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Characterization of Structure and Morphology in Two Poly(ether-*block*-amide) Copolymers

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ABSTRACT: The structure and morphology of two poly(ether-*block*-amide) polymers have been characterized by XRD, NMR, and DSC. Both polymers were found to be separated, multiphase systems that include a well-defined polyamide crystalline phase, a polyamide amorphous phase, and a predominantly amorphous polyether phase. The DSC data suggest the existence of polyether-based crystallites in both cases. However, a polyether crystalline phase was not detected by XRD, indicating either that it is a minor component or that the crystallites are very poorly defined compared to the homopolymer. In addition, the NMR and XRD results reveal that the crystalline polyamide phase in both polymers adopts a structure (α or γ) similar to that found in the corresponding polyamide homopolymer.

Introduction

Poly(ether-*block*-amide) (PEBA) copolymers are a relatively new family of thermoplastic elastomers with unique physical and processing properties.[1] The unique nature of these materials has been attributed to their structure (**I**), which conceptually consists of rigid polyamide (PA) segments and flexible polyether (PE) segments. By

$$\mathrm{HO{-}[C(O){-}PA{-}C(O)O{-}PE{-}O]{-}H}$$

I

altering the structure and molecular weight of the PA and PE segments, it is possible to design a system with varying properties. For example, the nature of the PA block can affect melting point, the nature of the PE block can affect hydrophobicity, and the ratio of PE to PA can affect flexibility.[1] Given the wide range of physical properties that can be designed into these polymers, it is not surprising that they are encountered in a number of applications from wire coatings to textile fibers to ski boots. In spite of this versatility, there has been little or no structural characterization of PEBA polymers reported in the literature. The purpose of this paper is to present our findings on the structure of two PEBA polymers. The two PEBA polymers under investigation here are block copolymers of poly(ethylene oxide) (PEO) and either nylon 6 (N6) or nylon 12 (N12). These cases will hereafter be referred to as P(EO,N6) and P(EO,N12), respectively, and are given in **II** and **III**.

$$\mathrm{-(CH_2CH_2O)_{3.6}{-}(C(O)(CH_2)_5NH)_{1.0}{-}}$$

II

$$\mathrm{-(CH_2CH_2O)_{6.0}{-}(C(O)(CH_2)_{11}NH)_{1.0}{-}}$$

III

The structure and morphology of **II** and **III** have been characterized by a combination of X-ray diffraction (XRD), differential scanning calorimetry (DSC), and solid-state nuclear magnetic resonance (^{13}C and ^{15}N NMR).

Experimental Section

Samples. All of the samples characterized in this work are commercially available and were analyzed as received. The homopolymers (N6, N12, and EO) were obtained from Standard Polymer Products. The poly(ether-*block*-amide) polymers are commercially available under the trade name PEBAX from Atochem. The polyether fraction of both PEBA copolymers was found to be 58 ± 1% (by weight), as determined by nitrogen content measured on a Perkin-Elmer 2400 elemental analyzer.

X-ray Diffraction. XRD experiments were carried out on a Siemens D500 automated powder diffractometer with a graphite monochromator. The instrument was set up with a Cu radiation (λ = 1.54 Å) X-ray source operating at 50 kV and 40 mA. The 2θ scan range was set to be 2–80° using a step scan window of 0.05°/1.0 s step. Beam slits were set at 1, 1, 1, 0.15, and 0.15° widths. 2θ calibration was performed using an NBS mica standard (SRM675). Data were collected and reduced with the use of a Micro VAX II computer.

NMR Spectroscopy. Solid-state ^{13}C and ^{15}N NMR spectra were acquired at 50.3 and 20.3 MHz, respectively, on a Bruker MSL200 NMR spectrometer. Data were obtained under magic-angle spinning (MAS) conditions using standard cross-polarization (CP) techniques.[2–4] The magic angle was adjusted to within 0.1° using the ^{79}Br spectrum of KBr.[5] ^{13}C CP/MAS spectra were acquired using a 3-s delay and a 1-ms contact time. ^{15}N CP/MAS spectra were acquired using a 2-s delay and a 1-ms contact time. All spectra were externally referenced relative to TMS (^{13}C, 0 ppm) or NH_3 (^{15}N, 0 ppm).

Differential Scanning Calorimetry. DSC thermograms were obtained using scanning rates of 5°/min on a Perkin-Elmer DSC 7 instrument with associated robotics.

Background

An understanding of structure in P(EO,N6) and P(EO,N12) requires some familiarity with structure in the homopolymer PEO, N6, and N12 cases. As a result, we briefly present a description of each to serve as reference points for the discussion below. In addition, some of the key XRD, DSC, and NMR data used to identify these structures are presented in Table I.

The structure of PEO has been extensively characterized by XRD, NMR, IR, and Raman spectroscopies.[6–8] The crystalline PEO chains form a helical structure (7_2 helix) with a succession of nearly trans (C–C–O–C), trans (C–O–C–C), and gauche (O–C–C–O) conformations in the polymer chain. Nylon 6 is known to exist in primarily two crystalline forms.[9,10] The most thermodynamically stable structure is called the α phase and consists of molecules in an extended chain conformation with hydrogen bonds between antiparallel chains. The second form is known as the γ phase. In this structure the molecules form pleated sheets in which the hydrogen bonds exist between parallel

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Table I

polymer	phase	XRD measd *d*-spacings (Å)	DSC measd peak mp (°C)	^{15}N NMR chem shift (ppm)	CH_2N ^{13}C NMR chem shift (ppm)
PEO		3.81, 4.63[a]	64[a]	–	–
		3.82, 4.69[b]			
N6	α	3.75, 4.39[a]	222[a]	116.5[e]	43.6[e]
		3.73, 4.45[c]	222–223[d]		
	γ	4.17[f]	214–217[d]	121.8[e]	39.9[e]
N12	α	3.73, 4.51[c,g]	179[h]	116.6[k]	43.0[k]
			173[i]		
			168[j]		
	γ	4.15[c,g]	174[j]	121.7[k]	40.3[k]
		4.23[a]	178[a]		
			180[i]		
			185[h]		
P(EO,N6)[a]		3.78, 4.41	12, 200	ca. 116	43.2[a]
P(EO,N12)[a]		4.16	10, 155	ca. 122	40.1[a]

[a] This work. [b] Reference 8. [c] Reference 22. [d] Reference 23. [e] Reference 16. [f] References 34 and 35. [g] Reference 28. [h] Reference 27. [i] Reference 29. [j] Reference 30. [k] Reference 26.

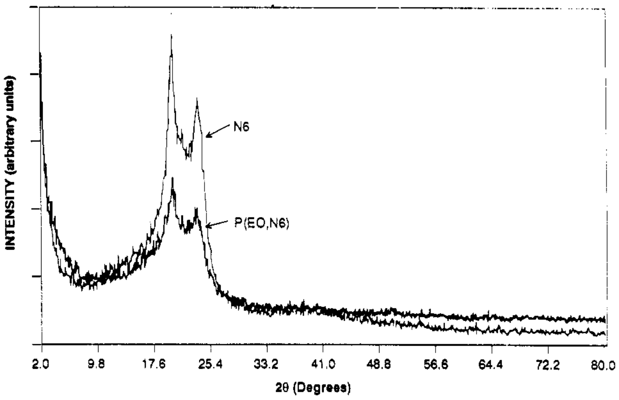

Figure 1. Wide-angle XRD patterns for P(EO,N6) and a N6 homopolymer. The N6 homopolymer is rich in α-phase.

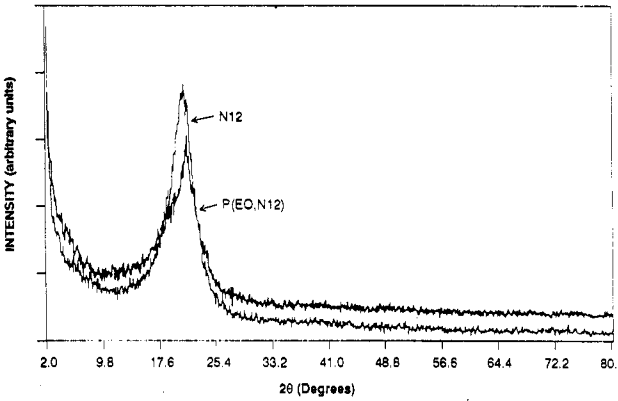

Figure 2. Wide-angle XRD patterns for P(EO,N12) and a N12 homopolymer. The N12 homopolymer is rich in γ-phase.

chains. Both of these phases have been extensively studied by a variety of techniques including NMR, XRD, and DSC.[11-25] The structure of nylon 12 has also been extensively studied,[22,26-30] and like nylon 6, it can adopt two crystalline structures called α and γ. However, unlike nylon 6, the predominant form of nylon 12 is the γ phase where the amide plane is twisted out of the methylene plane by ca. 60°.

Results and Discussion

Given in Figures 1 and 2 are XRD patterns for P(EO,N6), P(EO,N12), N6, and N12. As mentioned earlier, N6 and N12 preferentially crystallize in the α and γ forms, respectively. These two forms are readily distinguished by their XRD profiles. For both homopolymers, the α phases give rise to patterns with two maxima while the γ phases exhibit only a single maximum.[22,28] Examination of Figures 1 and 2 and the data given in Table I indicates that each PEBA polymer contains a polyamide crystalline phase. Furthermore, the structure of that phase appears to be identical to the thermodynamically stable structure found in the corresponding homopolymer.

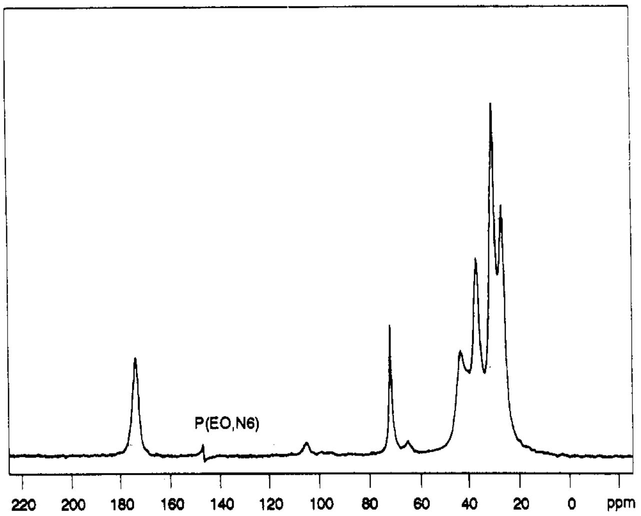

Figure 3. ^{13}C CP/MAS NMR spectrum of P(EO,N6).

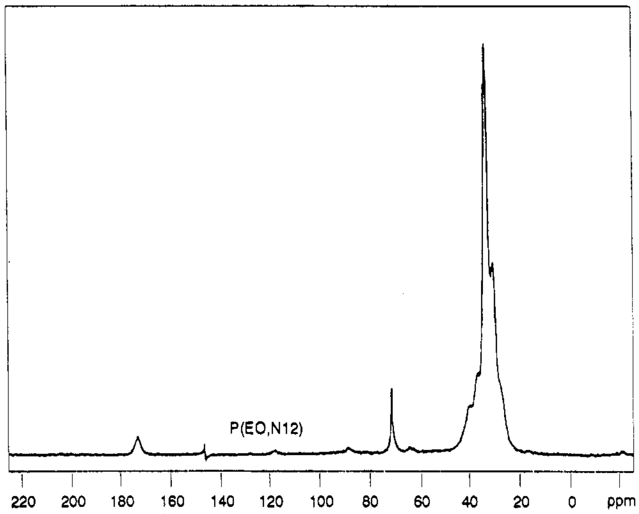

Figure 4. ^{13}C CP/MAS NMR spectrum of P(EO,N12).

This conclusion is supported by ^{13}C NMR studies. Given in Figures 3 and 4 are ^{13}C CP/MAS NMR spectra of P(EO,N6) and P(EO,N12). The NMR spectra are dominated by three regions of intensity: (1) 45–20 ppm due to amide segment methylenes, (2) 78–63 ppm due to polyether segment methylenes, and (3) the polyamide carbonyl resonance at 173–175 ppm. Previous studies of the homopolymers N6 and N12 have shown that several carbon sites yield different ^{13}C NMR shifts in the α and γ phases.[11-17] Of those carbons, one of the most readily diagnostic of phase type is the methylene adjacent to nitrogen. For both homopolymers, the shift of this carbon appears at 40 ppm in the γ phase and at 43 ppm in the α phase.[16,26] Comparison of Figures 3 and 4 and the data given in Table I confirms the fact that the polyamide crystalline phase exists in the α structure in P(EO,N6) and in the γ structure in P(EO,N12). These assertions were further supported by CPT1 experiments[16,36] (not shown) which confirmed that these peaks were due to crystalline carbons in each sample.

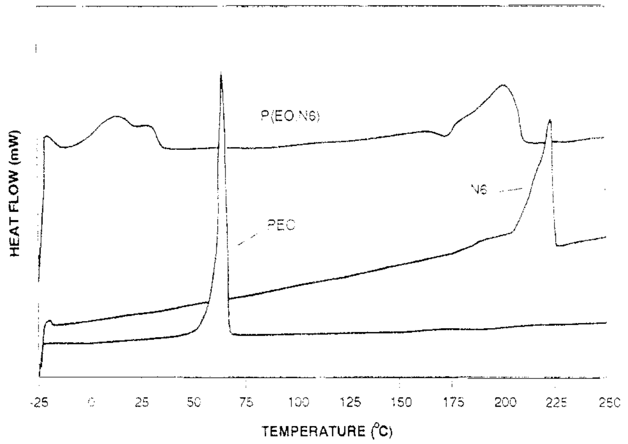

Figure 5. DSC traces for P(EO,N6), PEO, and a N6 homopolymer. The N6 homopolymer is rich in α-phase.

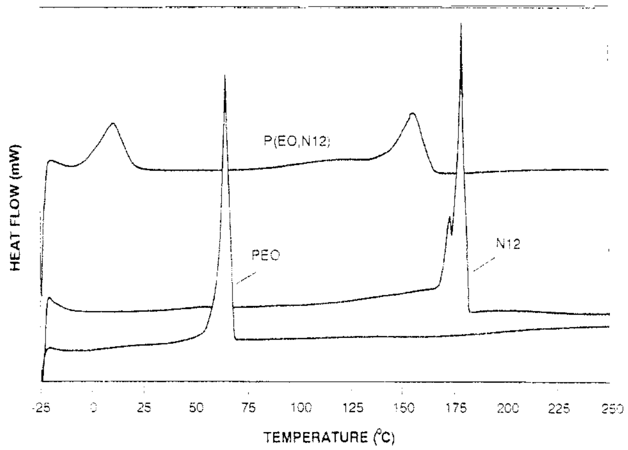

Figure 6. DSC traces for P(EO,N12), PEO, and a N12 homopolymer. The N12 homopolymer is rich in γ-phase.

The thermal behavior of both PEBA polymers was also investigated. Given in Figures 5 and 6 are DSC thermograms for P(EO,N6), P(EO,N12), N6, N12, and PEO. Note that the traces for both PEBA polymers exhibit two melting maxima which correspond to those for homopolymer-type PEO and N6 phases. The presence of these two maxima indicates that the PEBA polymers contain microscopically separated EO and N6 or N12 phases. This is the same conclusion reached earlier via XRD and NMR. In addition, the lower melting points for the crystalline phases in the copolymers, relative to the homopolymers, indicate that the degree of crystal perfection is lower.

In addition to confirming the phase-separated nature of P(EO,N6) and P(EO,N12), the DSC data indicate the existence of crystalline EO phases in both polymers. This is evidenced by the low melting endotherms at 10–12 °C (Figures 5 and 6). This is, perhaps, somewhat surprising since no crystalline EO-type phase was detected by XRD. Given in Figure 7 is an XRD pattern for semicrystalline PEO. Patterns for P(EO,N6) and P(EO,N12) are included again to facilitate comparison. The diffraction pattern for PEO contains two sharp and well-defined maxima at 19.2 and 23.3° (2θ). These features are not observed in the patterns for the two PEBA polymers. There are two likely explanations for this observation. The first is that the amount of crystalline PEO-type phase is small and obscured by the diffractions due to amorphous and crystalline nylon 6. By comparing the heats of fusion in the PEBA polymers with the heats of fusion obtained on the model homopolymers, it appears that the crystallinity in the EO domains is only about 20% of that in the homopolymer case. By comparison, the heats of fusion for the polyamide segments are more than 80% of that in the N6 and N12 cases. This is understandable given that the polyamide segments are much more crystallizable than the polyether segments. The second likely explanation for the apparent disparity between the XRD and DSC results is that the PEO-type crystallites are smaller and much more poorly defined in the PEBA polymers than in the PEO homopolymer. This reason would appear to be consistent with the smearing of the PEO melting endotherm in the DSC traces (Figures 5 and 6).

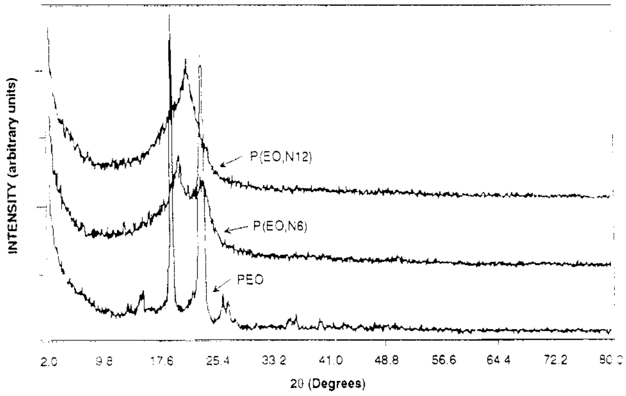

Figure 7. Wide-angle XRD patterns for P(EO,N6), P(EO,N12), and PEO.

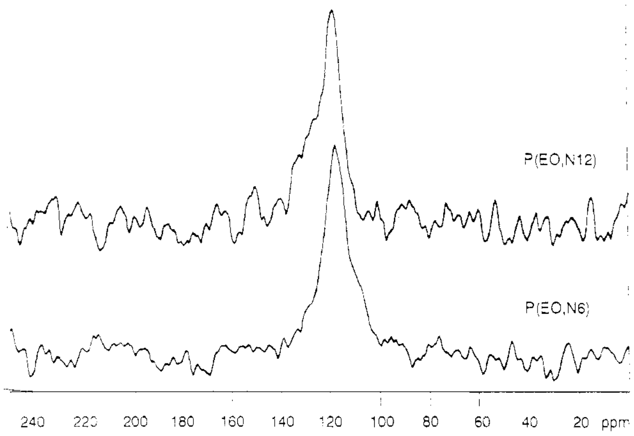

Figure 8. ^{15}N CP/MAS NMR spectra of P(EO,N6) and P(EO,-N12).

Finally, we also examined the structure of the two PEBA polymers using ^{15}N NMR. Several recent studies,[16,31] especially the systematic and thorough work of Mathias and coworkers,[12,17,26,30,32,33] have used ^{15}N NMR to probe the structure about the amide nitrogen in several nylons and model systems. These studies have shown that the ^{15}N NMR shift of polyamide α phases appears at 117 ppm while the shift for γ phases appears at 122 ppm. In addition to these shifts, an intermediate shift at roughly 119 ppm is observed for nitrogens in the amorphous phase. Given in Figure 8 are the ^{15}N (natural, abundance) CP/MAS NMR spectra of P(EO,N6) and P(EO,N12). Both spectra are dominated by peaks at roughly 119 ppm which can be assigned to the amorphous phase. In addition to this resonance, the ^{15}N spectra of both PEBA polymers exhibit a shoulder. In the case of P(EO,N6), this shoulder appears upfield of the amorphous peak and in the region of 117 ppm. By comparison, the ^{15}N spectrum of P(EO,N12) exhibits a downfield shoulder in the region of 122 ppm. Thus, the ^{15}N NMR data provide further evidence to support that the polyamide phases of P(EO,N6) and P(EO,N12) exists as α and γ structures, respectively.

In an effort to elucidate the degree of interaction between the polyether and polyamide blocks, NMR proton spin–lattice relaxation studies were also carried out on P(EO,N6) and P(EO,N12). For some polymeric systems, the rate constant describing this relaxation, $T_{1\mathrm{H}}$, has been shown to be a sensitive indicator of phase separation (or lack thereof).[36] The qualitative argument can be drawn that for a system where two blocks are distinct and separated, two $T_{1\mathrm{H}}$ processes can be observed. As the interfacial region becomes more pronounced and the contact between the two blocks becomes more intimate, spin diffusion between the two blocks also becomes more efficient. As a result, a single $T_{1\mathrm{H}}$ rate constant may be observed.[36] Proton spin–lattice relaxation studies of P(EO,N6) revealed a single $T_{1\mathrm{H}}$ value of 0.4 s for both the polyether and polyamide blocks. Similarly, both blocks in P(EO,N12) were found to have a single $T_{1\mathrm{H}}$ value of 0.3 s. These results suggest the presence of an extended interphase between the two blocks.

Summary

In summary, through a combination of NMR, XRD, and DSC studies, we are led to the conclusion that both PEBA polymers investigated here are microscopically separated, multiphase block copolymers. The evidence indicates that the polyamide segments prefer to associate with other polyamide segments and in doing so actually form well-defined crystals. For P(EO,N6), these crystals adopt a conformation similar to the α phase of the homopolymer N6. The P(EO,N12) crystals, on the other hand, prefer to adopt a conformation similar to the γ phase of the homopolymer N12. The DSC and XRD results suggest that, unlike the polyamide segments, the polyether segments associate in the form of poorly defined crystallites. From this information, it is possible to construct a visual image of poly(ether-*block*-amide) polymers best described as well-defined polyamide crystals and poorly defined polyether crystallites surrounded by interfacial amorphous polyamide and polyether phases.

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