Phase modification and polymorphism in two poly(ether-*block*-amide) copolymers

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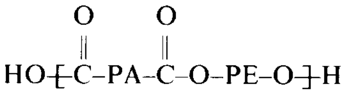
The crystalline polyamide phase in two representative poly(ether-*block*-amide) copolymers has been shown to be polymorphic in nature via an analysis by X-ray diffraction and solid-state ^{13}C nuclear magnetic resonance. In both polymers, this phase was found to adopt α and γ structures analogous to those that exist in the corresponding polyamide homopolymers. Furthermore, it has been shown that phase transformation between crystal types is possible using chemical modifications.

(Keywords: phase modification; polymorphism; block copolymers)

INTRODUCTION

Many of the unique physical and chemical properties of polymers are a direct result of their polymorphic nature[1]. This is certainly true for polyamides, or nylons. As a result, polymorphism in polyamides continues to be a subject of ongoing interest[2–23]. It has often been shown that nylons can adopt a variety of crystal structures depending upon conditions of crystallization (e.g. annealing or solution casting), chemical treatment (e.g. treatment with iodine or phenol) and mechanical processing (e.g. drawing or spinning). Apart from an attempt to understand structural and thermal differences, much of this work has been motivated by the fact that the various nylon polymorphs can also possess different properties such as pyroelectricity[24], three-dimensional elastic constants[25], crimp rigidity[26], dye uptake[26] and extensional compliance[27]. Differences such as these offer the potential for designing specific properties into nylon-based materials by selectively altering the polymorpic nature of the system.

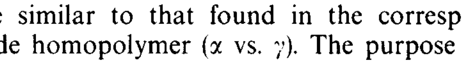
Poly(ether-*block*-amide) (PEBA) copolymers are a relatively new family of thermoplastic elastomers[28,29] containing polyamide, or nylon-like segments. The unique nature of these materials has been attributed to their structure (**I**), which conceptually consists of rigid polyamide (PA) segments and flexible polyether (PE) segments.



$$\mathrm{HO}\!\left[\overset{\overset{\displaystyle O}{\|}}{C}\text{–PA–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–O–PE–O}\right]\!\mathrm{H}$$

I

Previous studies[30] of two representative PEBA polymers (**II** and **III**) found them to be separated, multiphase systems containing a well-defined polyamide crystalline phase. In addition to the polyamide crystalline phase, which is the subject of this paper, amorphous polyamide and polyether segments were also detected, along with some evidence (from d.s.c.) for a minor polyether crystalline component. The two representative PEBA copolymers will hereafter be referred to as P(EO, N6) (**II**), and P(EO, N12) (**III**).



$$\left(CH_2CH_2O\right)_{3,6}\left(\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_2CH_2CH_2CH_2CH_2\text{–}\overset{\overset{\displaystyle H}{|}}{N}\right)_{1,0}$$

II

$$\left(CH_2CH_2O\right)_{6,0}\left(\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\text{–}\overset{\overset{\displaystyle H}{|}}{N}\right)_{1,0}$$

III

Within these multiphase systems, the crystalline polyamide phase in both polymers was found to adopt a structure similar to that found in the corresponding polyamide homopolymer (α vs. γ). The purpose of this paper is to present our findings regarding polymorphism and phase transformation in the same two representative PEBA polymers.

EXPERIMENTAL

Samples

The two PEBA polymers studied here 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.

Transformation of the α-N6 phase in P(EO, N6) to γ-N6 was carried out in a fashion similar to that described elsewhere[31]. A 0.52 g sample of powdered P(EO, N6) was

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stirred in 25 ml of KI/I_2 solution for 19 h. The KI/I_2 solution was decanted away from the resultant black powder which was then washed several times with water. The powder was then stirred in 25 ml of 1M $Na_2S_2O_3$ solution for 2 h. The resultant white precipitate was again washed with water, dried and analysed.

Transformation of the γ-N12 phase in P(EO, N12) to α-N12 was carried out according to a literature method[16] based on solution crystallization from a phenol/ethanol mixture. A 0.06 g sample of powdered P(EO, N12) was added to a solution containing 8.6 g of phenol and 1.4 g of ethanol. The mixture was poured into a 55 mm Petri dish to a depth of approximately 5 mm and allowed to stand uncovered in a hood. After 19 days, all of the phenol had volatilized, leaving a light tan polymer film which, after freezer milling to a powder, was then used for analysis.

X-ray diffraction

X.r.d. experiments were carried out on a Siemens D500 automated powder diffractometer with a graphite monochromator. The instrument was set up with a Cu radiation ($\lambda = 1.54$ 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 second 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.

N.m.r. spectroscopy

Solid-state ^{13}C n.m.r. spectra were acquired at 50.3 MHz on a Bruker MSL2000 NMR spectrometer. Data were obtained under magic-angle spinning (MAS) conditions using standard cross-polarization (CP) techniques[32–34]. The magic angle was adjusted to within 0.1° using the ^{79}Br spectrum of KBr[35]. ^{13}C CP/MAS spectra were acquired using a 3 s delay and a 1 ms contact time. All spectra were externally referenced relative to tetramethylsilane at 0 ppm.

RESULTS AND DISCUSSION

An understanding of structure in P(EO, N6) and P(EO, N12) requires some familiarity with structure in the homopolymer N6 and N12 cases. As a result, we briefly present a description of each to serve as reference points for the discussion below. Nylon 6 is known to exist in primarily two crystalline forms. 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 which the molecules form pleated sheets and the hydrogen bonds exist between parallel chains. The structure of nylon 12 has also been studied extensively and, like nylon 6, it can adopt the two crystalline structures, 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 about 60°. The α and γ phases of both nylon 6 and nylon 12 have been studied extensively[14,16,17,20,21,36–46] by a variety of techniques including n.m.r. and X.r.d.

Polyamide α and γ phases can be readily distinguished by either X.r.d. or n.m.r., as illustrated by the data given in *Table 1*. In X.r.d., the α phases give rise to patterns with two maxima corresponding to *d*-spacings of roughly 3.7 and 4.5 Å[16,38–41]. The γ phases, on the other hand, exhibit only a single maximum corresponding to a *d*-spacing of roughly 4.2 Å[16,38–41]. In n.m.r. there are a wide variety of spectral features that differ between the α and γ phases[14,20,42–44]. Of these, one of the most readily diagnostic of phase type is the methylene alpha to the nitrogen which appears at 40 ppm in the γ phase and at 43 ppm in the α phase[14,20]. In the case of nylon 6, a second diagnostic peak is that for the methylene beta to the nitrogen. In the α phase, this peak appears at 30 ppm while in the γ phase it appears at 34 ppm[14]. Unfortunately, the peak due to this carbon is not resolvable in nylon 12. Using diagnostic data such as these, we have previously shown[30] that the polyamide phases in P(EO, N6) and P(EO, N12) preferentially crystallize in the α and γ forms, respectively.

There are a variety of treatments known to convert the α phase of nylon 6 into the γ phase. One of the most efficient[31] involves sequential exposure to solutions of KI/I_2 and $Na_2S_2O_3$. Given in *Figure 1* are the X.r.d. patterns of P(EO, N6) before and after such treatment. Peaks marked with an asterisk are due to residual, elemental sulfur that had not been effectively washed away. A shift in intensity from two maxima (corresponding to *d*-spacings of 3.78 and 4.41 Å) to a single maximum (corresponding to a *d*-spacing of 4.18 Å) can be readily observed. As the data in *Table 1* reveal, this indicates that the α-like crystallites in P(EO, N6) have been transformed into a structure analogous to the γ phase found in the N6 homopolymer. This conclusion is also supported by ^{13}C n.m.r. Given in *Figure 2* are ^{13}C n.m.r.

Table 1 Key X.r.d. and ^{13}C n.m.r. data for characterizing polyamide phase type

Polymer	Polyamide phase	^{13}C n.m.r. chemical shift (ppm)		X.r.d. measured *d*-spacings (Å)
		$^{*}CH_2$–N	$^{*}CH_2CH_2$–N	
N6	α	43.6[a]	30.4[a]	3.73, 4.45[e]
	γ	39.9[a]	34.1[a]	4.17[f]
P(EO, N6)	α	43.2[b]	30.4[c]	3.78, 4.41[b]
	γ	ca. 40[c]	34.2[c]	4.18[c]
N12	α	43.0[d]	–	3.73, 4.51[e,g]
	γ	40.3[d]	–	4.15[e,g]
P(EO, N12)	α	42.9[c]	–	3.73, 4.47[c]
	γ	40.3[b]	–	4.16[b]

Data from: [a]ref. 14; [b]ref. 30; [c]this work; [d]ref. 20; [e]ref. 16; [f]ref. 38; [g]ref. 39

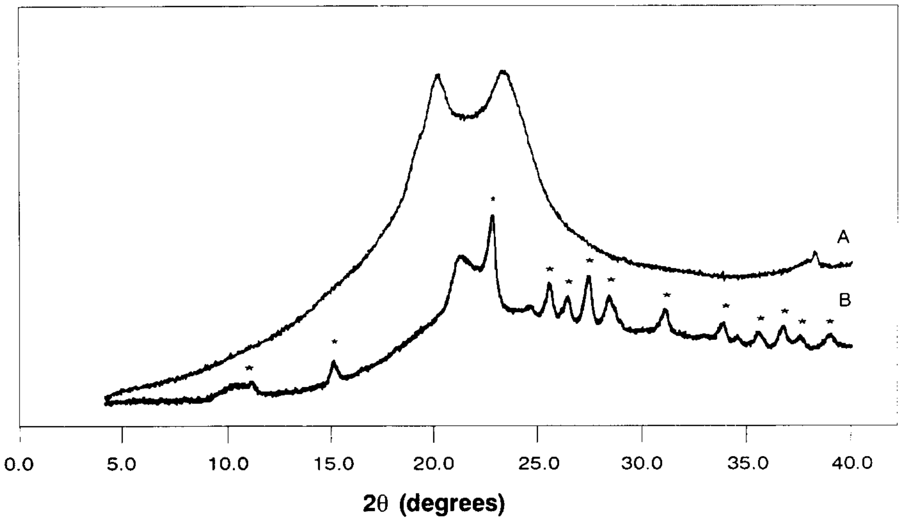

Figure 1 Wide-angle X.r.d. patterns for P(EO, N6) polymers rich in (A) α and (B) γ-N6 phases. Peaks marked with an asterisk are due to residual sulfur (see text)

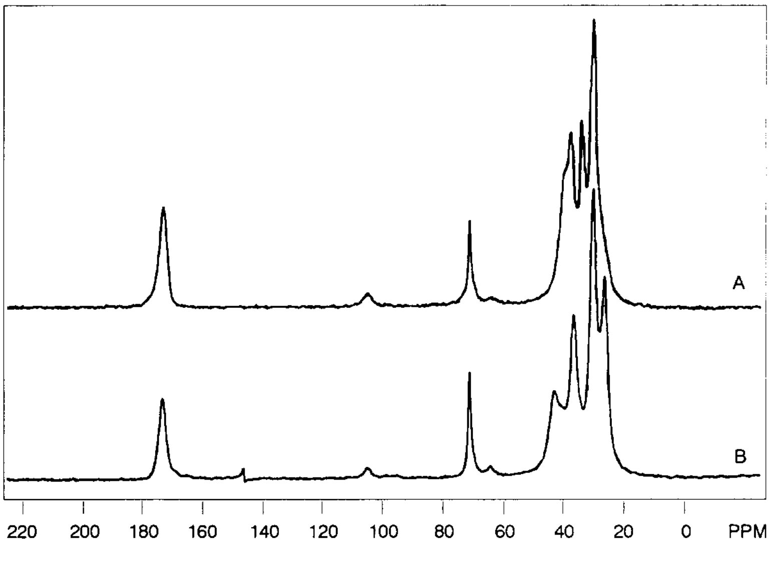

Figure 2 ^{13}C CP/MAS n.m.r. spectra of P(EO, N6) polymers rich in (A) γ and (B) α-N6 phases

spectra of P(EO, N6) before and after sequential treatment with KI/I_2 and $Na_2S_2O_3$. These spectra also reveal a shift in intensity that is consistent with transformation into the γ phase. This is most evidenced by a change in intensity from peaks at 43 and 30 ppm (indicative of the α phase) to peaks at 40 and 34 ppm (indicative of the γ phase), as detailed in *Table 1*. Thus, the X.r.d. and ^{13}C n.m.r. data confirm the fact that the polyamide phase in P(EO, N6) can exist in a structure analogous to either the α or γ phase observed in the N6 homopolymer.

There are a variety of treatments known to convert the γ phase of nylon 12 into the α phase. One of the most efficient involves solution crystallization from a phenol/ethanol mixture[16]. Given in *Figure 3* are the X.r.d. patterns of P(EO, N12) before and after such treatment. A shift in intensity from one maximum (corresponding to a *d*-spacing of 4.16 Å) to two maxima (corresponding to *d*-spacings of 3.73 and 4.47 Å) can be readily observed. As the data in *Table 1* reveal, this indicates that the γ-like crystallites in P(EO, N12) have been transformed into a structure analogous to the α phase found in the N12 homopolymer. This conclusion is also supported by ^{13}C n.m.r. Given in *Figure 4* are ^{13}C n.m.r. spectra of P(EO, N12) before and after solution crystallization from a phenol/ethanol mixture. These spectra also reveal a shift in intensity that is consistent with transformation into the α phase. This is most evidenced by a change in intensity from 40 ppm (indicative of the γ phase) to 43 ppm (indicative of the α phase), as detailed in *Table 1*. Thus, the X.r.d. and ^{13}C n.m.r. data confirm the fact that the polyamide phase in P(EO, N12) can exist in a structure analogous to either the α or γ phase observed in the N12 homopolymer.

SUMMARY

Through a combination of X.r.d., n.m.r. and established chemical treatments, the data presented here reveal the polymorphic nature of the polyamide phase in two representative poly(ether-*block*-amide) (PEBA) copolymers. We believe that this work has important implications.

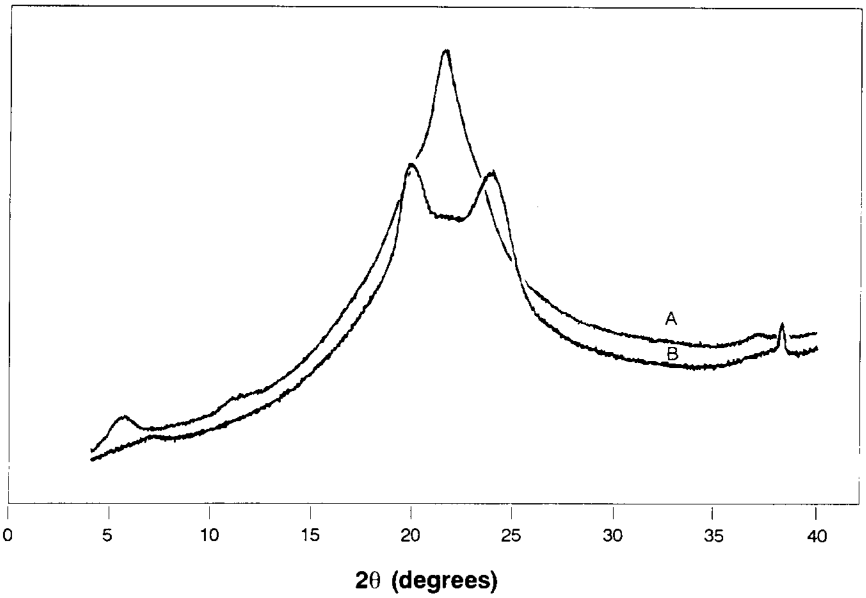

Figure 3 Wide-angle X.r.d. patterns for P(OE, N12) polymers rich in (A) γ and (B) α-N12 phases

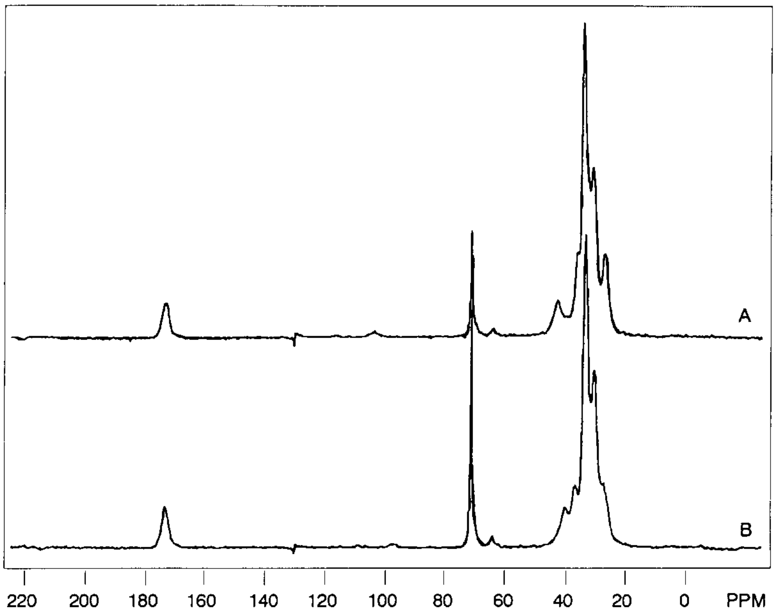

Figure 4 ^{13}C CP/MAS n.m.r. spectra of P(EO, N12) polymers rich in (A) α and (B) α-N12 phases

The physical properties of nylons are often governed by the type of crystalline phase present[2-27]. As a result, it is possible to design nylon-based materials with specific properties by altering the phase type. By analogy, it should be possible to use a materials-by-design approach in PEBA applications in order to enhance specific properties, while at the same time retaining the benefits imparted by the polyether component.

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