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Development of Multiphase Morphology in Poly(*cross*-butadiene)-*inter*-Poly(*cross*-styrene) Interpenetrating Polymer Networks

J. H. An, A. M. Fernandez, and L. H. Sperling*

Polymer Science and Engineering Program, Department of Chemical Engineering, Materials Research Center No. 32, Lehigh University, Bethlehem, Pennsylvania 18015.

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ABSTRACT: Domain formation processes in poly(*cross*-butadiene)-*inter*-poly(*cross*-styrene) interpenetrating polymer networks (IPN's) were investigated by small-angle neutron scattering (SANS) and transmission electron microscopy techniques. Partly polymerized IPN's were formed by reacting deuteriated styrene in swollen polybutadiene networks, terminating the reaction, and evaporating the remaining monomer. The polystyrene phase domain transverse length was found to be nearly constant, at several hundred angstroms, independent of the extent of reaction. Specific interfacial surface areas increased from 25 to 150 m^2/g and then slightly decreased as polymerization of the polystyrene was allowed to progress. The present data support the interconnected cylinder model of IPN's.

Introduction

An interpenetrating polymer network (IPN) may be defined as a combination of two polymers in network form, at least one of which is synthesized or cross-linked in the immediate presence of the other.[1] This class of multicomponent polymer is closely related to polymer blends, grafts, and blocks. Most such multicomponent materials phase separate. Early studies focused on understanding the morphological features of IPN's, such as domain size and the shape, as well as developing new synthetic methods.

Transmission electron microscopy combined with dynamic mechanical spectroscopy has been used to investigate the morphology of IPN's,[2,3] and theoretically derived equations were developed to predict domain size as a function of composition.[4] However, the kinetics of domain formation processes remain far from complete. Problems include the complex morphology of IPN's as well as limitations on experimental techniques. Recently, small-angle techniques such as small-angle X-ray scattering (SAXS)[5] and small-angle neutron scattering (SANS)[6,7] have been applied to the study of the morphological features of phase-separated block copolymers and IPN's. The IPN interfacial areas were estimated by SAXS[5] and SANS[6] to be in the range of 50–150 m^2/g, depending on composition.

In this study, the domain formation process in IPN's composed of polybutadiene (PB) and polystyrene (PS) will be investigated. The second phase, PS, is synthesized from deuteriated monomer to permit contrast necessary for SANS experiments. The content of PS was varied from 4% to 80% to investigate IPN morphological development during polymer II synthesis.

Theory

The SANS scattering theory can be summarized[6] as follows. For a two-phase system where one phase is completely deuteriated, the scattering intensity, described by the differential scattering cross section $d\Sigma/d\Omega$ per unit volume is given by the following equation in terms of the correlation function, $\gamma(r)$, at a characteristic distance r between scattering centers:

$$\frac{d\Sigma}{d\Omega}(K) = 4\pi\langle\eta^2\rangle_{av}\int_0^\infty \gamma(r) r^2 \frac{\sin(Kr)}{Kr}\,dr \qquad (1)$$

The quantity $\langle\eta\rangle_{av}$ is the mean square deviation of the neutron scattering length over all points, and $K = 4\pi\lambda^{-1}\sin(\theta/2)$, where λ is the wavelength and θ is the scattering angle. The quantity $d\Sigma/d\Omega$ represents the number of neutrons scattered per second into a solid angle Ω divided by the incident neutron flux. The quantity $d\Sigma/d\Omega$ is the equivalent of Rayleigh's ratio, used in light scattering.

For the simplest case, the correlation function can be given by an exponential form as proposed by Debye and co-workers:[8,9]

$$\gamma(r) = \exp(-r/a) \qquad (2)$$

where the quantity a represents the correlation distance defining the size of heterogeneities. It is often approprate to express the data by a summation of short- and long-range terms represented by an exponential and Gaussian terms[9–11]

$$\gamma(r) = f\exp(-r/a_1) + (1-f)\exp(-r^2/a_2^2) \qquad (3)$$

where the fractional factor, f, weighs the contribution of the exponential short-range term. The quantity f was determined by using eq 40 in ref 9 and the indicated plotting procedure.

The Gaussian term of eq 3 is postulated to work for the random cylindrical structures thought to exist in the present system. Equation 3, perfectly general for systems exhibiting two slopes,[9] was successfully applied to the case of well-defined spheres by Moritani et al.,[10] for example.

The specific interfacial surface area, S_{sp}, defined as the ratio of interfacial surface area, A, to the volume, V, is given by[9,10]

$$S_{sp} = \frac{A}{V} = -4\phi_p(1-\phi_p)\gamma'(0) = \frac{4\phi_p(1-\phi_p)}{a_1}f \qquad (4)$$

where ϕ_p represents the volume fraction of the polystyrene phase. In the present paper, it was convenient to convert S_{sp} to m^2/g, using the known density of the system.

The transverse lengths across the domains, the average dimension obtained from straight lines drawn through the whole sample, are given by[14]

$$l_1 = a_1/(\phi_2 f) \qquad (5a)$$

$$l_2 = a_1/(\phi_1 f) \qquad (5b)$$

Experimental Section

All IPN's were synthesized sequentially with poly(*cross*-butadiene) as the elastomeric phase and poly(*cross*-styrene) as the plastic phase.[3,6] Linear PB (Diene 35 NFA/AC, Firestone Synthetic Rubber and Latex) was purified by precipitation with methanol from tetrahydrofuran (THF). The purified PB was

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Table I
Phase Dimensions of Photopolymerized Poly(*cross*-butadiene)-*inter*-poly(*cross*-styrene) IPN's

sample ID	PS content (vol %) ϕ_p	correlation length,[a] Å			specific interfacial area S_{sp}, m²/g	transverse length,[b] Å	
		a_1	a_2	f		l_B	l_S
1	4.9	70.4	415.8	0.96	25.3	1500	77.3
2	6.8	71.6	615.7	0.93	33.0	1130	82.3
3	8.6	73.5	531.2	0.91	39.0	936	88.1
4	16.8	87.4	523.2	0.93	59.3	561	113
5	29.1	84.4	480.9	0.94	92.0	308	126
6	46	63	487.8	0.97	153	141	120
7	56.7	63.8	429.5	0.99	152	114	149
8	79.4	81.2	513.6	0.95	76.5	108	415

[a] a_1 = intraparticular short-range correlation length; a_2 = interparticular long-range correlation length. [b] l_B = transverse length of polybutadiene phase; l_S = transverse length of polystyrene phase.

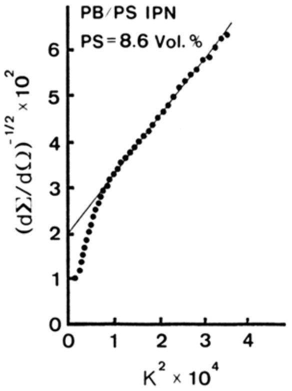

Figure 1. Debye scattering pattern showing two straight-line portions and the line used to calculate a_1.

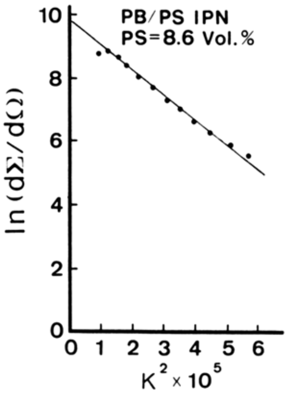

Figure 2. Small-angle excess intensity from Figure 1 replotted to determine a_2.

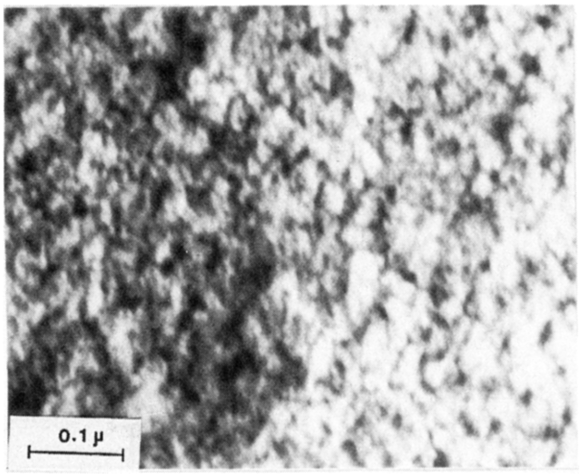

Figure 3. Electron micrograph of fully polymerized PB/PS IPN with PB phase stained dark with OsO_4.

dried and redissolved in THF and mixed with an appropriate amount of cross-linker (dicumyl peroxide, 0.2 wt %). After the solvent was evaporated, the PB network was cured in a compression mold and postcured in a nitrogen-filled oven to form a network. The unreacted linear PB was removed by toluene extraction.

The second phase, PS, was formed by swelling deuteriated styrene into the cross-linked PB and partially reacting the deuteriated styrene. The styrene monomer solution was prepared by mixing monomer with cross-linker (divinylbenzene, 1 mol %) and photoinitiator (benzoin, 0.3 g/100 mL of solution). A known weight of poly(*cross*-butadiene) was swollen in the monomer mixture up to the equilibrium point. Next the fully swollen network was placed in a UV chamber and allowed to react for a period of time. The partially reacted samples were vacuum-dried to remove the remaining monomer and weighed to determine the final composition.

All samples were characterized with the 30-m SANS spectrometer at the HFIR reactor in Oak Ridge National Laboratory. This instrument utilizes thermal neutrons of 4.75-Å wavelength. A sample-to-detector distance of 18.94 m was used. SANS measurements were performed on samples 1–2 mm thick, as well as on appropriate blanks made from fully protonated counterpart IPN's. The latter were used to subtract incoherent scattering from the data of the samples of interest. In all cases, the data were azimuthally averaged in both the sample and the blank before the above-mentioned subtraction was made. No correction for multiple scattering was deemed necessary.[12,13]

Results

Figure 1 shows a typical Debye plot[9] displayed in terms of $(d\Sigma/d\Omega)^{-1/2}$ vs. K^2. Two straight-line portions are observed. A straight line was drawn through the wide-angle portion, and the short-range correlation distance, a_1, was determined from eq 3. The excess intensity between the line determining a_1 and the lower angle slope was determined by obtaining the difference between the line used to calculate a_1 and the line characterizing the lower angle slope. This difference was replotted in the Guinier fashion as $\ln (d\Sigma/d\Omega)$ vs. K^2, (Figure 2). This second plot yields the correlation distance, a_2. The several phase dimensions determined from a_1 and a_2 are listed in Table I.

The transverse length, l_S, determined from a_1, increases slowly up to 55% polystyrene and then increases somewhat faster.

The most interesting quantity is S_{sp}, which appears to go through a slight maximum. Perhaps this suggests a reorganization of the phase domain structure. It must be pointed out that S_{sp} is independent of any morphological model.

Transmission electron microscopy was carried out on osmium tetraoxide stained, ultramicrotomed samples. While it was difficult to get good results on the rubber-rich samples, an electron micrograph of the fully polymerized

Table II
Phase Dimensions of Thermally Polymerized Poly(*cross*-butadiene)-*inter*-poly(*cross*-styrene) IPN's

sample ID	PS content (vol %) ϕ_p	correlation length,[a] Å			specific interfacial area S_{sp}, m²/g	transverse length,[b] Å	
		a_1	a_2	f		l_B	l_S
1	7	57.2	417.3	0.97	44.1	841	60.7
2	14.2	62.8	560.1	0.92	71.5	480	79.5
3	46.8	56.8	556.4	0.99	128.4	121	106
4	81.8	77.4	649.8	0.99	76.9	94.8	429

[a] a_1 = intraparticular short-range correlation length; a_2 = interparticular long-range correlation length. [b] l_B = transverse length of polybutadiene phase; l_S = transverse length of polystyrene phase.

material is shown in Figure 3. The photo supports the interconnected cylindrical model.[6]

The above results were based on a photopolymerization method. Preliminary data on thermally polymerized samples (Table II) yielded substantially the same overall findings. However, the experimental data do differ in detail. Most importantly, the elbow between the two straight-line portions occurs at a lower angle. This makes the small-angle data, represented by a_2, less reliable.

Discussion

As seen in Table I, a_2 is much larger than a_1 for each sample. Both remain virtually constant, independent of composition. The calculated transverse lengths of the PS domains, l_S, increase slowly from about 70 to 400 Å as the PS content is increased. This is a consequence of the increasing polystyrene content (eq 5). Most of the increase is at the very end of the polymerizations. The notion of the development of lengthening cylinders with continued polymerization is supported by these data.

The specific interfacial surface area of the final compositions is on the order of 100 m²/g, common for true colloid systems.[5,9] However, the quantity S_{sp} does not increase monotonously, reaching a maximum at around 50% PS and then decreasing. This might reflect the onset of dual phase continuity in the system.

SANS experiments provide valuable new information such as interfacial area. However, it is difficult to draw a detailed picture of domain morphology from SANS alone because it provides only a statistical description of the heterogeneities. On the other hand, the absence of such requirements makes the Debye model work best. Together with other methods such as TEM, however, SANS provides a powerful new method of analysis.

Even though the presence of two different correlation functions is suggested, the physical meaning of each is still unknown. The following models are not excluded by the current data:

1. The quantity a_1 measures the *intra*particle distance, and the quantity a_2 measures the *inter*particle distance. If the growth of irregular cylinders is assumed, both a_1 and a_2 might be nearly constant, as observed.

2. Taking into consideration that a fine structure of the order of 100 Å and larger domains of the order of 1000 Å have been observed by electron microscopy for poly(*cross*-butadiene)-*inter*-poly(*cross*-styrene),[15] the quantities a_1 and a_2 might represent the fine structure and larger domains, respectively.

3. It is possible that cocontinuous phases of the Gergen type[16,17] are being formed. These phase structures exhibit both concave and convex surfaces, with one phase, usually the one primarily convex, forming a "skeletal" phase. If the polystyrene phase is assumed to be the "skeletal" phase, then its dimensions are best represented by a_1. The "matrix" dimensions are then represented by a_2.

It is possible that some combination of the above, in a yet unidentified manner, will be closer to the truth.

Conclusions

This study indicates that the SANS technique is applicable to the analysis of IPN morphology in spite of the ambiguity in the physical meaning of the correlation functions. The specific interfacial surface area, which is clearly important for good mechanical behavior such as impact strength and toughness, cannot be obtained by classical techniques.

The polystyrene phase dimensions do not show significant change up to midrange compositions. The increase in S_{sp} is due to the increased amount of polystyrene. However, major changes were observed in the final stages of reaction, 60–80%. The quantity l_S is almost tripled. The S_{sp} value shows a maximum at around 50% PS composition and then decreases. This might indicate the onset of dual phase continuity in the latter stages of reaction.

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Registry No. (Styrene)(divinylbenzene) (copolymer), 9003-70-7; neutron, 12586-31-1.

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