Macromolecules **1989**, *22*, 1449–1453

Compatibilizing Effect of Block Copolymers Added to the Polymer/Polymer Interface

Spiros H. Anastasiadis[†]

Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

Irena Gancarz

Technical University of Wroclaw, Wroclaw, Poland

Jeffrey T. Koberstein*

Institute of Materials Science and Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06268. *Received April 28, 1988; Revised Manuscript Received August 3, 1988*

ABSTRACT: The compatibilizing effect of block copolymer addition on the interfacial tension between two immiscible homopolymers is studied as a function of the concentration of the additive for the ternary system polystyrene/1,2-polybutadiene/poly(styrene-*block*-1,2-butadiene). A sharp decrease in interfacial tension is observed with the addition of small amounts of copolymer, followed by a leveling off as the copolymer concentration is increased above the apparent critical micelle concentration (CMC). For concentrations below this critical concentration, the interfacial tension reduction is essentially linear in the copolymer content and compares well with the predictions of Noolandi and Hong.

Introduction

Polymer melt blending has proven to be a simple and efficient means for the development of new higher performance organic materials, starting from largely available monomers and polymers. In the case of immiscible systems, the overall physicomechanical behavior depends critically on two demanding structural parameters: a proper interfacial tension leading to a phase size small enough to allow the material to be considered as macroscopically "homogeneous", and an interphase "adhesion" strong enough to assimilate stresses and strains without disruption of the established morphology. That is unfortunately not the case for most immiscible polymer blends.[1-3]

It is widely known that the presence of certain polymeric species, usually suitably chosen block or graft copolymers, can alleviate to some degree these problems as a result of their interfacial activity.[4-12] The segments of these copolymers can be chemically identical with those in the respective phases[6,11,13-16] or miscible with or adhered to one of the phases.[17-19] As pointed out by Paul,[20] "this type of surface activity should (1) reduce the interfacial energy between the phases, (2) permit a finer dispersion during mixing, (3) provide a measure of stability against gross segregation, and (4) result in improved interfacial adhesion[21]."

Many experimental investigations have appeared that attempt to study the interfacial and surfactant properties of block copolymers. In addition to documenting the compatibilizing activity in polymer blend dispersions, these investigations have also provided evidence of the interfacial activity in polymeric systems,[14,22-25] surface activity,[26-29] and dispersant efficiency[30,31] of block copolymers.

Patterson et al.[25] used a rotating drop apparatus to study the effect of addition of poly(dimethylsiloxane-*block*-oxyethylene) copolymers on the interfacial tension between a commercial methyl terminated poly(dimethylsiloxane) and a commercial poly(oxyethylene-*block*-oxypropylene) copolymer. Starting with an interfacial tension of 8.3 dyn/cm, a 72% reduction in interfacial tension was obtained with the addition of 2% of a 60/40 poly(dimethylsiloxane-*block*-oxyethylene) block copolymer. Increasing the level of polar polyether substitution from 40% to 75% did not result in any further reduction. It rather showed less interfacial activity (64% reduction in interfacial tension). This agrees with the previous observation of maximum efficiency obtained with symmetric copolymers.[6,7,32] Substitution of a propylene oxide for the poly(ethylene oxide) in the 25/75 copolymer additive reduced its capability for reducing interfacial tension (51% reduction).

The effect of the concentration of the copolymer emulsifier was studied for the 60/40 poly(dimethylsiloxane-*block*-oxyethylene). A major reduction in interfacial tension (55%) took place with the addition of 0.17% of the copolymer, while 68% reduction was observed with 1% additive. Increasing the amount to 2% effected only a 4% further reduction. That is, a few percent of block copolymer additive is required to essentially saturate the interface and reach the limiting interfacial tension. A linear correlation was obtained when interfacial tension was plotted versus the logarithm of the concentration of the additive expressed as grams of additive per liter of mixed liquids.

Studies on star-shaped block copolymer additives[26] demonstrated that the limiting interfacial tension was identical with that for the corresponding diblock copolymer but that limiting behavior is achieved at significantly lower copolymer concentrations.

Gailard and co-workers[14,24] demonstrated the surface activity of block copolymers by studying the interfacial tension reduction in demixed polymer solutions. Addition of poly(styrene-*block*-butadiene) block copolymer to the polystyrene/polybutadiene/styrene ternary system showed first a characteristic decrease in interfacial tension followed by a leveling off, which is similar to the evolution of interfacial tensions for oil–water systems in the presence of surfactants.

The compatibilizing effect of block copolymer addition can therefore be demonstrated with the sharp reduction in interfacial tension observed with the addition of a small amount of the emulsifier followed by a leveling off indicative of saturation of the interface by the solubilizing agent. In this paper, the compatibilizing effect of diblock copolymer addition on the interfacial tension between two immiscible homopolymers is studied as a function of the concentration of the additive for the ternary system

---

* Author to whom correspondence should be addressed.

[†] Present address: IBM Research Division, Almaden Research Center, 650 Harry Rd, San Jose, CA 95120-6099.

0024-9297/89/2222-1449$01.50/0

Table I
Characteristics of the Materials

	M_n	M_w/M_n	chemical structure		wt % PS
			1,4	1,2	
PS[a]	2 200	1.06			100
PB[b]	7 800	1.02	95	5	0
P(S-b-B)[b]	18 600	1.06	95	5	49

[a] Polymer Laboratories, Ltd. [b] Synthesized in house.

polystyrene(PS)/1,2 polybutadiene(PB)/poly(styrene-*block*-1,2-butadiene)(P(S-b-B)). The interfacial tension data are compared to the predictions of current theories[33-37] which treat the emulsification behavior of block copolymers.

Experimental Section

Materials. Polystyrene oligomer (Polymer Laboratories, Ltd.) was used in this study as received. The number-average molecular weight is 2200, and the sample is monodisperse (M_w/M_n = 1.06). Its characteristics are listed in Table I.

The 1,2-polybutadiene homopolymer was anionically synthesized in house. The reaction was carried out at room temperature in benzene under high-purity argon by using a glass manifold equipped with Teflon valves. *n*-Butyllithium (*n*-BuLi) was the initiator and dipiperidinoethane[38] was used as a modifier at a molar ratio of 10:1 (modifier:initiator) to produce homopolymers with more than 95% 1,2-butadiene isomer. More details on the synthesis procedure are given by Owens[39] and Anastasiadis.[40] The microstructure of the butadiene sequence was evaluated by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and showed predominantly the 1,2 isomer (95% 1,2 and 5% 1,4). The number-average molecular weight was measured with membrane osmometry[39] in toluene on a Knauer osmometer. The number-average molecular weight for our sample (sample PB-9 in ref 39) was found to be 7800. The polydispersity of the 1,2-polybutadiene homopolymer measured by high-pressure size-exclusion chromatography (HPSEC) was M_w/M_n = 1.02.

The block copolymerization was carried out in benzene with dipiperidinoethane as a polar modifier to yield primarily 1,2-butadiene. More details on the synthesis procedure are given elsewhere.[39,40] The composition and microstructure of the diblock copolymer were determined by ^{1}H NMR on a 250-mHz Bruker instrument. The copolymer was determined to be 49 wt % polystyrene and the polybutadiene microstructure was determined to be 95% 1,2 microstructure. The number-average molecular weight for the P(S-b-B) diblock copolymer, measured by membrane osmometry,[39] was reported as 18 600. The polydispersity measured by HPSEC was 1.06. The characteristics of all the materials are summarized in Table I.

The density of the PB 7800 sample used in this study was estimated using the density values reported[40,41] for two different molecular weight 1,4-polybutadienes, a hydrogenated 1,2-polybutadiene, and literature values[42,43] for the 1,2 homopolymers. The estimated butadiene density value at the temperature of the interfacial tension measurements (145 °C) was 0.856 g/cm^3. The density data of Bender and Gaines[44] and Fox and Flory[45] were used to estimate the density for the PS 2200 sample. It was estimated as 0.980 g/cm^3. Thus, the density difference across the interface was estimated to be 0.124 g/cm^3 at the temperature of our experiments. It was also assumed that the addition of the very small amounts of the P(S-b-B) (less than 3.5%) does not affect appreciably the density difference across the interface.

Interfacial Tension Measurements. Interfacial tension for the binary homopolymer blend and the ternary systems containing the block copolymer additive were measured by using the automated pendant drop apparatus,[46] which utilizes video digital image processing techniques. The copolymer emulsifier was preblended with PS and a fluid drop of the mixture was formed, at the tip of a glass capillary tube of a Drummond positive displacement syringe, in a fluid matrix of the PB phase. That is, the copolymer was preblended with the dispersed phase in order to control more precisely the amount that can diffuse to the interface and to minimize the distance traveled by the copolymer molecules to reach the polymer/polymer interface. The same preblending procedure was also adopted by Fayt and co-workers[11,47-49] in preparation of specimens for transmission electron microscopy experiments. The microcuvette containing the polymer matrix was placed in a Rame-Hart C-2033 environmental chamber under argon atmosphere. The temperature was controlled at 145 °C. Details regarding the experimental setup and data aquisition procedure are discussed elsewhere.[40,41] Images of the drops were recorded every 15 min for a period of time of more than 1 h. The drop profiles were then analyzed by using a robust shape comparison algorithm.[46] When the calculated interfacial tension did not change with time, equilibrium was considered to be attained.

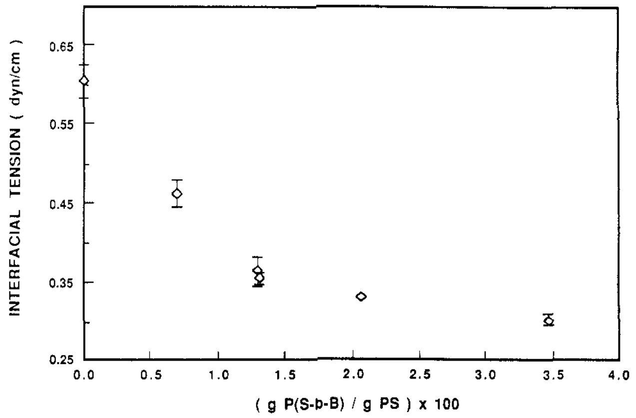

Figure 1. Interfacial tension for the system PS/PB/P(S-b-B) at 145 °C as a function of P(S-b-B) diblock copolymer concentration.

Results and Discussion

Interfacial Tension Data. The interfacial tension data for the PS 2200/PB 7800/P(S-b-B) system as a function of the copolymer concentration, at a constant temperature of 145 °C, appear in Figure 1. The copolymer concentration is expressed as weight of copolymer per weight of the PS. The average standard deviation of the data is 3.0%, whereas the maximum standard deviation is 5.1%. A sharp decrease in the interfacial tension is observed with addition of a small amount of copolymer (40% reduction with 1.29% addition), illustrating the surfactant-like behavior of the diblock copolymer. The interfacial tension levels off as the copolymer concentration is increased (50% reduction with addition of 3.5% copolymer).

Similar behavior was observed by Patterson et al.[25] and by Gailard et al.,[14,24] as discussed in the Introduction. Their results, however, indicate a much higher reduction obtained by the addition of the copolymer to the phase-separated system. Patterson et al. do not provide information on the molecular weights or the polydispersities of the polymers they used, so one cannot really assess why they achieved higher reductions. It may be attributed to the specific interactions that might be present in the poly(dimethylsiloxane)/poly(oxyethylene-*block*-oxypropylene)/poly(dimethylsiloxane-*block*-oxyethylene) system, especially since the reduction was lower when the oxyethylene sequence was replaced by oxypropylene. The augmented reduction (68% with 2.6% copolymer) observed by Gailard et al. may also be associated with either the high molecular weight of the copolymer used (M_n = 225000, 48% PS), compared to that of the homopolymers [PS (M_n = 76 200, M_w/M_n = 1.1) and commercial polybutadiene (M_n = 120 000)] or to the interactions (e.g., excluded volume) that are caused by the presence of the styrene solvent in the polystyrene/polybutadiene/poly(styrene-*block*-butadiene)/styrene system.

The leveling off of interfacial tension observed at high block copolymer concentrations in these ternary systems is an indication of interfacial saturation by the copolymer.

The addition of more copolymer is wasteful, since it does not affect the interfacial situation but rather produces micelles of the copolymer dispersed in the homopolymer phases.[35] The critical micelle concentration (CMC), defined as the concentration at which micelles are formed, can be estimated from Figure 1. For block copolymers in solutions, the CMC is evaluated using surface tension data of the solutions versus the copolymer concentration. As reported by Nakamura et al.[50] and Riess and co-workers[23,32,51] the surface tension of block copolymer solutions decreases linearly with increasing concentration below the CMC and attains an almost constant value when the concentration exceeds the CMC. If the same approximation is used for the polymer A/polymer B/copolymer interfacial tensions, a CMC of ca. 1.6 g of copolymer per gram of PS can be estimated. Clearly, at concentrations higher than the CMC, there is a coexistence equilibrium between copolymer at the saturated interface and copolymer micelles dispersed within the two homopolymer phases.

Comparison with Theory. Statistical thermodynamic theories considering the emulsifying effect of compolymers have recently been proposed by Noolandi and co-workers[33-36] and Leibler.[37]

Hong and Noolandi previously constructed a general theory[52,53] of inhomogeneous systems, beginning with the functional integral representation of the partition function as introduced by Edwards.[54] The free-energy function was minimized by the saddle-function method, including the constraints of no volume change upon mixing and a constant number of molecules of each component, to obtain the mean-field equations for the fundamental probability distribution functions for a system of two immiscible homopolymers A and B diluted with solvent in the presence of a diblock copolymer AB. These equations were solved numerically to obtain the polymer density profiles in the interfacial region. The difference between the total free energy and that of the bulk polymers was used to evaluate the interfacial tension.

The assumption was made that the part of the copolymer that does not localize itself at the interface will be randomly distributed in the bulk of the homopolymers. Because of this assumption, their results[34] should be reliable only for low copolymer concentrations below the critical micelle concentration. Numerical solutions of their model[35,36] were used to identify the relative importance of the various contributions that affect the interfacial tension reduction. For a symmetric diblock copolymer, homopolymers of infinite molecular weight, and a symmetric solvent, they found that the interfacial tension reduction, $\Delta\gamma$, with increasing copolymer molecular weight and concentration arose mainly from the energetically preferred orientation of the blocks at the interface so as to extend into their respective compatible homopolymers. The main counterbalancing term in the expression for $\Delta\gamma$ is the entropy loss of the copolymer that localizes at the interface. The loss of conformational or "turning back" entropy of both the copolymer and homopolymer chains at the interface was shown to contribute little to $\Delta\gamma$.

Neglecting, thus, the loss of conformational entropy, they were able to obtain an analytical expression for the interfacial tension reduction, given by

$$\Delta\gamma = d\phi_c\left\{\left(\frac{1}{2}\chi\phi_p + \frac{1}{Z_c}\right) - \frac{1}{Z_c}\exp(Z_c\chi\phi_p/2)\right\} \qquad (1)$$

The total amount of the copolymer residing at the interface was shown to be

$$\phi_c(0) \cong \phi_c \exp(Z_c\chi\phi_p/2) \qquad (2)$$

d is the width at half height of the copolymer profile, reduced by the Kuhn statistical segment length. Numerical calculations showed that d was almost constant for varying copolymer molecular weights. ϕ_c denotes the bulk copolymer volume fraction of the copolymer in the system, which is very close to the nominal amount of the block copolymer present,[36] whereas $\phi_c(0)$ is the copolymer volume fraction at the interface. ϕ_p is the bulk volume fraction of polymer A or B (assumed equal), Z_c is the degree of polymerization of the symmetric copolymer, and χ is the Flory–Huggins interaction parameter between A and B segments. It was assumed that $\chi_{AS} = \chi_{BS} = 0$, between the solvent and segments A and B, respectively. The simplified theory does not provide an expression for d directly, and thus, it is left as an adjustable parameter. For $Z_c\chi\phi_p \ll 1$, eq 1 reduces to

$$\Delta\gamma = -\frac{d}{8}Z_c\phi_c\chi^2\phi_p^2 \qquad Z_c\chi\phi_p \ll 1 \qquad (3)$$

The important features of the approximate relations (1 and 3) were verified by the exact numerical calculations. An exponential dependence of the interfacial tension reduction on the block copolymer molecular weight, as well as the total homopolymer volume fraction, is predicted that can explain the remarkable effectiveness of using large molecular weight diblocks as surfactants for concentrated mixtures of immiscible homopolymers. For small Z_c, a linear dependence of $\Delta\gamma$ on Z_c (eq 3) was predicted by the exact numerical calculations, as well. A linear dependence of $\Delta\gamma$ on the block copolymer volume fraction was predicted by the exact numerical solution in agreement with (1) and (3).

Noolandi and Hong[35,36] pointed out that both copolymer concentration and molecular weight are equally important in reducing the interfacial tension. They noted, however, that the interfacial tension surface (γ plotted against Z_c and ϕ_c) is bounded by a critical micelle concentration (CMC) curve, since blocks of large molecular weight tend to form micelles in the bulk of the homopolymers, rather than congregating at the interface. Their theoretical treatment is valid for concentrations well inside the CMC boundary.

Leibler[37] developed a mean-field formalism to study the interfacial properties of nearly compatible mixtures of two homopolymers, A and B, and a copolymer AB. The free energy was expressed in terms of monomer concentration correlation functions that were calculated in a self-consistent way within the random-phase approximation.[55,56] For the very broad interface of nearly miscible systems, a gradient expansion was carried out giving a generalization of the Cahn–Hilliard theory.[57] As mentioned by Noolandi and Hong,[36] with the gradient expansion in Leibler's theory, the diblock copolymer was effectively treated as a small-molecule solvent compared to the large width of the interfacial region, and the structure of the copolymer became irrelevant. The system, thus, behaved as a mixture of two homopolymers driven to the consolute point by the addition of an excess of solvent. For the nearly compatible species ($2 < \chi N < 4(2)^{1/2}$), two mechanisms of the interfacial activity of the copolymer chains were distinguished: (i) species A and B, which are more closely mixed as copolymer chains, are present in both phases, and (ii) the copolymer chains have a certain tendency to locate at the interface. In the case of nearly miscible species (near the consolute point), the first mechanism dominates, whereas for the highly incompatible case the second is the most important.

To summarize, the mechanisms thought to control the decrease in interfacial tension in highly immiscible systems compared to nearly compatible blends are quite different. In the first case, it is the surfactant activity of the block copolymer chains that causes the interfacial tension reduction, whereas it is the presence of copolymer molecules dissolved in the bulk homopolymer phases that causes the compatibilizing behavior in the second. These theories remain relatively untested to date, primarily as a result of the scarcity of data on homopolymer/copolymer interfaces.

The theory of Leibler[37] holds for nearly compatible polymer systems, whereas the theories of Noolandi and Hong[34-36] apply to the case of highly incompatible systems for concentrations less than the critical micelle concentration (CMC) of micelle aggregation. For concentrations below the CMC, interfacial tension is expected to decrease linearly with copolymer concentration, whereas for concentrations higher than the CMC a leveling off is expected, as observed in Figure 1. For the immiscible system polystyrene/polybutadiene, the theories of Noolandi and Hong will be examined for their applicability in predicting the interfacial tension reduction upon the addition of the diblock copolymer.

The Flory–Huggins interaction parameter for this system has been determined by Owens[39] by small-angle X-ray scattering analysis of the disordered state of poly(styrene-*block*-1,2-butadiene) diblock copolymer (the same sample used in our study), using the theory of Leibler.[58] It was found to be given by the expression

$$\chi = -0.021 + 25/T \tag{4}$$

in very good agreement with the data of Hewel and Ruland,[59] where T is the absolute temperature. For the temperature of 145 °C of our experiments, $\chi = 0.0388$. The degree of polymerization[39] of the diblock is $Z_c = 261$.

Noolandi[60] suggested that the theory can be applied to the system PS/PB/P(S-b-B), i.e., to a concentrated system without solvent, by letting the total polymer volume fraction, ϕ_p, go to 1. In this case, (1) reduces to

$$\Delta\gamma \cong d\phi_c\left\{\frac{1}{2}\chi + \frac{1}{Z_c} - \frac{1}{Z_c}\exp(Z_c\chi/2)\right\} \tag{5}$$

or, by use of the values for χ and Z_c,

$$\Delta\gamma \cong -0.583d\phi_c \tag{6}$$

with d being the width at the half height of the copolymer profile in units of b, which is essentially a parameter not determined by the simplified theory. It is related to the thickness of the interface.

In order to compare our data with the Noolandi and Hong theory, we need the bulk volume fractions of the copolymer. We assume that the same volume fraction of copolymer exists in both bulk phases. By use of the densities of PS and PB used earlier ($\rho_{PS} = 0.980$ g/cm^3 and $\rho_{PB} = 0.856$ g/cm^3), the copolymer bulk volume fraction is related to the concentration, c, used in Figure 1, by

$$\phi_c = \left(1 + \frac{1.959}{c}\right)^{-1} \tag{7}$$

The interfacial tension reduction or increment $\Delta\gamma$ is referred to the average value of the interfacial tension for the binary blend without the copolymer (0.60 dyn/cm).

The plot of interfacial tension increment as a function of the copolymer volume fraction, calculated as discussed above, appears in Figure 2, together with the linear fit of the data for low concentration (less than the CMC) of the copolymer additive. The slope of this line is −37.0, and thus, by the use of eq 6, $d \cong 63.5b$, or by the use of the geometric mean of the Kuhn statistical segment lengths of the two segments[39] as 0.6 nm, it is found that $d \cong 38$ nm. This value of d (~63.5 monomer units) is about 24% of the contour length of the copolymer chains (degree of polymerization of 261) and, thus, is very reasonable for our system. A similar extended configuration of the chains has been found for diblock copolymers adsorbed onto mica surfaces, with the solvent being a good solvent for one block and a nonsolvent for the other.[61] The approximate theory, however, should be considered reliable only for

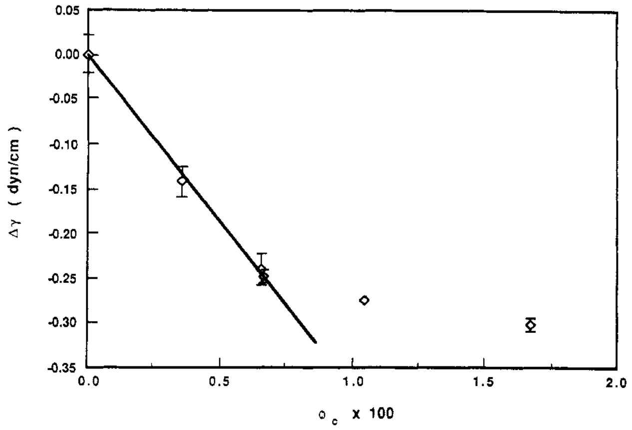

Figure 2. Interfacial tension reduction versus copolymer volume fraction for the system PS/PB/P(S-b-B) at 145 °C. Solid line is the linear fit of the data for concentrations below the CMC, according to the theory of Noolandi and Hong.[36]

$$\chi Z_c\phi_p \leq 2 \tag{8}$$

For larger values of this parameter (as in our system $\chi Z_c\phi_p \approx 10$), the effects shown in the calculations are "accentuated but they have to be interpreted with care, because of the possibility of third-phase formation in the system".[36]

More experiments with carefully tailored systems are needed, both for highly immiscible and for nearly compatible polymer systems, in order to fully test the applicability of the thermodynamic theories for the homopolymer/copolymer interfaces and thus gain the fundamental ability to optimize interfacial activity in these systems.

Summary

An initial study has been performed on the effect of low amounts of diblock copolymer compatibilizing agents on the interfacial tension between two immiscible homopolymers. The effect of addition of poly(styrene-*block*-1,2-butadiene) in reducing the interfacial tension between polystyrene and 1,2-polybutadiene is investigated as a function of copolymer concentration.

The interfacial tension data demonstrate the surfactant-like behavior of the added diblock copolymer. A sharp decrease in interfacial tension is observed with addition of a small amount of copolymer (40% reduction with 1.29% additive), followed by a leveling off as the copolymer concentration is increased (50% total reduction with 3.5% copolymer). The leveling off at higher concentrations is an indication of interfacial saturation by the copolymer and subsequent formation of copolymer micelles dispersed in the homopolymer phases. An estimate of the critical micelle concentration (CMC) of 1.6 g of copolymer per gram of polystyrene can be extracted from these data.

For concentrations less than the CMC, the theories of Noolandi and Hong predict a linear decrease of interfacial tension with copolymer volume fraction in agreement with the data, with a slope that depends on the configuration of the copolymer at the homopolymer/homopolymer interface. The comparison with theory suggests that the copolymer chains adopt extended configurations at the interface.

Acknowledgment. This research was supported by a joint grant from NSF (DMR-8504727) and the Army Research Office and by the E. I. du Pont de Nemours & Company, Inc.

Registry No. PS, 9003-53-6; PB, 9003-17-2; (S)(B) (block copolymer), 106107-54-4.

References and Notes

(1) Paul, D. R.; Vinson, C. E.; Locke, C. E. *Polym. Eng. Sci.* **1972**, *12*, 157.
(2) Schrenk, W. J.; Alfrey, T., Jr. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2, p 129.
(3) Paul, D. R. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2, p 167.
(4) Gaylord, N. G. (U. S. Plywood—Champion Papers, Inc.) U.S. Patent 3,485,777, Dec. 23, 1969.
(5) Gaylord, N. G. In *Copolymers, Polyblends, and Composites*; Platzer, N. A. J., Ed.; Advances in Chemistry 142; American Chemical Society: Washington, DC, 1975; p 76.
(6) Riess, G.; Jolivet, Y. In *Copolymers, Polyblends, and Composites*, Platzer, N. A. J., Ed.; Advances in Chemistry Series 142; American Chemical Society: Washington, DC, 1975; p 243.
(7) Riess, G.; Kohler, J.; Tournut, C.; Banderet, A. *Makromol. Chem.* **1967**, *101*, 58.
(8) Kohler, J.; Riess, G.; Banderet, A. *Eur. Polym. J.* **1968**, *4*, 173.
(9) Kohler, J.; Riess, G.; Banderet, A. *Eur. Polym. J.* **1968**, *4*, 187.
(10) Riess, G.; Periard, J.; Jolivet, Y. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 339.
(11) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 25.
(12) Fayt, R.; Jérôme, R.; Teyssié, Ph. In *Polyblends—'86*; Utracki, L. A., Ed.; NRCC/IMRA Polymers Symposium Series; IMRA:[15] Montreal, Canada, 1986.
(13) Ramos, A. R.; Cohen, R. E. *Polym. Eng. Sci.* **1977**, *17*, 639.
(14) Gailard, P.; Ossenbach-Sauter, M.; Riess, G. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 771.
(15) Marie, P.; Selb, J.; Rameau, A.; Duplessix, R.; Gallot, Y. In *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; NATO Advanced Science Institute Series; Mortinus Nijhoff: Dordrecht, The Netherlands, 1985; p 449.
(16) Barentsen, W. M.; Heikens, D.; Piet, P. *Polymer* **1974**, *15*, 119.
(17) Ouhadi, T.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *Polym. Commun.* **1986**, *27*, 212.
(18) Ouhadi, T.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 973.
(19) Ouhadi, T.; Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Appl. Polym. Sci.* **1986**, *32*, 5647.
(20) Paul, D. R. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 2; p 35.
(21) Molau, G. E. In *Block Copolymers*; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970; p 79.
(22) Cantor, R. *Macromolecules* **1981**, *14*, 1186.
(23) Riess, G.; Nervo, J.; Rogez, D. *Polym. Eng. Sci.* **1977**, *17*, 634.
(24) Gailard, P.; Ossenbach-Sauter, M.; Riess, G. In *Polymer Compatibility and Incompatibility: Principles and Practice*; Solc, K., Ed.; MMI Symposium Series 2; Harwood: New York, 1982.
(25) Patterson, H. T.; Hu, K. H.; Grindstaff, T. H. *J. Polym. Sci., Part C* **1971**, *34*, 31.
(26) Gia, H. B.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Phys.* **1980**, *18*, 2391.
(27) Owen, M. J.; Kendrick, T. C. *Macromolecules* **1970**, *3*, 458.
(28) Gaines, G. L., Jr.; Bender, G. W. *Macromolecules* **1972**, *5*, 82.
(29) O'Malley, J. J.; Ronald Thomas, H.; Lee, G. N. *Macromolecules* **1979**, *12*, 996.
(30) Meier, D. J. *J. Phys. Chem.* **1967**, *71*, 1861.
(31) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: New York, 1983.
(32) Wilson, D. J.; Hurtrez, G.; Riess, G. In *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; NATO Advanced Science Institute Series; Mortinus Nijhoff: Dordrecht, The Netherlands, 1985; p 195.
(33) Noolandi, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 46.
(34) Noolandi, J.; Hong, K. M. *Macromolecules* **1982**, *15*, 482.
(35) Noolandi, J. *Polym. Eng. Sci.* **1984**, *24*, 70.
(36) Noolandi, J.; Hong, K. M. *Macromolecules* **1984**, *17*, 1531.
(37) Leibler, L. *Macromolecules* **1982**, *15*, 1283.
(38) Antkowiak, T. A.; Oberster, A. E.; Halasa, A. F.; Tate, D. P. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 1319.
(39) Owens, J. N. Ph.D. Thesis, Princeton University, Princeton, NJ, 1986.
(40) Anastasiadis, S. H. Ph.D. Thesis, Princeton University, Princeton, NJ, 1988.
(41) Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2980.
(42) Quan, X. S.-W. Ph.D. Thesis, Princeton University, Princeton, NJ, 1986.
(43) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1975.
(44) Bender, G. W.; Gaines, G. L., Jr. *Macromolecules* **1970**, *3*, 128.
(45) Fox, T. G., Jr.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(46) Anastasiadis, S. H.; Chen, J.-K.; Koberstein, J. T.; Siegel, A. F.; Sohn, J. E.; Emerson, J. A. *J. Colloid Interface Sci.* **1987**, *119*, 55.
(47) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 79.
(48) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 1269.
(49) Fayt, R.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 2209.
(50) Nakamura, K.; Endo, R.; Takada, M. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1287.
(51) Riess, G.; Rogez, D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 19.
(52) Noolandi, J.; Hong, K. M. *Ferroelectrics* **1980**, *30*, 117.
(53) Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 72.
(54) Edwards, S. F. *Proc. Phys. Soc., London* **1965**, *85*, 613.
(55) de Gennes, P. G. *J. Phys. (Les Ulis, Fr.)* **1978**, *39*, 951.
(56) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(57) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258.
(58) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(59) Hewel, M.; Ruland, W. *Makromol. Chem., Makromol. Symp.* **1986**, 4, 197.
(60) Noolandi, J., private communication, 1987.
(61) Patel, S.; Hadziioannou, G.; Tirrell, M. In *Composite Interfaces*; Ishida, H., Koenig, J. L., Eds., Elsevier Science: Amsterdam, 1986; p 65.