

Segmented Block Copolyetheramides Based on Nylon 6 and Polyoxypropylene. III. SAXS Analysis

YEONG CHOO L YU,¹ WON HO JO,¹ MOO SUNG LEE²

¹ Department of Fiber and Polymer Science, Seoul National University, Seoul 151-742, Korea

² Department of Textile Engineering, Chonnam National University, Kwangju 500-757, Korea

Received 15 January 1996; accepted 6 October 1996

ABSTRACT: Morphologic characteristics of segmented block copolyetheramides based on nylon 6 and polyoxypropylene (POP) were investigated as a function of the compositions and block lengths of the hard and soft segments using small angle X-ray scattering (SAXS). Three POPs with different molecular weights were used as a soft segment. One-dimensional correlation functions were obtained from the desmeared intensity SAXS curves using the method developed by Vonk and Kortleve. The interdomain spacings were determined from the correlation distance at the peak position of the correlation function. From the dependence of the correlation distance on soft segment content, we deduced that an increase in the hard-segment length may lead to crystal formation by a chain-folding mechanism. The thickness of phase boundary was determined from the smeared intensity data using the method of Koberstein. A decrease in the phase boundary thickness with increasing soft-segment content suggests that an increase in the chain mobility by soft segment facilitates the regular arrangement of the hard segment, resulting in the formation of the hard domain with a narrow interfacial region. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2155–2163, 1997

Key words: copolyesteramides; SAXS; interfacial thickness; morphology

INTRODUCTION

Small angle X-ray scattering (SAXS) is a very useful tool for the characterization of morphology and microstructure in polymeric materials. The SAXS technique can be employed to measure a structural feature on the order of 1–100 nm in size if sufficient contrast in scattering power exists. The angular dependence of the scattered intensity yields morphologic information.^{1–7}

For dilute systems, the scattering curve can provide information about the shape, size and volume of the particles. On the other hand, for dense systems, where the interaction between particles

is very important, the SAXS scattering curve gives various morphologic information depending on the angular region examined. The overall intensity is related to the degree of phase separation, while the breadth of the intensity distribution is related to the size distribution of the inhomogeneities. If a periodic structure exists, the interdomain spacing may be estimated from the angular position of the maximum in the scattering curve or the correlation function. The shape of the tail region can provide information about the thickness of the diffuse boundary between phases.^{6,8–15}

In previous papers,^{16,17} we reported some results about synthesis, structure, and property of segmented block copolyetheramides composed of nylon 6 as a hard segment and polyoxypropylene (POP) as a soft segment. To investigate the effect

Correspondence to: W. H. Jo.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/112155-09

of block length on the structure–property relationship, three POPs with different molecular weights were used. From thermal analyses of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) and from tensile property it was clear that the variation in block length and the composition of the hard and soft segments affect the microphase separation, the composition of each phase, and the crystallinity of the hard domain, resulting in the change in the block copolymers' tensile properties. As the block length of soft segments becomes longer, better phase separation is induced and the purity of the phase-separated domains is enhanced. From the results of DSC and DMA, we concluded that the POP units having molecular weight of 452 g/mol are miscible with the amorphous phase of nylon 6. Therefore, the block copolymers of nylon 6 and POP with shorter chain consist of two different phases of a crystalline domain of nylon 6 and a miscible amorphous domain of nylon 6 and the POP, whereas the other POP units having higher molecular weights are immiscible with nylon 6. Therefore, the resultant copolymers of these POP units have three different phases: a crystalline domain of nylon 6, and nylon 6-rich and POP-rich amorphous domains.

The objective of this study is to obtain information about the microstructure of the nylon 6–POP block copolymers using SAXS analysis. More specifically, the interdomain spacings and interfacial thicknesses of the block copolymer are determined from SAXS intensity curves and discussed as functions of the soft segment content and its length.

EXPERIMENTAL

Materials

Nylon 6–POP block copolymers were synthesized by melt polymerization of caprolactam, polyoxypropylene diamine (PODP), and adipic acid at 240°C, as described in the preceding paper.¹⁶ Their compositions and block lengths, which were calculated from ¹H-NMR data and a statistical theory of Sorta and Melis,¹⁸ are listed in Table I. In sample codes, D4, D20, and D40 stand for the D-400 (mol wt 462), D-2000 (mol wt 2104), and D-4000 (mol wt 4540) grades of PODP, respectively, and the numbers that follow D4-, D20-, and D40- represent the PODP contents in the feed of

polymerization. While the soft-segment block lengths correspond nearly to 1 POP unit, the block lengths of hard segments are varied with the content and chain length of the soft segment used. As the POP content decreases and the chain length of POP unit increases, the hard block length becomes longer.

Preparation of Specimens

Test specimens for measurements of small angle X-ray diffraction were compression-molded by a laboratory press equipped with a thermometer and a cavity for the circulation of cooling water. The samples were molded at a temperature 10 to 20°C higher than the melting temperature of the samples and at a pressure of 250 kg/cm² for 5 min. The samples were then cooled at a rate of 20°C/min to 100°C, the pressure was released, and the samples were removed. The average thickness of the test specimens was 0.8 mm.

SAXS Measurement

A Kratky small angle X-ray camera (MXP3; MAC Science Co., Japan) equipped with a step scanning device was used for SAXS experiments. The X-ray source was operated at 45 kV and 40 mA by a Phillips PW2253/H X-ray generator. Experiments were carried out under the conditions of infinite slit optics using the entrance slit of 70 μm and the receiving slit of 140 μm, but the slit-width effect was assumed to be negligible. The absolute scattered intensity was not calculated because the intensity of the primary beam could not be measured.

Raw data were smoothed using a progressive piecewise cubic least-squares fitting method before the subtraction of a background intensity.¹⁹ The smoothing procedure is important to minimize errors in desmearing procedures and to facilitate the diffuse boundary analysis by reducing the statistical scatter of the data in the Porod's law region. In this work the background scattering was determined using the method of Vonk,²⁰ then the background intensities were subtracted from the observed intensities.

RESULTS AND DISCUSSION

Figure 1 shows the effect of desmearing procedure on the raw SAXS intensity curve for D20-40. The

Table I Nylon-POP Block Copolymers Used in Study

Sample Code	CPL/PODP Feed Ratio	Molecular Weight (g/mol)	Copolymer Composition (wt %)		Number of Units	
			Soft Segment	Hard Segment	Soft Segment	Hard Segment
D4-10	100/10	21,500	12.9	87.1	1.03	32.1
D4-20	100/20	22,900	21.5	78.5	1.05	18.1
D4-40	100/40	24,300	36.2	63.8	1.11	9.50
D4-60	100/60	22,500	46.7	53.3	1.17	6.57
D4-80	100/80	21,200	55.6	44.4	1.25	4.91
D20-10	100/10	17,600	11.4	88.6	1.01	87.6
D20-20	100/20	21,200	20.7	79.3	1.01	56.0
D20-40	100/40	26,800	31.9	68.1	1.02	35.0
D20-60	100/60	28,800	41.8	58.2	1.04	23.6
D20-80	100/80	30,600	49.3	50.7	1.05	21.3
D40-10	100/10	19,900	10.0	90.0	1.00	133.0
D40-20	100/20	24,300	19.6	80.4	1.01	90.5
D40-40	100/40	22,500	32.4	67.6	1.01	55.2
D40-60	100/60	32,700	44.1	55.9	1.02	52.6
D40-80	100/80	28,700	50.9	49.1	1.03	30.1

raw intensity curve was desmeared according to the method of Vonk.²⁰ The desmearing procedure used in this work is well described elsewhere.²¹ As discussed by Vonk and colleagues,²² the desmeared intensity curve shows a more prominent peak than does the smeared one. The Bragg distance corresponding to the interdomain repeat

distance, d , may be calculated from the maximum of the SAXS curve by the Bragg's law equation. The desmeared value of d for D20-40 was shifted to a lower value by a factor of 1.26 as compared with the smeared value.

Figure 2 shows the desmeared scattering intensity curves for D4 copolymers with the shortest

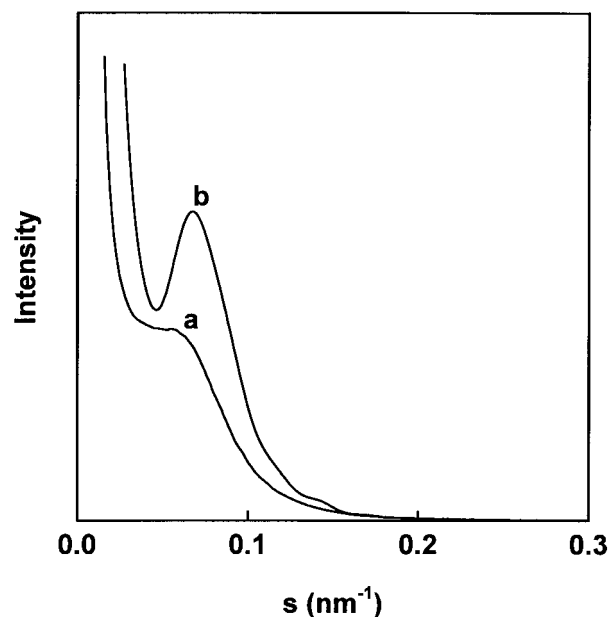


Figure 1 Effect of desmearing procedure on the SAXS intensity curve for D20-40 copolymer: (a) smeared; (b) desmeared SAXS intensity curves.

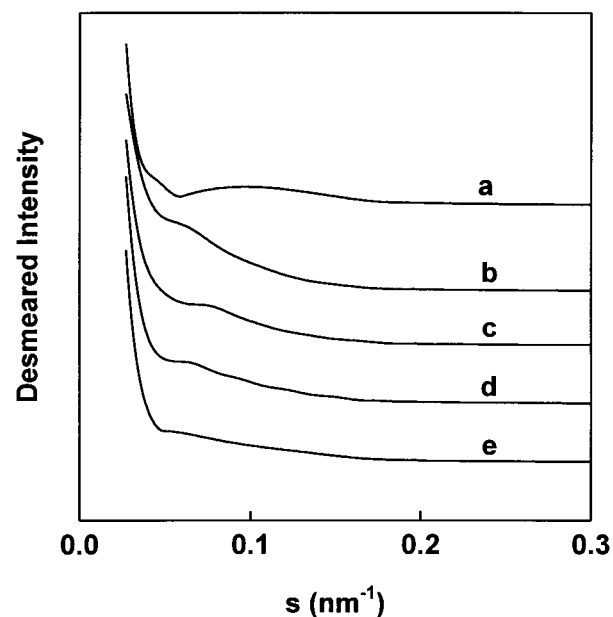


Figure 2 Desmeared SAXS intensity curves for D4 copolymers: (a) D4-10; (b) D4-20; (c) D4-40; (d) D4-60; (e) D4-80.

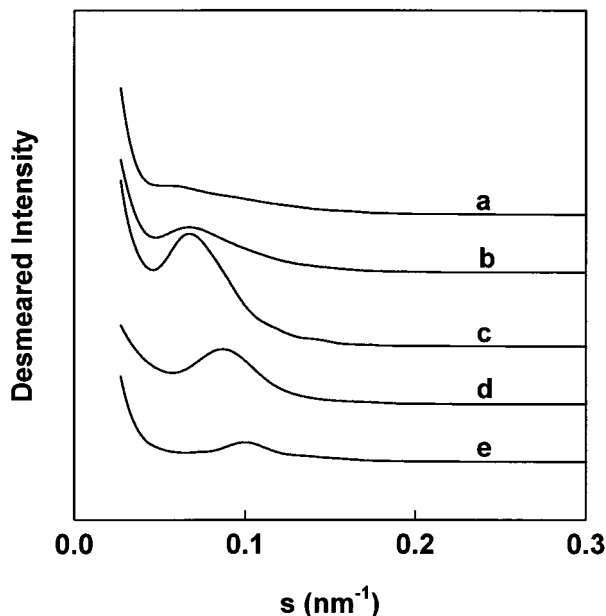


Figure 3 Desmeared SAXS intensity curves for D20 copolymers: (a) D20-10; (b) D20-20; (c) D20-40; (d) D20-60; (e) D20-80.

POP block length. The scattering profiles for these copolymers exhibit weak discernible peaks. The scattering curve for D4-10 shows a broad peak and its Bragg distance is 10.4 nm. The D4-20 copolymer shows the strongest peak intensity. However, the intensity peaks are gradually broadened as the POP content increases. These results suggest that a periodic structure exists in D4 copolymers but the structure disappears with high content of soft segment. As discussed in the previous paper,¹⁷ the D4 copolymers consist of two different domains: one is a crystalline domain of nylon 6 and the other is a miscible amorphous domain of POP and nylon 6. From the results of DSC, DMA, and wide-angle X-ray scattering of the previous study and SAXS of this study, it is clear that for D4 copolymers the crystalline domain of nylon 6 becomes progressively smaller as the POP content increases. Note that the hard block length of nylon 6 decreases with increasing soft segment content. Except for D4-10, the interdomain spacings of the copolymers are in the range of 14.5 to 16.7 nm.

Figure 3 shows the desmeared SAXS intensity curves for D20 copolymers. The intensity profiles of the copolymers are very dependent on the soft-segment content. The peak intensity first increases with the soft-segment content and then decreases. The maximum peak intensity is ob-

served for D20-40 having the soft-segment content of 32 wt %. When the POP content is lower than 32 wt %, hard nylon 6 segments may form interconnected microphases with crystalline domains of irregular shape. As a result, D20-10 and D20-20 show broad SAXS intensity peaks. At the soft-segment content of 32 wt % the hard and soft domains are arranged regularly, resulting in a well-developed periodic structure. When the soft-segment content is higher than 32 wt %, the regularity of the lamellar structure is gradually reduced due to perturbation of the regular structure by the increase of the flexible soft segments and the reduction in the lamellar size. The interdomain spacing decreases from 15 nm to 10 nm as the soft-segment content increases from 32 wt % (D20-40) to 50 wt % (D20-80). This is because the lamellar thickness decreases with increasing soft-segment content, while the interlayer thickness of the amorphous POP domain between the lamellae remains constant to convert from a discrete phase into a continuous phase.

Figure 4 shows the desmeared SAXS intensity curves for D40 copolymers of the longest POP length. None of the copolymers exhibit any characteristic scattering peaks. As shown in Table I, at the same content of soft segment, D40 copolymers have the longest hard segment of nylon 6. Therefore, the D40 copolymers have the most prominent

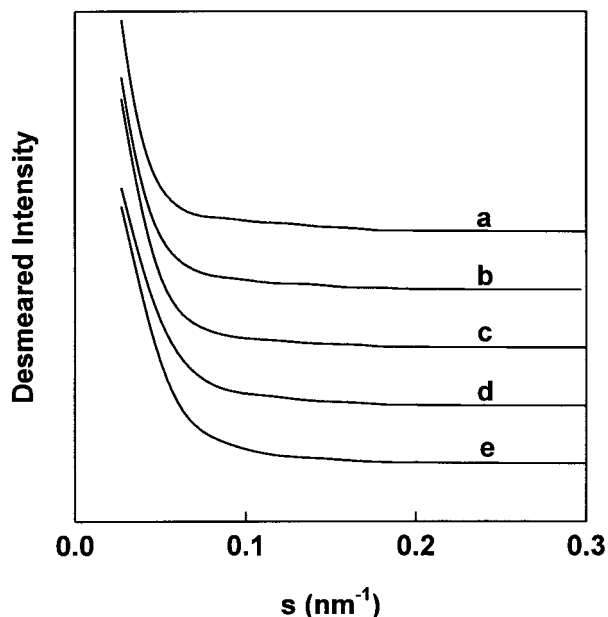


Figure 4 Desmeared SAXS intensity curves for D40 copolymers: (a) D40-10; (b) D40-20; (c) D40-40; (d) D40-60; (e) D40-80.

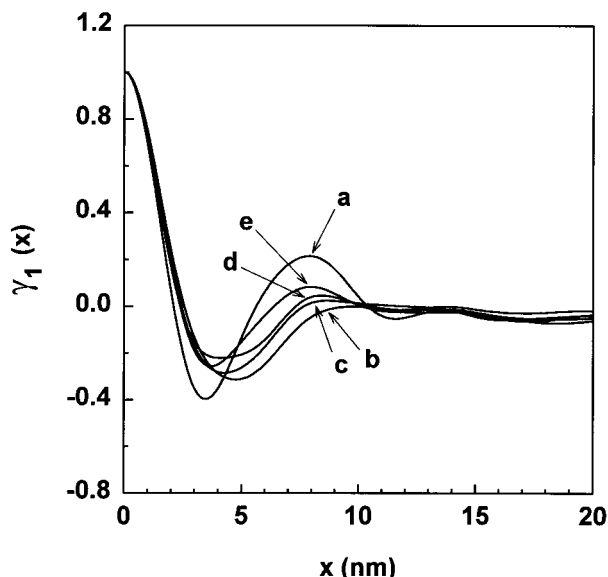


Figure 5 One-dimensional correlation functions of D4 copolymers: (a) D4-10; (b) D4-20; (c) D4-40; (d) D4-60; (e) D4-80.

interconnected structures of the hard domains at the same content of soft segment. In this case, soft POP domains are randomly distributed in the matrix of hard nylon 6. Thus irregular structures, which lack periodicity, are developed.

One-dimensional correlation functions for nylon 6-POP block copolymers can be obtained from the desmeared SAXS intensity curves according to the method developed by Vonk and Kortleve²³:

$$\gamma_1(x) = \frac{\int_0^{\infty} s^2 I(s) \cos(2\pi xs) ds}{\int_0^{\infty} s^2 I(s) ds} \quad (1)$$

where s is the scattering vector, $I(s)$ is the scattered intensity, and x is the correlation distance. Scattering curves should be extrapolated from the observed minimum angle to $s = 0$ for the calculation of the correlation function. This extrapolation was performed by fitting a Gaussian curve to the first five experimental points of the scattering curve.²⁴ The existence of a maximum in the one-dimensional correlation function indicates a periodicity in the phase correlation and is often related to the average interdomain spacing in segmented block copolymers which show microphase separation.

In Figure 5, which shows one-dimensional cor-

relation functions for D4 copolymers, $\gamma_1(x)$ for D4-10 shows a strong oscillation up to long correlation distance. This implies that periodic lamellar structures with a narrow distribution are well developed in D4-10. The oscillation of $\gamma_1(x)$ diminishes very rapidly with increasing soft-segment content due to a broad distribution of the interdomain spacing. Another point to be mentioned is that the interdomain spacing corresponding to a maximum peak increases slightly as the soft-segment content decreases from D4-80 to D4-20. This result is attributed to the fact that the lamellar thickness increases due to the increase of hard block length as the soft-segment content decreases, while the interlayer thickness of amorphous phase remains constant. However, a further decrease of the soft-segment content to D4-10 causes the decrease in the interdomain spacing. An increase of hard block length does not always yield the increase of lamellar thickness, because the increase of hard block length may induce crystal formation by a chain-folding mechanism. This type of crystal has constant lamellar thickness. Therefore, the decrease of the soft-segment content will reduce the interlamellar thickness, resulting in the decrease of the interdomain spacing.

Figure 6 shows the one-dimensional correlation functions for D20 copolymers. The copolymers exhibit the chain-folding phenomenon at the soft-segment content of 32 wt %. The oscillation of

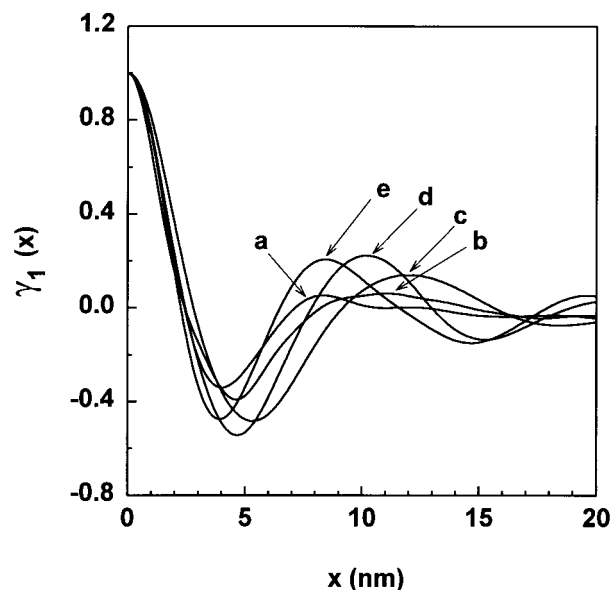


Figure 6 One-dimensional correlation functions of D20 copolymers: (a) D20-10; (b) D20-20; (c) D20-40; (d) D20-60; (e) D20-80.

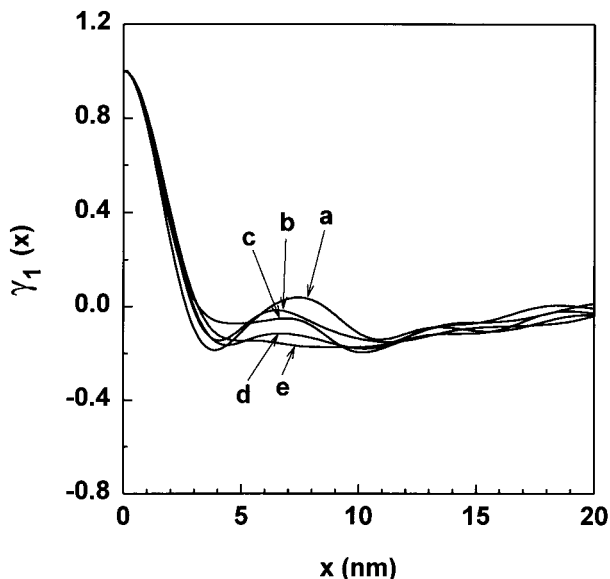


Figure 7 One-dimensional correlation functions of D40 copolymers: (a) D40-10; (b) D40-20; (c) D40-40; (d) D40-60; (e) D40-80.

$\gamma_1(x)$ becomes stronger with increasing soft-segment content. It is well known that $\gamma_1(x)$, which shows periodicity, indicates the existence of two-phase structure, which can be described as alternating layers of the soft and hard segments on a local scale.¹ Therefore, the strong oscillation shown in Figure 6 implies that alternating structures are well developed for D20 copolymers. At a low soft-segment content, the hard domains become interconnected and are distributed irregularly, resulting in a rapid disappearance of the oscillation. At the soft-segment content of 32 wt %, the soft domains seem to form a co-continuous phase with the hard domains. This co-continuous phase is better developed at the higher content of soft segment, resulting in a good alternating lamellar structure.

Figure 7 shows the one-dimensional correlation functions for D40 copolymers. Differently from the above two block copolymers, the interdomain spacings for D40 copolymers are almost independent of the soft-segment content as represented by almost the same position of maximum peaks. The oscillation vanishes rapidly, however, with increasing soft-segment content. This phenomenon may be explained by the following speculation. The lamellar thickness of nylon 6 in D40 copolymers may decrease with increasing soft-segment content because the block length of nylon 6 is shortened and the continuity of the soft seg-

ment is increased. This structural evolution causes disalignment of the crystalline hard domains and progressively destroys the regularity of the lamellar structure.

Three-dimensional correlation function can be determined by taking the inverse Fourier transform of the intensity function in the equation of Debye and Bueche.²⁵ However, three-dimensional correlation functions for nylon 6-POP block copolymers do not exhibit characteristic peaks (not shown here).²¹ This means that the microstructure of the copolymers can be better described by one-dimensional correlation function, assuming a lamellar model.

The presence of diffuse phase boundaries can be confirmed from the SAXS intensity data because diffuse phase boundaries lead to a negative deviation from Porod's law.^{8,26} Figure 8 shows a representative plot of $s^3 \tilde{I}(s)$ against s for D20-40 copolymer, where $\tilde{I}(s)$ is the slit-smear intensity, which is free from background scattering. The negative slope at higher s of Figure 8 indicates the presence of a diffuse phase boundary for D20-40.

The thickness of diffuse phase boundary, called "interfacial thickness," was determined from the intensity data using the method of Koberstein and associates.²⁶ According to the suggestion of Hashimoto et al.,²⁷ the smeared intensity data was used. A parameter for phase boundary thickness, σ , which is a measure of the interfacial thickness, is calculated from intensity data and their val-

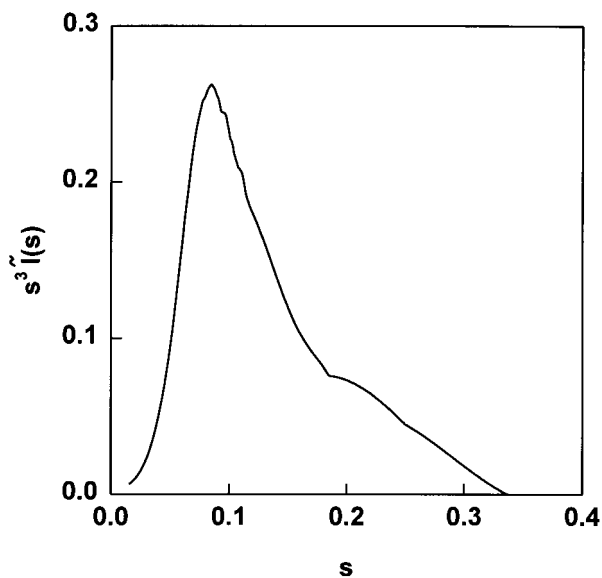


Figure 8 Porod plot for D20-40 copolymer.

Table II Diffuse Phase Boundary Thickness Determined by the Koberstein Method

Sample Code	Sigmoidal Parameter, σ (nm)	Linear Dimension, ^a E (nm)
N-6	1.18	4.09
D4-10	1.05	3.64
D4-20	0.87	3.01
D4-40	0.87	3.01
D4-60	0.79	2.74
D4-80	0.75	2.60
D20-10	1.14	3.95
D20-20	0.87	3.01
D20-40	0.99	3.43
D20-60	1.08	3.74
D20-80	1.25	4.33
D40-10	1.20	4.15
D40-20	1.17	4.05
D40-40	1.00	3.46
D40-60	0.95	3.29
D40-80	1.01	3.50

^a Parameter E represents the full width of an interfacial gradient. This parameter is related to σ by the relation: $E = \sqrt{12}\sigma$.

ues are listed in Table II. The values of σ range from 0.7 to 1.2 nm. These values are in a similar range to segmented polyurethane block copolymers.^{1,3,14,28} Although σ is related to the interfacial thickness, it does not represent the actual thickness but can be used to qualitatively compare interfacial thicknesses. The thickness of linear diffuse phase boundary, E , corresponding to the effective linear dimension of the sigmoidal gradient, was also calculated from the relation $E = \sqrt{12}\sigma$. In D4 copolymers having two domains, the interfacial thickness decreases with increasing soft-segment content. This may be explained by two different effects: one is the reduction of lamellar thickness by the decrease of the hard block length; another is the increase of the boundary sharpness by the improved chain arrangement of hard segment in the mobile soft domain. In D20 copolymers having three different domains, σ exhibits a minimum value at the soft-segment content of 20 wt %. The inclusion of a small amount of soft POP units in the amorphous hard domain induces the increase of the boundary sharpness between the crystalline hard domain and the amorphous hard domain, resulting in decreased thickness of the overall phase boundary. However, further inclusion of POP units causes

an increase in the diffuse phase boundary between the amorphous nylon 6-rich and POP-rich domains. This acts as a dominant factor for increasing the thickness of the overall diffuse phase boundary. The interfacial thickness of D40 copolymers decreases with increasing soft-segment content. This trend may be attributed to the decrease in the lamellar thickness of the hard domain. Similar to D20, D40 copolymers are composed of three phases. However, the thickness of phase boundary between the amorphous hard and amorphous soft domains becomes nearly constant because the amorphous hard domains contain little of the soft segments due to their higher compositional purity. Therefore, the thickness of overall phase boundary depends on the thickness of phase boundary between the crystalline hard and amorphous hard domains. Since the lamellar thickness of the hard domain decreases with increasing soft-segment content, the thickness of phase boundary between the crystalline hard and amorphous hard domains also decreases. An increase in the thickness of phase boundary for D40-80 seems to be caused by a diffuse effect between the amorphous hard and amorphous soft domains at high soft-segment contents.

From of this and previous studies^{16,17} of the microstructure of the segmented nylon 6-POP block copolymers, morphologic models for these copolymers are schematically illustrated in Figure 9. The morphologic character of D4 copolymers with the shortest POP block length is expressed in Figure 9(a). The POP units of 452 g/mol are miscible with the amorphous phase of nylon 6. Therefore, D4 copolymers have two distinct domains: one is a crystalline domain of nylon 6 and the other is a miscible amorphous domain of nylon 6 and POP. Nylon 6 chains form fringed micelle crystals due to their short length in D4 copolymers. The crystalline hard domain exists as a discrete phase in an amorphous matrix such as a plasticized thermoplastic. The periodicity of the two-phase structure is very weak on a local scale. In D20 copolymers with middle POP block length, the crystalline domains are developed by some chain-folding mechanism. The amorphous regions are phase-separated into two distinct domains: POP-rich and nylon 6-rich. The domains of D20 copolymers form well-defined periodic structures at least on a local scale and the crystalline domains may be connected by tie molecules of hard segments as described in Figure 9(b). The D40 copolymers with the longest hard and soft block

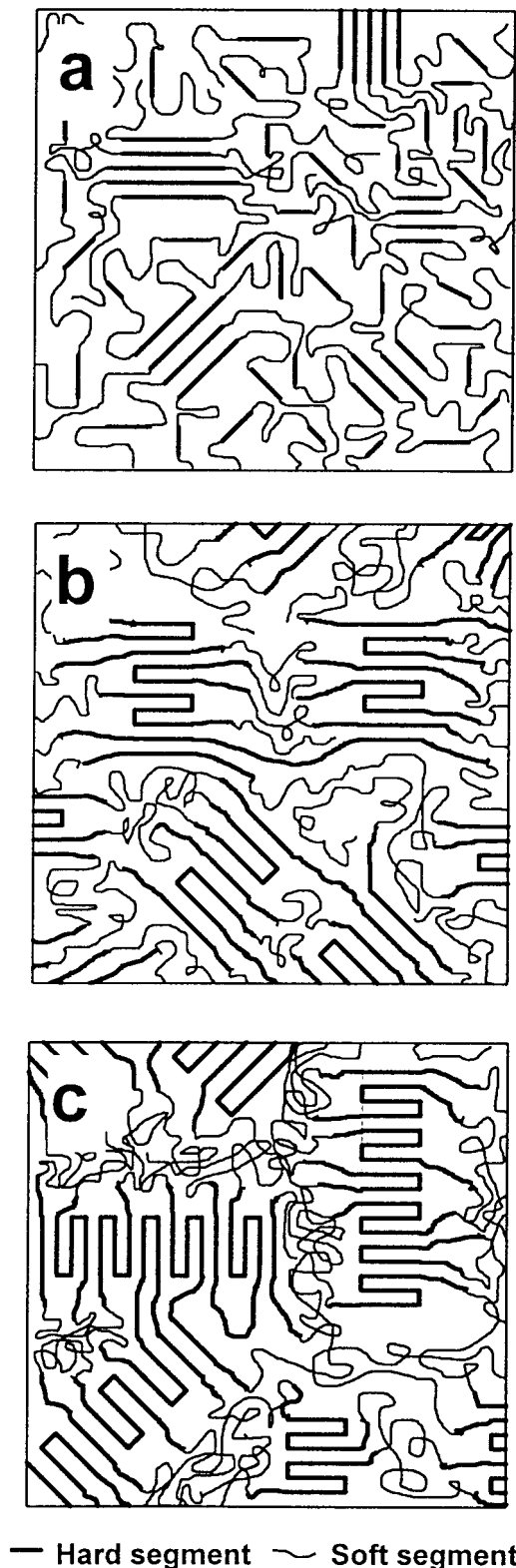


Figure 9 Schematic microstructure for nylon 6-POP block copolymers: (a) D4; (b) D20; (c) D40.

lengths exhibit pronounced chain-folding structures in the hard domain which have a longer dimension in the direction perpendicular to the chain alignment. The interconnectivity of the hard domain and the continuity of the soft domain are enhanced as compared with those of D20 copolymers. From the analysis of the correlation function, each phase is irregularly distributed and its local periodicity is very weak [see Fig. 9(c)].

CONCLUSIONS

The SAXS study gives various important information about the microstructure of the segmented block copolyetheramides based on nylon 6 and POP. The interdomain spacings between two lamellae determined from the analysis of the one-dimensional correlation function range from 6 to 12 nm, and their dependence on the block composition indicates the crystal formation of a chain-folding mechanism. The thickness of linear diffuse phase boundary calculated by the method of Koberstein lies in the range of 2.6 to 4.3 nm. The dependence of interfacial thickness on the copolymer composition seems to be related to the chain mobility and the lamellar thickness. Especially, the amorphous hard domain between the crystalline hard domain and the amorphous soft domain influences the interfacial thickness in three-phase systems of D20 and D40 copolymers.

REFERENCES

1. Z. Ophir and G. L. Wilkes, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1469 (1980).
2. S. Abouzahr, G. L. Wilkes, and Z. Ophir, *Polymer*, **23**, 1077 (1982).
3. J. T. Koberstein and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1439 (1983).
4. L. M. Leung and J. T. Koberstein, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 1883 (1985).
5. B. Chu, T. Gao, Y. Li, J. Wang, C. R. Desper, and C. A. Byrene, *Macromolecules*, **25**, 5724 (1992).
6. J. T. Koberstein, A. F. Galambos, and L. M. Leung, *Macromolecules*, **25**, 6159 (1992).
7. Y. Li, Z. Rem, M. Zhao, H. Yang, and B. Chu, *Macromolecules*, **26**, 612 (1993).
8. E. J. Roche, Ph.D. dissertation, University of Massachusetts, 1979.
9. G. Porod, in *Small Angle X-ray Scattering*, O. Glatter and O. Kratky, eds., Academic Press, Inc., London, 1982, p. 17.

10. L. E. Alexander, in *X-ray Diffraction Method in Polymer Science*, Wiley-Interscience, New York, 1969, p. 280.
11. R. J. Roe, M. Fishkis, and J. C. Chang, *Macromolecules*, **14**, 1091 (1981).
12. D. Tyagi, J. E. Mcgrath, and G. L. Wilkes, *Polym. Eng. Sci.*, **26**, 1371 (1986).
13. J. W. C. van Borgart, P. E. Gibson, and S. L. Cooper, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 65 (1983).
14. P. E. Gibson, J. W. C. van Borgart, and S. L. Cooper, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 885 (1986).
15. Y. Li, T. Gao, J. Liu, K. Linbu, C. R. Desper, and B. Chu, *Macromolecules*, **25**, 7365 (1992).
16. Y. C. Yu and W. H. Jo, *J. Appl. Polym. Sci.*, **54**, 585 (1994).
17. Y. C. Yu and W. H. Jo, *J. Appl. Polym. Sci.*, **56**, 895 (1995).
18. E. Sorta and A. Melis, *Polymer*, **19**, 1153 (1978).
19. J. T. Koberstein and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 2181 (1983).
20. C. G. Vonk, *J. Appl. Cryst.*, **6**, 81 (1973).
21. Y. C. Yu, Ph.D. dissertation, Seoul National University, 1994.
22. C. G. Vonk, G. Kotleve, and A. Dijkstra, *Kolloid Z. Z. Polym.*, **210**, 121 (1966).
23. C. G. Vonk and G. Kotleve, *Kolloid Z. Z. Polym.*, **220**, 19 (1967).
24. C. G. Vonk, *J. Appl. Cryst.*, **8**, 340 (1975).
25. P. Debye and A. M. Bueche, *J. Appl. Phys.*, **20**, 518 (1949).
26. J. T. Koberstein, B. Morra, and R. S. Stein, *J. Appl. Cryst.*, **13**, 34 (1980).
27. A. Todo, J. Hashimoto, and H. Kawai, *J. Appl. Cryst.*, **11**, 558 (1978).
28. R. Bonart and E. H. Muller, *J. Macromol. Sci., Phys.*, **B10**, 345 (1974).