

Blends of Polypropylene with Poly(*cis*-butadiene) Rubber.

II. Small-Angle X-ray Scattering Studies of the Phase Structure of Immiscible Blends of Polypropylene with Poly(*cis*-butadiene) Rubber

GUI-QIU MA,¹ XU-BO YUAN,¹ JING SHENG,¹ DONG-CAI BIAN²

¹ School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

² Department of Materials, The Tianjin Institute of Textile Science and Technology, Tianjin 300160, People's Republic of China

Received 29 August 2000; accepted 16 April 2001

ABSTRACT: Pressed films of the blends of polypropylene (PP) with poly(*cis*-butadiene) rubber (PcBR) were studied by IR spectra, small-angle X-ray scattering, and scanning electron microscopy. The problem of the interaction between different macromolecules in the blends of PP/PcBR is discussed by melt-mixing at a temperature of 210°C using IR. X-ray scattering from the relation of the phase was analyzed using Porod's law, and the interface layer thickness was calculated. The immiscibility of the blends of PP/PcBR was proved. The structure parameters, the correlation distance a_c , average chord lengths \bar{l} , and radius of gyration \bar{R}_g were obtained by the Debye–Buech statistical theory of scattering. Porod's index was calculated and the shape of the dispersed phase is discussed in relation to Porod's index in the blends. The morphology and structure of the blends were investigated by scanning electron microscopy. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2088–2094, 2002

Key words: poly(propylene) blends; polybutadiene rubber blends; SAXS of polymer

INTRODUCTION

In the preceding paper,¹ the phase structure and morphology of binary blends of isotactic polypropylene (PP)/poly(*cis*-butadiene)rubber-*g*-ethyl acrylate (PcBR-*g*-EA) were studied by small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM), and IR spectra. The semimiscibility of PP with PcBR-*g*-EA was proved by SAXS, and an interface layer exists between two phases

in the blends of PP/PcBR-*g*-EA. This suggests that a dilute dispersed PcBR-*g*-EA or PP in the blends is molecularly distributed. The aggregates increase in size with an increasing concentration of PcBR-*g*-EA or PP.

PP and PcBR are nonpolar, but the macromolecule of PP and PcBR is immiscible. The mixing of immiscible polymers is an excellent way for developing new materials with improved properties. The properties of such mixtures depend on the properties of the ingredients, the blend morphology (spatial distribution of the two polymer phases), the interface characteristics, and the composition. Controlling the morphology during processing of the blend is the key to obtaining a product with improved specific properties such as impact strength^{2,3} or permeability.⁴

Correspondence to: J. Sheng.

Contract grant sponsor: National Natural Foundation of China; contract grant number: 59733070.

Journal of Applied Polymer Science, Vol. 83, 2088–2094 (2002)
© 2002 John Wiley & Sons, Inc.
DOI 10.1002/app.10162

Most of the widely used thermoplastic materials show marked limitation in their use when toughness and high impact resistance are required.⁵ These limitations may be overcome by melting and mixing these materials with a rubber polymer. But if two phases in thermoplastic/rubber (or thermoplastic) blends are immiscible, the thermoplastic cannot be modified. However, before we investigate the miscibility of the blends, study on the phase behavior and the relation between macromolecules in immiscible blends of a polymer/polymer is important.

In this article, the phase structure and morphology of PP/PcBR blends are discussed. SAXS and IR spectra were used to study the relation of the phases in the PP/PcBR blends. The morphology of the blends was observed by SEM.

EXPERIMENTAL

Materials

Polybutadiene rubber (high *cis*-1,4 content; Mooney viscosity 46) and PP [melt index (MI) = 8] from the Beijing Yanshan Petrochemical Co. (Beijing, China) were used.

Preparation of Blends

Binary PP/PcBR was prepared by melt-mixing the polymer in a mixing apparatus (XXS-30 mixer, China) at a temperature of 210°C with a residence time of 10 min at 30 rpm. The compositions of the binary blends (PP/PcBR) proposed were 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90 (wt/wt) and 90.23/9.77, 80.21/19.79, 70.2/29.8, 60.18/39.8, 50.13/49.87, 40.11/59.89, 30.08/69.92, 20.05/79.95, and 10.03/89.97 (v/v).

Specimen Preparation

The premixed material was compression-molded to obtain a slab of 1-mm thickness and a film of 20 μm at 230°C with a residence time of 5 min in a common heated press at 24.5 MPa. The slab was quickly moved to a cool press with a residence time of 4 min at room temperature and at 24.5 MPa. A slab, 1 mm thick, was cut by a cutter from a 2 \times 4-mm specimen on which SAXS tests were performed. The same slab was broken in liquid nitrogen on which SEM tests were executed. A 20- μm -thick film was used in the IR spectra tests.

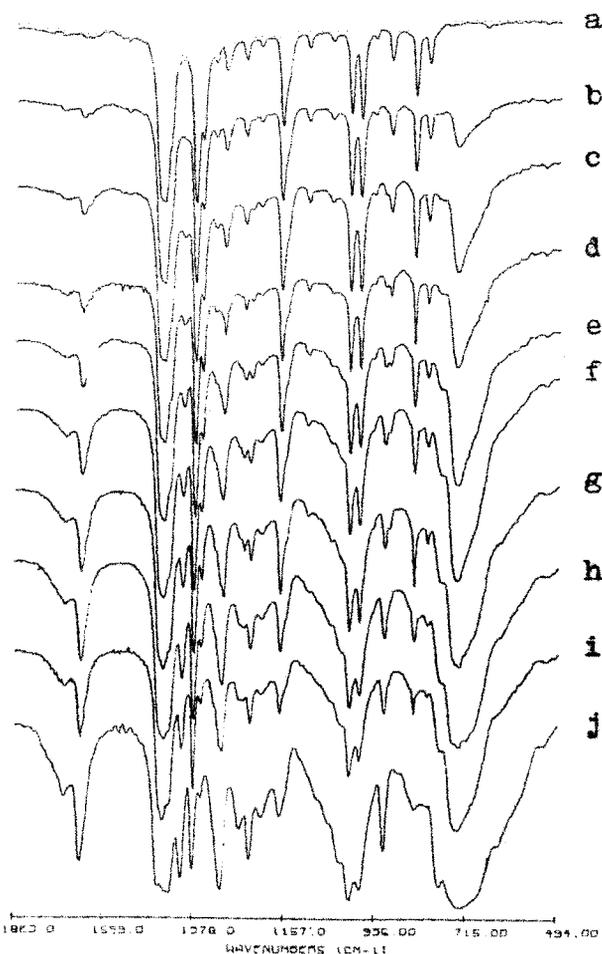


Figure 1 IR spectra of PP and PP/PcBR blends: (a) PP; (b) PP/PcBR(10); (c) PP/PcBR(20); (d) PP/PcBR(30); (e) PP/PcBR(40); (f) PP/PcBR(50); (g) PP/PcBR(60); (h) PP/PcBR(70); (i) PP/PcBR(80); (j) PP/PcBR(90).

Characterization

The IR spectra of PcBR, PP, and PP/PcBR blends was measured by a Nicolet-5DX IR spectrometer. The SAXS data were obtained on a Rigaku D/max-rA. The morphology of the fracture surface of the blends was observed on a Hitachi X-650 scanning electron microscope.

RESULTS AND DISCUSSION

IR Spectrum Studies

Figure 1 show the IR spectra for a series of blends of PS/PcBR. There are absorption bands at 1304, 1167, 998, and 841 cm^{-1} , with a crystalline phase of PP. Clearly, vibration peaks at 1167, 998, and 841 cm^{-1} exist in the blends (see Fig. 1), as the crystalline phase of PP is not affected by PcBR.

The IR spectra show an overlapping of pure PP and PcBR in Figure 1. The characteristic spectra of PP (or PcBR) are not moved, and new spectra did not appear. Clearly, the affinity between different macromolecules is not existent. This blend of PP/PcBR is an immiscible system.

SEM Studies

The overall morphology of blends of PP/PcBR was investigated on the fractured surface of specimens broken in liquid nitrogen. The fractured surface of the samples is etched by cyclohexane. Hereby, the rubber phase was etched on as a black area. SEM images of cryogenically fractured surfaces of the PP/PcBR blends are shown in Figure 2. As can be seen, the blend exhibits a holelike morphology uniformly distributed throughout the whole sample before 60/40 (PP/PcBR). The phase-inversion region is from a composition of 40/60/(PP/PcBR) to 60/40 (see Fig. 2). The rubber is the dispersed phase before the ratio of 40/60(PP/PcBR), and after 30/70, PP is the dispersed phase and the rubber phase is etched. In the phase-inversion region, a double continuous phase is formed in the blend of PP/PcBR. The diameter of the dispersed phase that varies with the content of PcBR in the blends was calculated by a graph technique and Table I shows these results. The relation of the average diameter \bar{D} of the dispersed phase with the PP concentration is shown in Figure 3. The value of \bar{D} is approximate in the phase-inversion region because it is difficult to calculate the size of the dispersed phase by a graph.

SAXS Studies

The relationship between the two phases in the blends may be characterized by the SAXS intensity. According to Porod's law,^{6,7} the intensity in the tail of a diffraction curve from a two-phase structure with sharp phase boundaries is given by

$$\lim_{s \rightarrow \infty} I(s) = C/s^4 \quad (1)$$

where $I(s)$ is the intensity of scattering and $s = 2 \sin \theta$. It is assumed that the interface layer (compatible domain) exists. Porod's law is given by

$$I(s) \cong \frac{C}{s^4} (1 - 4\pi^2\sigma_b s^2) \quad (2)$$

where σ_b is the interface layer thickness between the two phases of the blends. In a four-slit system, eq. (2) may be approximated by

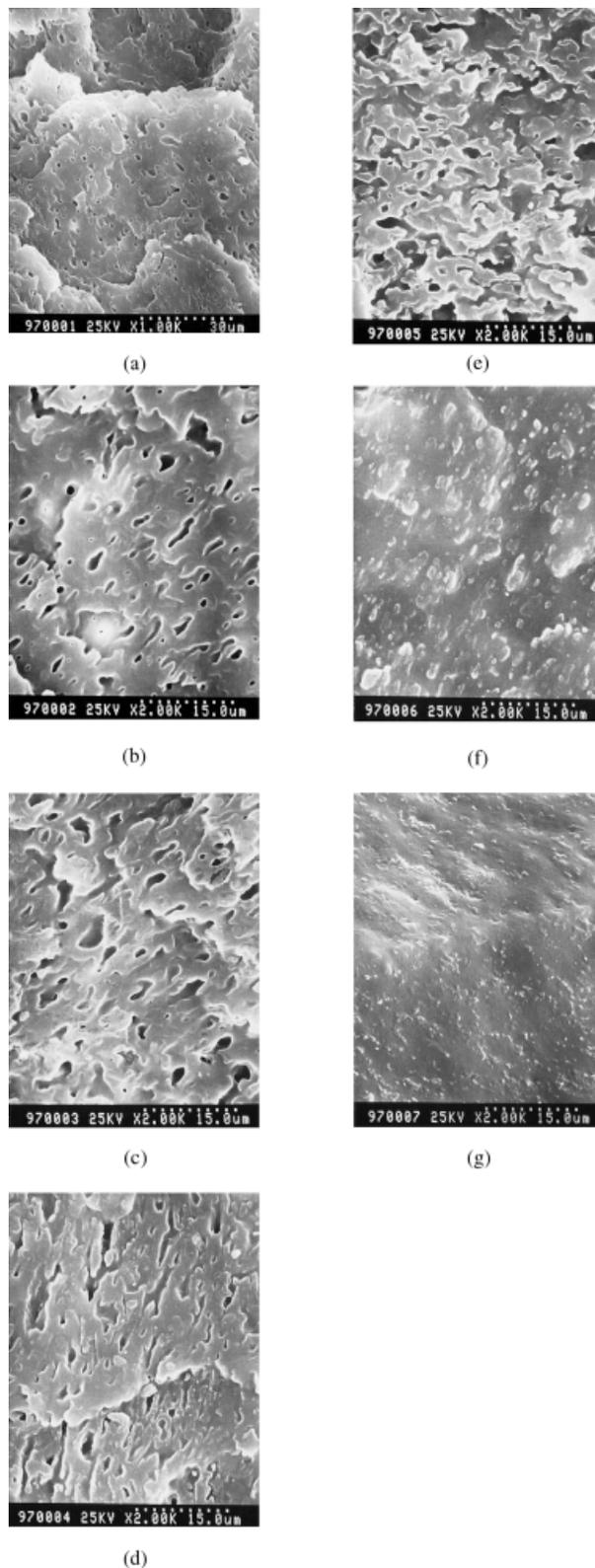


Figure 2 SEM micrographs of PP/PcBR blends: (a) PP/PcBR(20%); (b) PP/PcBR(30%); (c) PP/PcBR(40%); (d) PP/PcBR(50%); (e) PP/PcBR(60%); (f) PP/PcBR(70%); (g) PP/PcBR(80%).

Table I Relation of Size of Dispersed Phase with Compositions in the Blend

Measurement	Composition (wt/wt)					
	20/80	30/70	40/60	50/50	60/40	70/30
\bar{D} (μm)	0.805	1.075	1.299	—	0.571	0.377
\bar{D}_{max} (μm)	3.048	3.513	4.464	—	1.897	1.338
\bar{D}_{min} (μm)	0.183	0.294	0.281	—	0.047	0.033

$$I(s) \cong \frac{K}{s^4} \exp[-38(\sigma_b s)^{1.81}] \quad (3)$$

A plot of $\ln[I(s)s^3]$ versus $s^{1.81}$ is used and the results are shown in Figure 4. The curves remain level with s increasing because a sharp phase boundary existed in the blends of PP/PcBR, so then the σ_b are equal to zero. The blends of PP/PcBR are immiscible.

If the dispersed phase can be regarded as a particle in polymer blends, we can calculate the size of the particle using a correlation function. For this purpose, we used a modification of the Debye–Bueche^{7,8} description of scattering from random heterogeneous media, which gives for spherically symmetrical systems

$$I(h) = K \langle \eta^2 \rangle_{av} \int_0^\infty \gamma(r) \frac{\sinh r}{hr} r^2 dr \quad (4)$$

where K is a proportionality constant and $h = (4\pi/\lambda)\sin \theta$. $\gamma(r)$ is the correlation function. For systems not having a clearly defined structure, $\gamma(r)$ often decreases monotonically with r

and may be represented by an empirical equation such as

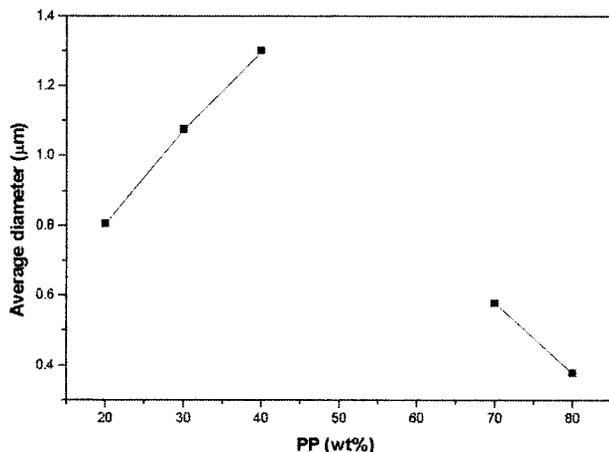
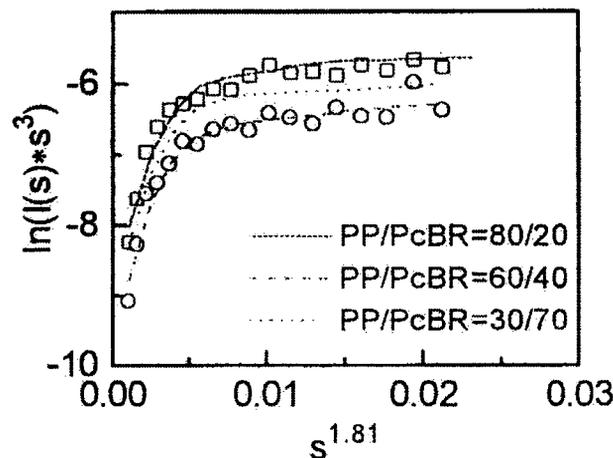
$$\gamma(r) = \exp(-r/a_c) \quad (5)$$

where the parameter a_c is known as a correlation distance and defines the size of the heterogeneity. For dilute discrete particles, a_c is related to the particle size. Thus, for spheres, a_c is $(\frac{4}{3}R$. For more concentrated systems, a_c is not simply related to the size of the structural unit but depends upon both interparticle and intraparticle distances. It may be considered as an average wavelength of $\eta(x)$ fluctuations, whereas $\langle \eta^2 \rangle$ is a mean-square amplitude.

If eq. (5) is substituted into eq. (4), one obtains, upon rearrangement,

$$\frac{1}{[I(h)]^{1/2}} = \frac{1}{(K' a_c^3)^{1/2}} (1 + h^2 a_c^2) \quad (6)$$

Consequently, a plot of $I(h)^{-1/2}$ against h^2 should lead to a straight line having a ratio of the slope to the intercept of a_c^2 . Figure 5 shows that the value of a_c is calculated and relates to the compositions


Figure 3 Mean size of dispersed phase of PP/PcBR.

Figure 4 Plot of $\ln[I(s)s^3]$ versus $s^{1.81}$.

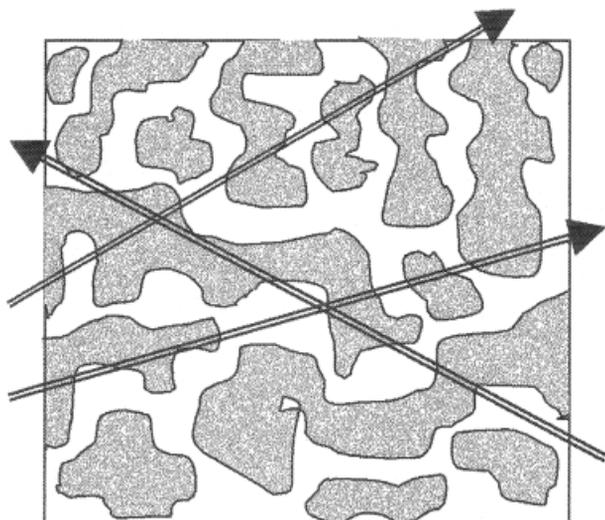


Figure 5 Average chord lengths of a random two-phase system.⁹

of the blends. For the dilute phase [before 70/30(PP/PcBR) and after 30/70], the varied law of a_c is the same as that of \bar{D} . In the phase-inversion region, a_c relates to the size of the two phases in the blends. Also, the value of a_c shows complication of the morphology in the phase-inversion region and the varied law is the same as the variation of \bar{D} . The variation of \bar{R}_g is the same as that of \bar{D} .

An analysis may be made using the approach of Debye et al.⁷ for a random dispersion of two phases of the volume fractions ϕ_1 and ϕ_2 and a definite composition for which the ratio of the interphase surface area S to the volume V related to the correlation distance by

$$S/V = 4\phi_1\phi_2/a_c \quad (7)$$

Porod^{10,11} defined the average chord lengths \bar{l}_1 and \bar{l}_2 , which are illustrated in Figure 6. If lines are randomly drawn, the system is in three dimensions; \bar{l}_1 represents, for example, the mean length of the line segments through the regions of phase 1. These chord lengths are given by

$$\bar{l}_1 = 4\phi_1/(S/V) \quad (8)$$

$$\bar{l}_2 = 4\phi_2/(S/V) \quad (9)$$

from which it follows that

$$\bar{l}_1 = a_c/\phi_2 \quad (10)$$

$$\bar{l}_2 = a_c/\phi_1 \quad (11)$$

The relation of \bar{l}_{PP} and \bar{l}_{PcBR} with compositions of the blends is shown in Figure 7. The value of the variation for \bar{l}_{PcBR} with the PP content decreasing is quickly reduced. Also, the value of the variation for \bar{l}_{PP} with the PP content increasing is slowly increased, and the variation of the value of \bar{l}_{PP} is larger. This result makes clear that the PP phase is a continuous phase at a larger region of compositions in the blends. The value of \bar{l}_{PcBR} for the 20% PcBR blend is of the order 29.71 Å (if the content of PcBR is smaller in the blends, the value of \bar{l}_{PcBR} is less than 29.71 Å), which is about the size of an isolated PcBR molecule, assuming it to be a collapsed sphere. The suggests that a dilute dispersion of PcBR in PP is molecularly

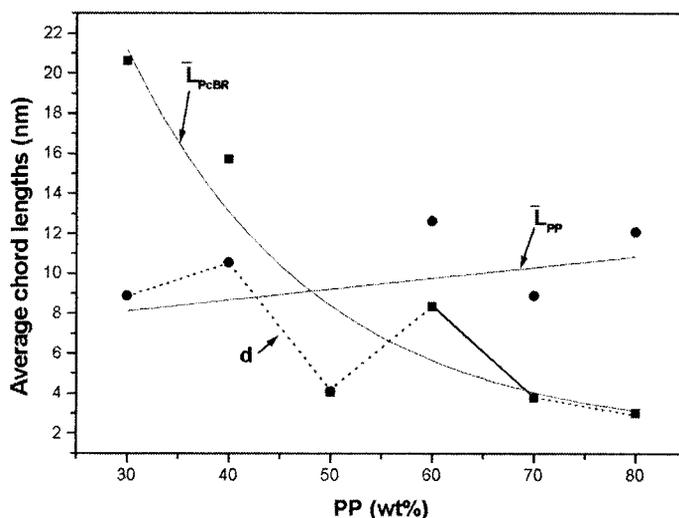


Figure 6 Relation of average chord lengths with composition of blends.

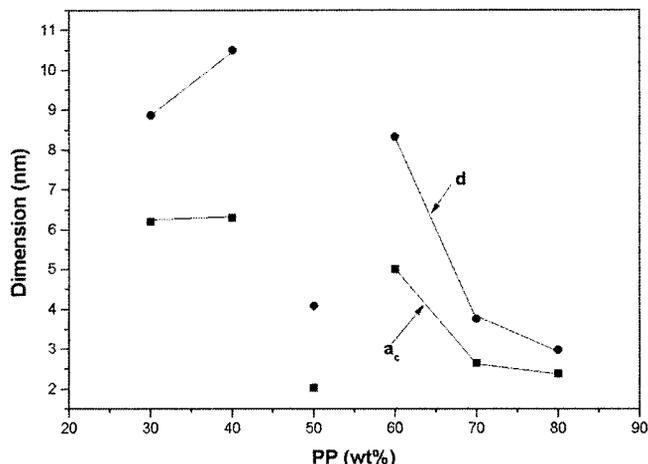


Figure 7 Relation of a_c and average chord lengths (d) of dispersed phase with composition of blends.

distributed. The aggregates increase in size with an increasing concentration of PcBR. Curve (d) shows variation of the dispersed phase in the blends.

If we regard the blend of a polymer as a solid solution, the size of the dispersed phase (domain) in the blend can be expressed using the radius of gyration (\bar{R}_g).^{12a} The \bar{R}_g of the whole particles (dispersed phase) is given by⁷

$$P(\theta) = \frac{I_s(\theta)}{I_s(0)} = 1 - \frac{\bar{R}_g^2}{3} h^2 + \dots \quad (12)$$

A plot of $P(\theta)$ versus h^2 was used, and we obtained a curve. The curve leads to a straight line at very small angles, and the slope of 1 is equal to $(-\bar{R}_g^2/3)$; \bar{R}_g is the radius of gyration. Figure 8

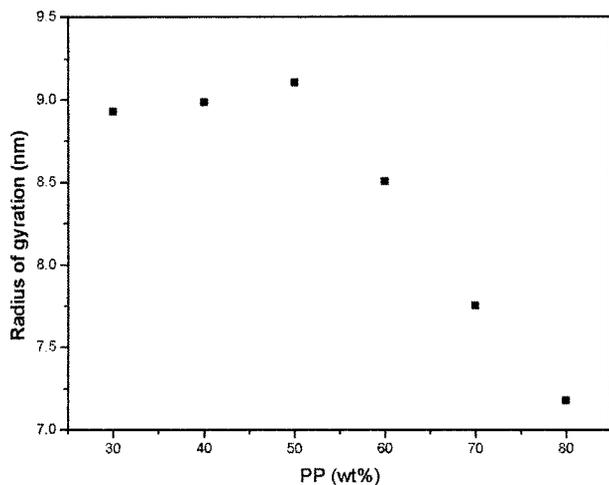


Figure 8 Relation of \bar{R}_g with composition of blends.

represents the relation of the value of \bar{R}_g with compositions of the blends. The varied law of \bar{R}_g is the same as that of \bar{D} . To further characterize the structure of the dispersed phase (particle) in the blends, we analyzed the scattering spectra using Guinier and Fournet^{12b} and the Porod¹³ analyses. We examined the Porod region to evaluate approximately the shape of the dispersed particles. Porod derived that $\ln I(h)$ as a function of $\ln(h)$ should be equal to $-\alpha$ at α large h value. If α is equal to (or approaches) -4 , these particles are spherical in shape and have a smooth surface. When α is equal to -2 , these particles are flat particles. In the case of α equal to -1 , the particles are rodlike in shape. The value of α is shown in Table II. The value of α is near 3 except for the composition of 30/70(PP/PcBR). Clearly, the shape of the dispersed phase is not spherical and flat. One of dispersed phases is random (near ellipselike) and has a definite volume. This result is the same as that of the SEM image.

CONCLUSIONS

The results of SAXS and IR showed that the blends of PP/PcBR are immiscible polymer

Table II Porod's Index α for PP/PcBR Blends

Index	Composition (wt/wt)					
	20/80	30/70	40/60	50/50	60/40	70/30
α	2.825	3.357	2.966	2.253	2.548	2.859

blends. The characteristic spectra of PP (or PcBR) are not moved, and new spectra have not appeared. The affinity between different macromolecules is not existent. This blend of PP/PcBR is an immiscible system.

The SEM images of the PP/PcBR blends show the typical morphology of an immiscible mixture: large, coarse, and irregular domains were found. But the interface was clear. The phase-inversion region is from the composition of 40/60/(PP/PcBR) to 60/40. The rubber was the dispersed phase before the ratio of 40/60(PP/PcBR), and after 30/70, PP is the dispersed phase.

The \bar{R}_g , a_c , and \bar{l} of the dispersed phase in the blends was calculated by SAXS. The varied law of \bar{R}_g and \bar{l} was the same as that of \bar{D} . The variation of a_c shows the complexity of the morphology in the blends.

The shape of the dispersed phase was shown by Porod's index α , and α was near 3. Therefore, the shape of the dispersed phase is not spherical and flat. One of dispersed phases is random (near ellipselike) and has a definite volume.

REFERENCES

1. Sheng, J.; Qi, L.-Y.; Yuan, X.-B.; Shen, N.-X.; Bian, D.-C. *J Appl Polym Sci* 1997, 64, 2265.
2. Yoshida, M.; Ma, J. J.; Min, K.; White, J. L.; Quirk, R. P. *Polym Eng Sci* 1990, 30, 30.
3. Shung, T. S. *Plast Eng* 1987, Oct., 39.
4. Kamal, M. R.; Garmabli, H.; Hozhabr, S.; Arghyris, L. *Polym Eng Sci* 1995, 35, 41.
5. Morero, D.; Santambrogio, A.; Porri, L.; Ciampelli, F. *Chim Ind (Milano) A* 1959, 1, 758.
6. Porod, G. *Z Z Koll Polym* 1952, 125, 51–57, 108–122.
7. Debye, P., Jr.; Anderson, H. R.; Brumberger, H. *J Appl Phys* 1957, 28, 679–683.
8. Debye, P.; Bueche, A. *J Appl Phys* 1944, 20, 518.
9. Khambatta, F. B.; Warner, F.; Russell, T.; Stein, R. S. *J Polym Sci Polym Phys Ed* 1976, 14, 1391.
10. Kratky, O. *Pure Appl Chem* 1966, 12, 483.
11. Stern, F. *Trans Faraday Soc* 1955, 51, 430.
12. Guinier, A.; Fournet, G. *Small Angle Scattering of X-rays*; Wiley: New York; Chapman and Hall: London, 1955; (a) p 104, (b) p 340.
13. Porod, G. In *Small Angle X-ray Scattering*; Glatter, O.; Kratky, O., Eds.; Academic: New York, 1982, p 34.