

Thermoplastic Interpenetrating Polymer Networks Based on a Poly(*Styrene-*b**-Butadiene) Copolymer and an Ionically-Terminated Polybutadiene Ionomer

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SYNOPSIS

Thermoplastic interpenetrating polymer networks (IPN) are mixtures of two physically crosslinked polymers. Thermoplastic IPNs were prepared by blending an SBS triblock elastomer with a 1,2-polybutadiene that was ionically-terminated at both ends. The morphologies of these IPNs were studied using differential scanning calorimetry and dynamic mechanical thermal analysis. It was concluded that the ionomer was incompatible with the SBS elastomer, since the T_g s of both the 1,2-polybutadiene from the ionomer and the essentially 1,4-polybutadiene from the SBS component were observable at temperatures that were close to those of the individual components. The addition of the polybutadiene material had, however, an influence on the relaxation processes of the polystyrene blocks. The polystyrene glass transition in the pure SBS copolymer is broadened by the interfacial region between polystyrene and polybutadiene. The low temperature shoulder was much more pronounced when the ion-terminated polybutadiene was present, indicating it has a preference to be located in these interfacial regions. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

An interpenetrating polymer network (IPN) is defined as a combination of two polymers in network form, at least one of which has been synthesized and/or crosslinked in the immediate presence of the other.¹⁻⁷ The IPN component networks may be synthesized sequentially or simultaneously. Since both polymers are covalently crosslinked at the end of the reaction sequence, these IPNs are thermosets.

Three classes of polymer are recognized as having noncovalent or physical crosslinks: multiblock copolymers, which phase separate, semicrystalline polymers, and polymers possessing ionic charges. In

all cases, such materials have segregated regions of the polymer chains, which impart physical crosslink properties to the polymer. Combinations of two such physically crosslinked polymers, especially where both polymers have some degree of dual-phase continuity, belong in a relatively new class of interpenetrating polymer networks, designated as thermoplastic IPNs.⁸⁻¹⁸ Thus, thermoplastic IPNs are hybrid polymer materials possessing physical crosslinking capabilities and frequently possessing the interpenetration of phases. These materials flow at elevated temperatures, yet behave as thermosets at use temperature.

These three modes of network formation allow a vast number of potential thermoplastic IPNs to be identified. This investigation concentrates on thermoplastic IPN systems that are based on a poly(*styrene-*b**-butadiene) triblock copolymer (SBS) and a polybutadiene that is terminated at both ends by ionic groups (it-PB). The morphology and dynamic mechanical behavior of this blend system is discussed.

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Table I Characterization Data for the SBS Copolymer

Method of Analysis		Data	
GPC	M_n 86,000	Polydispersity 1.28	
Membrane osmometry	M_n 101,000		
$^1\text{H-NMR}$ spectroscopy	PS	1,4-PB	1,2-PB
	19 mol %	75 mol %	6 mol %

EXPERIMENTAL

Materials

*Poly(Styrene-*b*-Butadiene) Triblock Copolymer*

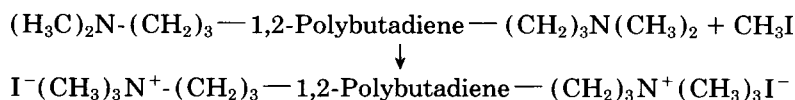
The contamination of commercial grades of SBS with SB diblock, and with possibly homopolymer, is undesirable, in that neither the diblock nor the homopolymer contribute to the network. Consequently, the SBS sample used in this study was synthesized¹⁹ by sequential anionic polymerization. The final product was virtually free (< 0.5%, as indicated by gel permeation chromatography) of homopolymer and diblock contamination. The polymer had a polystyrene content of 19 mol %. The terminal polystyrene blocks had molecular weights of 16,200 and the midblock had a molecular weight of 73,800.

Double-Ended Methyl Iodide Quaternized Amino Polybutadiene

The ionically-terminated 1,2-polybutadiene (it-PB) was synthesized²⁰ by anionic polymerization. Two-hundred mL of tetrahydrofuran (THF) was placed in a 500 mL, 3-necked, round-bottom flask, equipped with a serum cap, nitrogen inlet/outlet, and a mag-

netic stirrer. Dry nitrogen was bubbled through the solvent, which was cooled to -78°C before 73 mL (1.0 mole) butadiene was distilled into the system. The solution was allowed to warm to 0°C and 30 mL of a 0.66 M solution of lithium naphthalene in THF²¹ was introduced by injection in order to initiate polymerization. Polymerization was allowed to proceed to completion over a 90 min period at this temperature. Up to 50% molar excess of the previously prepared α,ω -alkylene-chloroamine was then added neat to terminate the living polybutadiene solution. The resulting difunctionally-terminated polymer was precipitated from excess methanol, was dried, and was stored under vacuum at room temperature.

Quaternization (see below) was performed by placing 30 g of the amine-terminated 1,2-polybutadiene in a 100 mL round-bottom flask, and to this was added 100 mL of methylene chloride and a 20-fold molar excess of the quaternizing agent, methyl iodide. The mixture was then left to react in the dark at ambient for a minimum of 72 h. The solvent and excess quaternizing agent were removed by vacuum distillation, and the residual polymer was then vacuum dried for 48 h to remove trace contaminants. It was finally stored at -20°C until required.



QUATERNIZATION PATHWAY

Table II Characterization Data for the it-PB Polymer

Method of Analysis	Data	
Vapor pressure osmometry	M_n (g/mol)	3700
Dynamic mechanical analysis	T_g ($^\circ\text{C}$)	0
Differential scanning calorimetry	Ionic dissociation transition ($^\circ\text{C}$)	66
$^{13}\text{C-NMR}$ spectroscopy	1,2-PB (mol %)	86
	1,4-PB (mol %)	14

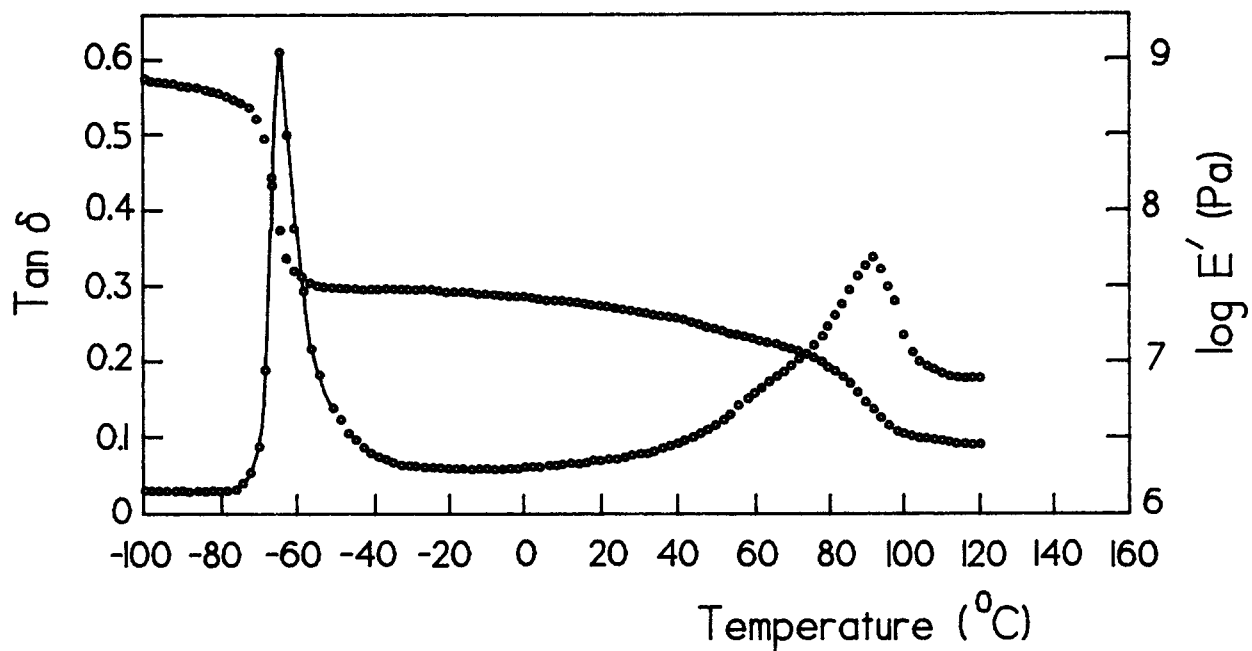


Figure 1 Tan δ and $\log E'$ -temperature plots of the SBS copolymer at 1 Hz.

Characterization

A Waters Associates model 502/401 GPC apparatus was used to obtain the molecular weights and molecular weight distributions of the polymers. The instrument was fitted with a Waters R401 refractive index detector. All the GPC tests were made in tetrahydrofuran with 0.5% solutions (w/v) at a flow rate of 1 mL per min. The data were evaluated using a Waters 730 Data Module, which was calibrated with standard polystyrene samples.

The number-average molecular weight of the low molecular weight it-PB material was determined using a Knauer vapor pressure osmometer (type 11.00) with a Knauer digital meter (type 06.00). Tetrahydrofuran was used at 37°C as the solvent and the apparatus was calibrated with benzil.

The number-average molecular weight of the SBS triblock copolymer was obtained with a Knauer membrane osmometer (type 01.00), using toluene at 37°C as a solvent. Linear plots were obtained of reduced osmotic pressure (π/c) vs. concentration. The number-average molecular weight was then calculated from the intercept using $(\pi/c)_{\lim c \rightarrow 0} = RT/M_n$.

Proton nuclear magnetic resonance spectra ($^1\text{H-NMR}$) and carbon-13 nuclear magnetic resonance spectra ($^{13}\text{C-NMR}$) were used to study the polymer microstructures to determine the extent of the termination and quaternization processes and the

polybutadiene microstructures. NMR spectra were obtained with a JEOL FX 100 ($^1\text{H-NMR}$) and a Varian CFT-20 ($^{13}\text{C-NMR}$) spectrometer.

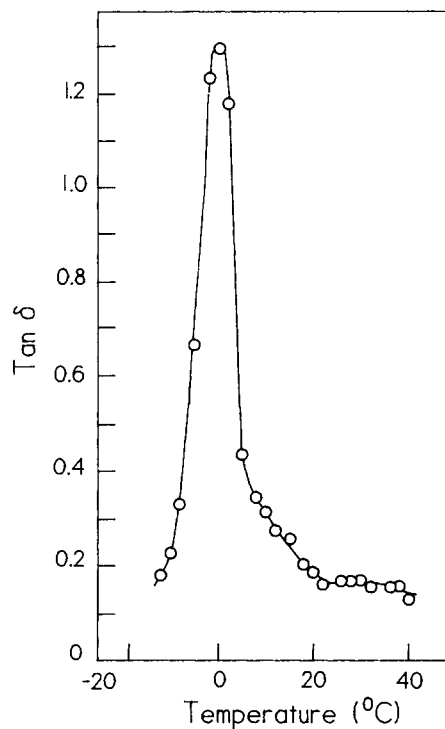


Figure 2 Tan δ -temperature plot of the it-PB at 1 Hz.

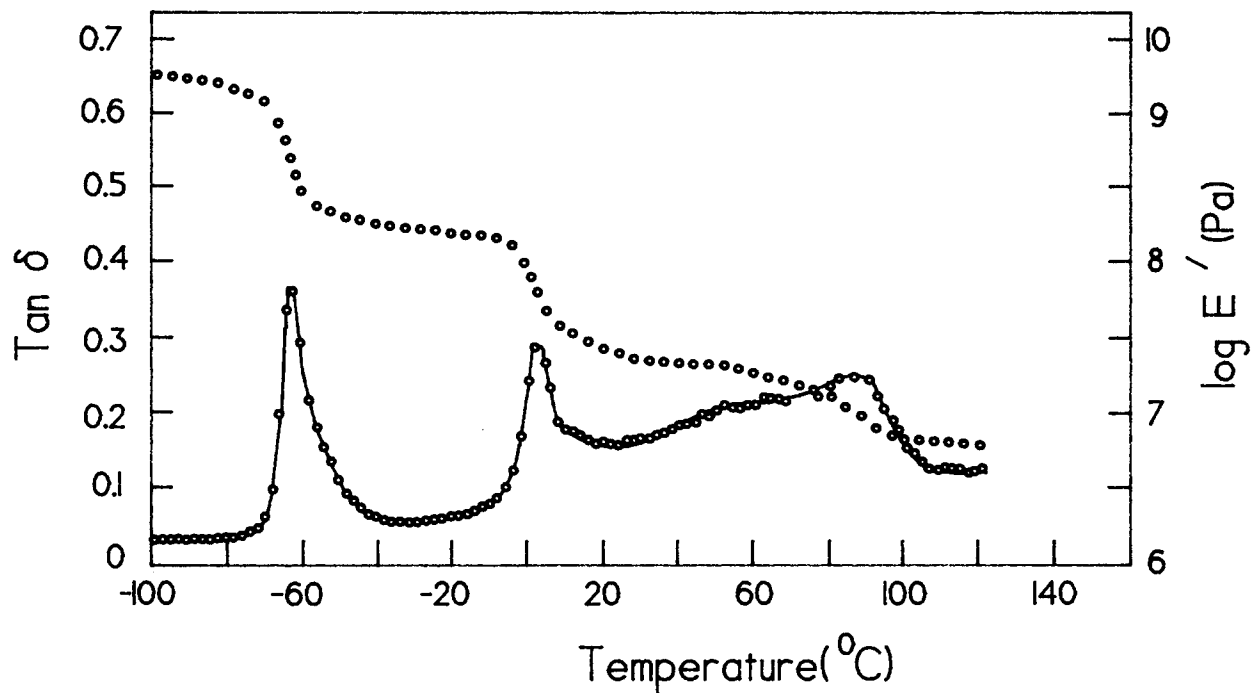


Figure 3 $\tan \delta$ and $\log E'$ -temperature plots of the solvent cast 75% SBS copolymer and 25% it-PB blend at 1 Hz.

Blending

A series of blends of the SBS triblock copolymer and the ionically-terminated polybutadiene of various compositions were prepared in a common sol-

vent (THF). Sheet was then prepared by two different methods. Either the solvent was evaporated at room temperature from casting trays, and the samples were then heated at 30°C in a vacuum oven

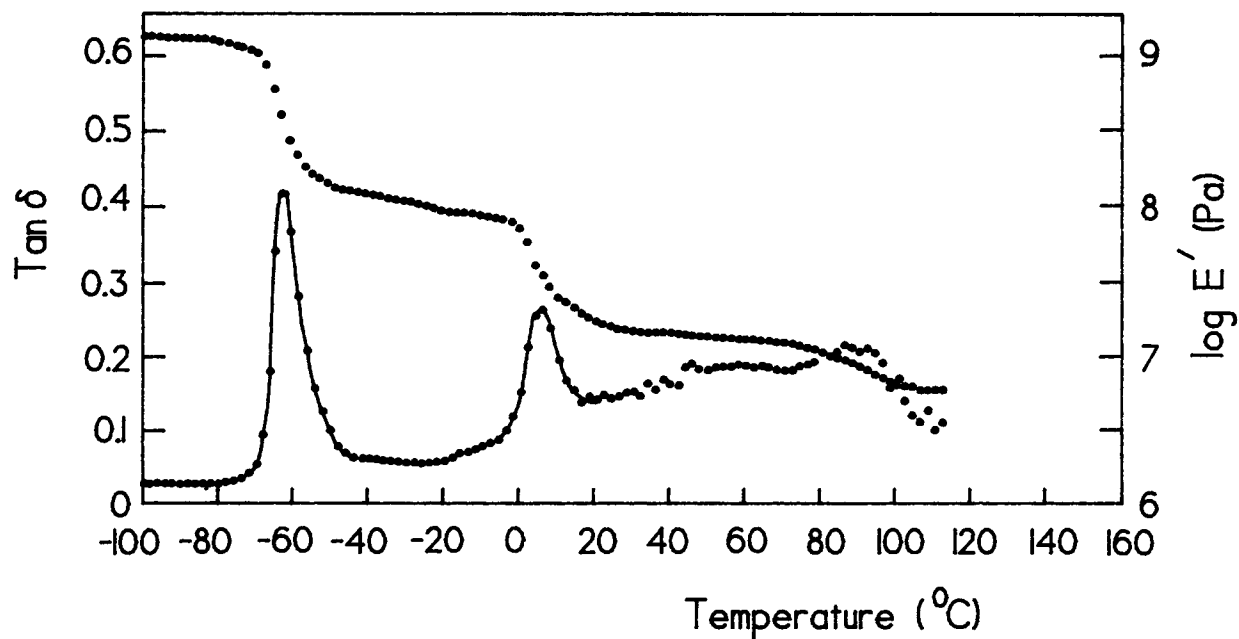


Figure 4 $\tan \delta$ and $\log E'$ -temperature plots of the solvent cast 50% SBS copolymer and 50% it-PB blend at 1 Hz.

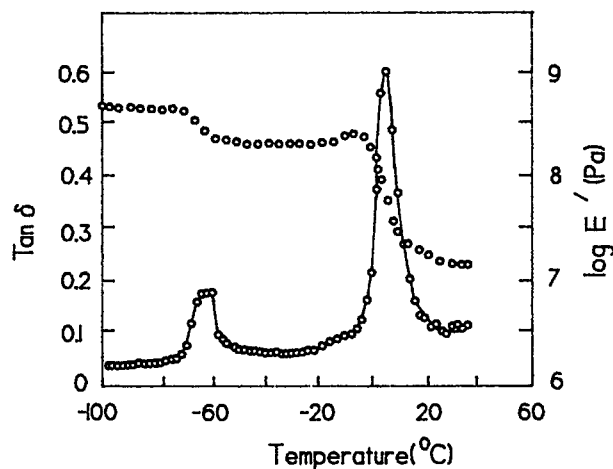


Figure 5 $\tan \delta$ and $\log E'$ -temperature plots of the solvent cast 25% SBS copolymer and 75% it-PB blend at 1 Hz.

to remove residual solvent, or methanol was used to precipitate the blends, which were then similarly vacuum dried prior to sheeting, using a hot press at 140°C.

Testing

Differential scanning calorimetry (DSC) thermograms were obtained using a Perkin-Elmer DSC-1B, at a heating rate of 8°C/min.

A nonresonance, forced-vibration, dynamic mechanical thermal analyzer (DMTA), supplied by Polymer Laboratories Ltd., was used to obtain morphological information. The dimensions of the test pieces were generally about $1.3 \times 0.8 \times 0.04$ cm and the samples were scanned over the desired temperature range at a heating rate of 2°C per min and at a frequency of 1 Hz.

RESULTS AND DISCUSSION

The characterization data for the SBS copolymer are shown in Table I. The polybutadiene blocks are predominantly of the 1,4-type of repeat unit. The characterization data for the it-PB polymer are given in Table II. The ionic cluster dissociation at 66°C indicates that the it-PB material can form networks.

Dynamic mechanical thermal analysis was used to examine the physical properties of these thermoplastic IPNs containing 25, 50, and 75% by weight of the SBS copolymer. Figure 1 shows that for the pure SBS, there are two transitions arising from the phase-separated nature²² of this material.

The peak at -64°C is the glass transition, T_g , of the polybutadiene midsegment, while the other peak, at 92°C, is the T_g of the polystyrene end blocks. This latter peak shows a secondary transition, or shoulder, on the low temperature side. It is well-known²²⁻²⁵ that polystyrene has a β -transition in this region, but that is generally much less prominent than in Figure 1. Consequently, in SBS copolymers, it is believed²⁶⁻³² that this shoulder is concerned with relaxation processes occurring in an interfacial region between the spherical phases formed by the polystyrene end blocks in the continuum formed by the polybutadiene midblocks. In other words, there is not believed to be a sharp boundary between the spherical polystyrene domains and the rubbery continuous phase. This region has been studied by a variety of techniques,^{27,28,33,34} including small angle neutron scattering.^{35,36}

Figure 2 shows that the T_g of the it-PB occurs at 0°C. The T_g of 1,2-polybutadiene is quoted³⁷ to be -15°C, determined by a static technique. Consequently, the dynamic value of 0°C at 1 Hz is indicative of the high 1,2-content of this low molecular weight polymer. Figures 3-5 for the solvent-cast blends show that the polybutadiene from SBS copolymer and from the it-PB still give rise to their individual glass transitions. However, the magnitude of each peak is proportional to the concentration of each material in the blend. As 1,4-polybutadiene has a solubility parameter of $8.9 \text{ (cal/cm}^3)^{1/2}$, while 1,2-polybutadiene has a value of $8.2 \text{ (cal/cm}^3)^{1/2}$, it is not surprising that incompatibility is observed. When the solvent-cast blend contained 75 wt % of the it-PB component, it was too soft to be run up to temperatures above the polystyrene T_g . The observed T_g values for the component polymers and the thermoplastic IPNs are listed in Table III.

Table III Dynamic Mechanical Data (1 Hz) for the SBS Copolymer and the Solvent-Cast it-PB Blends

Compositions	T_g (°C)		
	1,4-PB ^a	1,2-PB ^a	PS ^b
SBS copolymer	-64	—	92
25 wt % it-PB	-63	2	86
50 wt % it-PB	-62	6	90
75 wt % it-PB	-60	8	—
it-PB	—	0	—

^a Polybutadiene component.

^b Polystyrene component.

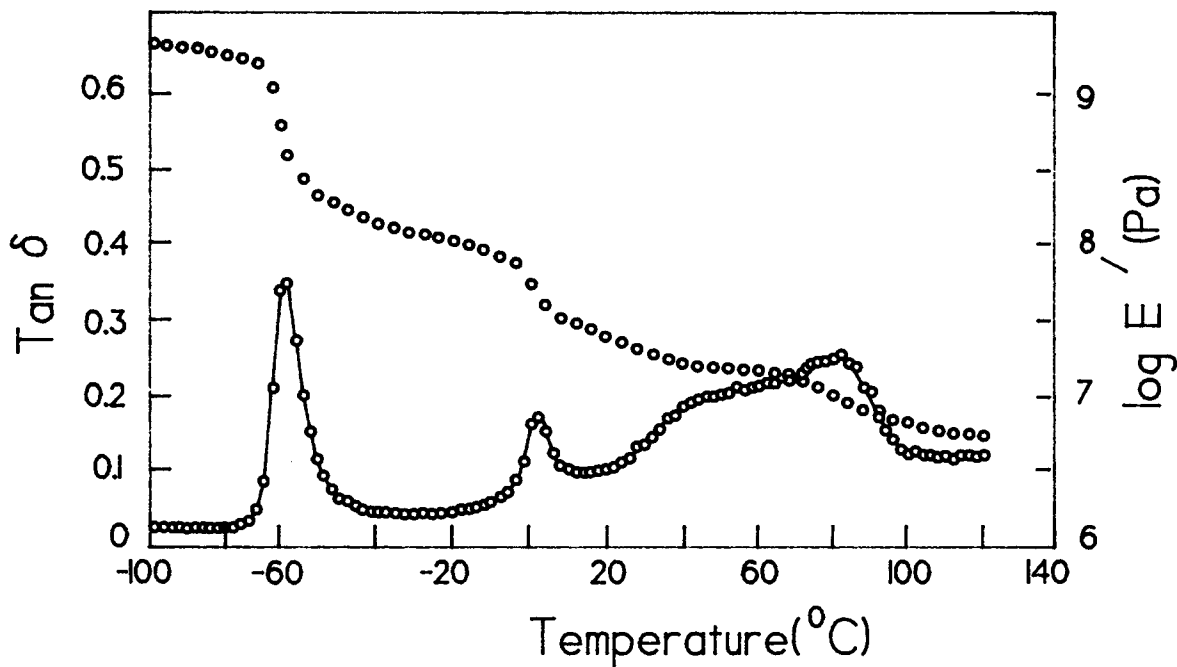


Figure 6 $\tan \delta$ and $\log E'$ -temperature plots of the hot pressed 50% SBS copolymer and 50% it-PB blend at 1 Hz.

It is obvious from Figures 3 and 4 that the shoulder on the polystyrene transition is enhanced by the addition of it-PB and there are small, but real, shifts in the it-PB and polystyrene T_g s, indicating some degree of mixing. These shifts, plus the enlargement of the low temperature shoulder on the polystyrene transition, indicate that the it-PB is preferentially located in the SBS interphase regions. This is also the case for the 50/50 hot-pressed sample (see Fig. 6). Here, the broadening of the shoulder region is even more conspicuous and the it-PB T_g is more reduced than for the solvent-cast case (Fig. 4).

As the it-PB is incompatible with either 1,4-polybutadiene or with polystyrene, it is reasonable that this low molecular weight it-PB is located, substantially or entirely, in the polystyrene-polybutadiene interfacial regions, because these regions consist of an immiscible mixture of polystyrene and 1,4-polybutadiene segments, where the free volume available could be larger than for any of the other phases. Thus, the location of the it-PB may be governed by both thermodynamic and free volume considerations.

REFERENCES

1. L. H. Sperling, *J. Polym. Sci. Macromolec. Rev.*, **12**, 141 (1977).
2. S. C. Kim, D. Klempner, K. C. Frisch, N. Radigan, and H. L. Frisch, *Macromolecules*, **9**, 258 (1976).
3. Y. S. Lipatov and L. M. Sergeeva, *Russ. Chem. Rev.*, **45**, 63 (1976).
4. L. H. Sperling, in: *Polymer Blends and Mixtures*, D. J. Walsh, J. S. Higgins, and A. Maconnachie, Eds., Martinus Nijhoff, Dordrecht, Netherlands, 1985.
5. E. F. Cassidy and H. L. Frisch, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1839 (1984).
6. J. K. Yeo, L. H. Sperling, and D. A. Thomas, *Polym. Eng. Sci.*, **22**, 190 (1982).
7. J. K. Yeo, L. H. Sperling, and D. A. Thomas, *Polymer*, **24**, 307 (1983).
8. D. L. Siegfried, D. A. Thomas, and L. H. Sperling, *Polym. Eng. Sci.*, **21**, 39 (1981).
9. D. L. Siegfried, D. A. Thomas, and L. H. Sperling, *J. Appl. Polym. Sci.*, **26**, 177 (1981).
10. J. M. Crosby and M. K. Hutchins, 40th Annual Conference, Society of the Plastics Industry, Atlanta, Georgia, January 1985.
11. B. A. Arkles, U.S. Pat. 4,500,688 (1985).
12. D. L. Siegfried, D. A. Thomas, and L. H. Sperling, U.S. Pat. 4,468,499 (1984).
13. A. Eisenberg, P. Smith, and Z. L. Zhou, *Polym. Eng. Sci.*, **17**, 1117 (1982).
14. M. Ruthowska and A. Eisenberg, *Macromolecules*, **17**, 821 (1984).
15. M. Hara and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
16. W. P. Gergen, *Kautschuk Gummi*, **37**, 284 (1984).
17. W. K. Fischer, U.S. Pat. 3,806,558 (1974).

18. Y. Nishiyama and L. H. Sperling, *J. Appl. Sci.*, **32**, 5903 (1986).
19. A. Noshay and G. E. McGrath, *Block Copolymer—Overview and Critical Survey*, Academic, New York, 1977.
20. D. H. Richards, D. M. Service, and M. J. Stewart, *Brit. Polym. J.*, **16**, 117 (1984).
21. P. Guyot, J. C. Favler, H. Vytterhoeven, M. Fontanille, and P. Sigwalt, *Polymer*, **22**, 1724 (1981).
22. K. Schnieder and K. Wolf, *Kolloid Z.*, **134**, 149 (1953).
23. K. H. Illers, *Z. Electrochem.*, **65**, 679 (1961).
24. K. M. Sinnott, *Trans. Soc. Plast. Eng.*, **2**, 65 (1962).
25. K. H. Illers and E. Jenckel, *Rheol. Acta*, **1**, 322 (1958).
26. D. J. Meier, *Polym. Prepr.*, **15**, 171 (1974).
27. M. Shen and D. H. Kaelble, *J. Polym. Sci. Polym. Phys. Ed.*, **8**, 149 (1970).
28. G. Krause and K. W. Rollmann, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1133 (1976).
29. Y-D. M. Chen and R. E. Cohen, *J. Appl. Polym. Sci.*, **21**, 629 (1977).
30. C. P. Henderson and M. C. Williams, *J. Polym. Sci. Polym. Lett. Ed.*, **17**, 257 (1979).
31. J. Diament, D. S. Soong, and M. C. Williams, *Contemporary Topics in Polymer Science*, Vol. 4, Plenum, New York, 1982.
32. B. Djermouni and H. Ache, *Macromolecules*, **13**, 168 (1980).
33. A. Todo, T. Hashimoto, and H. Kawai, *J. Appl. Cryst.*, **11**, 558 (1978).
34. T. Hashimoto, K. Nagatoshi, A. Todo, H. Hasegawa, and H. Kawai, *Macromolecules*, **7**, 364 (1974).
35. R. W. Richards and J. L. Thomason, *Polymer*, **22**, 581 (1981).
36. R. W. Richards and J. L. Thomason, *Polymer*, **24**, 1089 (1983).
37. Q. A. Trementozzi, *J. Polym. Sci.*, **22**, 187 (1956).

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