 and 1490 cm^{-1}, respectively. These two bands at 1658 and 1490 cm^{-1} are also present in the *n*-hexadecane urea IC(H-U-IC) and poly(L-lactic acid) urea IC(PLLA-U-IC). These shifts were previously attributed to hexagonal IC. These ICs have also been studied by wide-angle X-ray diffraction, and similar diffractograms were observed for PEC-U-IC,[5] H-U-IC,[9] and PLLA-U-IC.[10] A unique reflection was observed at $2\theta = 12.6°$, which was assigned to the hexagonal structure. From these observations it was confirmed that the overall structures of these ICs are similar. However, the bands at 1682 and 1467 cm^{-1} due to tetragonal urea are shifted to 1655 and 1498 cm^{-1} in the PEC-PB-U-IC, indicating that the crystal structure of this PEC-PB-U-IC might be slightly different from the usual hexagonal IC crystal structure. Further supporting evidence is obtained from the X-ray diffractogram of PEC-PB-U-IC (not presented) which does not show the peak at $2\theta = 12.6°$.

Vibrational bands due to the included polymer can be seen in the region between 1400 and 700 cm^{-1}, and appreciable differences between these two ICs are not evident. Our molecular modeling[11] of PB in the narrow urea channel (5.5 Å) also indicates that the structurally irregular PB blocks do not form IC with urea. This suggests that only PEC blocks of the diblock copolymer form an IC with urea, while the PB blocks are rejected during the IC formation. Detailed studies of this IC might afford an opportunity to increase our understanding of the morphologies, conformations, and motions of crystalline-amorphous diblock copolymers in the bulk.

Solid-state NMR spectroscopic and scanning electron microscopic investigations are currently in progress and will be compared to similar observations performed on the diblock copolymer sample. By this approach we hope to compare the morphologies, conformations, and motions of isolated IC and bulk PEC-PB diblock copolymer chains. Complete results will be published later.

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References and Notes

(1) Farina, M. In *Proceeding of the International Symposium on Macromolecules*; Mano, E. B., Ed.; Elsevier: New York, 1975; p 21.
(2) De Silvestro, G.; Sozzani, P. In *Comprehensive Polymer Science*; Eastman, G. C., et al., Eds.; Pergamon Press: Oxford, U. K., 1988; Chapter 18, p 303.
(3) Tonelli, A. E. *Polymer (British)* **1994**, *35*, 573.
(4) Tonelli, A. E. *Macromolecules* **1991**, *24*, 1275.
(5) Choi, C.; Davis, D. D.; Tonelli, A. E. *Macromolecules* **1993**, *26*, 1468.
(6) Vasanthan, N.; Shin, I. D.; Tonelli, A. E. *Macromolecules*, in press.
(7) Nojima, S.; Kato, K.; Yamamoto, S.; Ashida, T. *Macromolecules* **1992**, *25*, 2237.
(8) Bhoopathy, T. J.; Baskaran, M.; Mohan, S. *Indian J. Phys.* 1988, *62B* (1), 47.
(9) Vasanthan, N.; Shin, I. D.; Tonelli, A. E. Unpublished results.
(10) Howe, C.; Vasanthan, N.; MacClamrook, C.; Shin, I. D.; Sankar, S.; Simonson, I. K.; Tonelli, A. E. *Macromolecules*, in press.
(11) Tonelli, A. E. *Macromolecules* **1990**, *23*, 3129.