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(9) One can also consider a regime in which the modulation amplitude is small. However, when the polymerization index is extremely large such that the domain size becomes much greater than the domain wall thickness, the reduced amplitude again reaches the size of the order unity and then we are no longer in the weak segregation regime. In fact, the relevant dimensionless parameter that decides the degree of segregation is χN_K where χ is the Flory–Huggins interaction parameter and N_K is the smaller of N_A and N_B.[1,5,10]

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Interfacial Tension of Immiscible Polymer Blends: Temperature and Molecular Weight Dependence

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ABSTRACT: Interfacial tensions between immiscible homopolymers are measured by using an automated pendant drop apparatus, which utilizes video digital image processing techniques. A recently developed robust shape analysis algorithm is used to analyze the experimental drop profiles. The data show the effect of temperature and number average molecular weight (M_n) on the interfacial tension for the immiscible blends polystyrene–poly(methyl methacrylate), polybutadiene–poly(dimethylsiloxane) and polystyrene–hydrogenated 1,2-polybutadiene. Interfacial tension decreases linearly with temperature and increases with molecular weight. The data are well represented by an $C_1 + C_2M_n^{-z}$ dependence on molecular weight but are not of sufficient precision to determine a precise value for the exponent. The interfacial tension data for the latter blend system are compared with thermodynamic theories of polymeric interfaces. A square gradient theory approach, in conjunction with the Flory–Huggins expression for the free energy of mixing, predicts a magnitude and temperature dependence of interfacial tension which are in reasonable agreement with experimental data. The predicted molecular weight dependence corresponds well with experimental data at high molecular weights but severely underestimates the interfacial tensions for low molecular weights.

Introduction

The structure and thermodynamic state of polymeric interfaces are important features in many polymeric materials of current technological interest. This is especially true for multiconstituent systems such as immiscible polymer blends or microphase separated copolymers, where interface structure can affect greatly the mechanical properties.[1] Interfacial tension is important due to its influence on the morphology of multiphase polymers. A number of experimental investigations, for example, have shown that the phase structure (e.g. dispersed particle size) in incompatible polymer blends is directly proportional to the interfacial tension.[2–4]

Fundamentally, interfacial tension is a thermodynamic property of the system which may be calculated directly from statistical thermodynamic theories. Experimental measurement of interfacial tensions is therefore a straightforward means for evaluating the validity of these theories.

The existent data pertaining to the interfacial properties of multiphase polymers have been well summarized in several reviews[5–7] and a monograph by Wu.[8] Interfacial tension generally decreases linearly with temperature with a temperature coefficient in the range of 10^{-2} dyn/(cm °C). An increase in molecular weight leads to an increase in the interfacial tensions; however, there are only a few studies which have examined this dependence in any detail. Experimental interfacial tensions[9,10] between n-alkanes and a perfluoroalkane ($C_{12.5}F_{27}$), poly(dimethylsiloxane) (PDMS) and $C_{12.5}F_{27}$ or C_8F_{18}, and alkanes with poly(ethylene glycol) all exhibit an apparent $M_n^{-2/3}$ dependence on molecular weight (where M_n is the number average molecular weight), similar to what has been found for homopolymer surface tension.[8]

This similarity is predicted by several empirical theories which relate interfacial tension to the pure component surface tensions.[11,12] A number of thermodynamic theories[13–20] have appeared that predict the interfacial tensions of polymer blends. The applicability of these theories has been discussed in detail in several review articles.[5,7,8,21,22] To date, these theories have not been compared to data

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Table I
Characteristics of the Materials

	M_n	M_w/M_n	chemical structure 1,4	chemical structure 1,2	hydrogenatn, %
PDMS 770[a]	770	2			
PDMS 1250[a]	1250	2			
PDMS 2000[a]	2000	2			
PDMS 3780[a]	3780	2			
PBD 1000[b]	982	1.07	49 (trans); 32 (cis)	14	
PS 1790[c]	1790	(M_v = 2111)			
PS 2200[b]	2200	1.06			
PS 4000[b]	4000	1.04			
PS 9000[b]	9000	1.06			
PS 10200[b]	10200	1.07			
PS 34500[c]	34500	1.05			
PS 41260[d]	41260	1.05			
PS 43700[d]	43700	1.18			
PBDH 4080[d]	4080	1.04		91	100
PMMA 1000[e]	10000	1.05			

[a] Petrarch Systems, Inc. [b] Polysciences, Inc. [c] Polymer Laboratories, Ltd. [d] Synthesized in house. [e] Supplied by Dr. R. Khanna of E. I. du Pont de Nemours & Co.

with systematic changes in molecular weight and temperatures. In general, the theories either assume infinite molecular weight or do not reproduce the observed empirical $M_n^{-2/3}$ dependence. Several theoretical treatments, valid near the critical temperature, lead to a predicted $M_n^{-1/2}$ dependence.[19,22]

In this paper, the effect of temperature and molecular weight on the interfacial tension is studied for three binary polymer blend systems: polystyrene (PS) with poly(methyl methacrylate) (PMMA); poly(dimethylsiloxane) (PDMS) with 1,4-polybutadiene (PBD); and polystyrene (PS) with hydrogenated 1,2-polybutadiene (PBDH). The experimental data for PS/PBDH blends are compared to the predictions of Helfand and co-workers[13,14] and to a theory based upon an extension[23] of the square gradient theory.[24]

Experimental Section

Materials. Trimethylsiloxy-terminated PDMS (Petrarch Systems, Inc.) 1,4-polybutadiene (Polysciences, Inc.), poly(methyl methacrylate), and polystyrene (Polysciences, Inc. and Polymer Laboratories, Ltd.) were used as received. Their characteristics, quoted from the suppliers, are listed in Table I. The PMMA was prepared by group transfer polymerization and was provided by Dr. R. Khanna of E. I. du Pont de Nemours & Co. The 1,2-polybutadiene polymer was anionically synthesized in our laboratory. The reaction was carried out at room temperature in benzene under high-purity argon using a glass manifold equipped with Teflon valves. *n*-Butyllithium (*n*-BuLi) was the initiator and dipiperidinoethane[25] was used as a modifier at a molar ratio of 10:1 (modifier:initiator) to produce homopolymers with mainly 1,2-butadiene isomer. A homogeneous catalytic reaction was adapted from a method described by Falk[26] to saturate the butadiene sequences. The catalyst used was a complex of *n*-BuLi and the cobalt salt of 2-ethylhexanoic acid in cyclohexane. A molar ratio of Li/Co of 2.5 was found necessary for the reaction to go to completion. The hydrogenation reaction was carried out at 50 °C and 50–60 psi reactant gas pressure with stirring for 1–4 h. More details on the synthesis procedure are given by Quan.[27] The microstructure of the butadiene sequence and the extent of the hydrogenation reaction were evaluated by proton nuclear magnetic resonance spectroscopy. The M_n and the molecular weight distributions were estimated by using gel permeation chromatography using a calibration curve by Quan.[27] The characteristics of the PBDH 4080 are given in Table I.

The densities, necessary to calculate interfacial tension, were measured for PDMS, PBD, and PBDH with a digital density meter (Mettler Instrument Corp., Model DMA45, DMA46, and external cell DM4512) capable of measuring density as a function of temperature to five significant digits. The densities depend approximately linearly on temperature. The results of linear regression are expressed in the following empirical equations which are used for the purpose of interpolation:

$$\text{PDMS 770:}\quad \rho = 0.94762 - 9.968 \times 10^{-4}t$$

$$\text{PDMS 1250:}\quad \rho = 0.96093 - 9.158 \times 10^{-4}t$$

$$\text{PDMS 2000:}\quad \rho = 0.98006 - 9.384 \times 10^{-4}t$$

$$\text{PDMS 3780:}\quad \rho = 0.99773 - 1.055 \times 10^{-3}t$$

$$\text{PBD 1000:}\quad \rho = 0.88787 - 5.358 \times 10^{-4}t$$

$$\text{PBDH 4080:}\quad \rho = 0.88395 - 5.267 \times 10^{-4}t$$

with ρ in g/cm^3 and t in °C. The density data of Bender and Gaines[28] and Fox and Flory[29] are used for PS. For PMMA, the density data of Somani[30] were employed.

Interfacial Tension Measurements. Interfacial tensions were measured by using an automated pendant drop apparatus which utilizes video digital image processing techniques.[31] A fluid pendant drop of the more dense constituent is formed at the tip of a glass capillary tube of a Drummond positive displacement syringe. The syringe is inserted into a fluid matrix of the second polymer which is contained in a quartz microcuvette. The microcuvette is placed in a Rame-Hart C-2033 environmental chamber under argon atmosphere. The temperature of the chamber is controlled to within 1 °C.

The optical system consists of a Quester M1 microscope coupled to an NEC TI-22A CCD video camera. The optics are focussed by optimizing the video image of a reticle containing a finely ruled grid that is placed at the drop location. The grid also serves in determination of the actual magnification of the instrument.

The video image of the drop is digitized by a Tecmar Video Van Gogh frame grabber board resident within an IBM XT microcomputer. The resulting image is analyzed by using global thresholding[32] and near-neighbor analysis to extract the experimental profile.

The equilibrium profile of a pendant drop can be expressed by the dimensionless set of equations[33]

$$\frac{d\phi}{dS} = \frac{2}{B} + Z - \frac{\sin\phi}{X} \tag{1a}$$

$$\frac{dX}{dS} = \cos\phi \tag{1b}$$

$$\frac{dZ}{dS} = \sin\phi \tag{1b}$$

which is solved with boundary conditions applied at the drop apex.

$$X(0) = Z(0) = \phi(0) = 0 \tag{1d}$$

The dimensionless variables are defined as $X = x\sqrt{c}$, $Z = z\sqrt{c}$, $S = \sqrt{c}$, and $B = b\sqrt{c}$. The shape of the drop is specified in terms of the x and z coordinates, the arc length s, the angle ϕ between a tangent to the drop profile and the horizontal axis, at a point (x,z), and the radius of curvature at the drop apex, b. The shape factor B is defined as

$$B = b\sqrt{c} = b\left(\frac{\Delta\rho g}{\gamma}\right)^{1/2} \tag{2}$$

where γ is the interfacial tension, g is the gravitational constant, and $\Delta\rho$ is the mass density difference across the interface.

The experimental profile is analyzed with a robust shape comparison algorithm,[31] which is resistant to outlying points that may result during the computerized drop profile discrimination procedure. In addition these routines minimize the number of parameters that must be searched numerically in the subsequent optimization (i.e., shape comparison). Images of the drop are recorded every ca. 20 min for a period of time of ca. 2 h. When the calculated interfacial tension does not change with time, equilibrium is considered to be attained. The experimental points represent the average of measurements for a minimum of four different drops. Approximately 30 min is allowed prior to each measurement for the establishment of thermal equilibrium. Figure

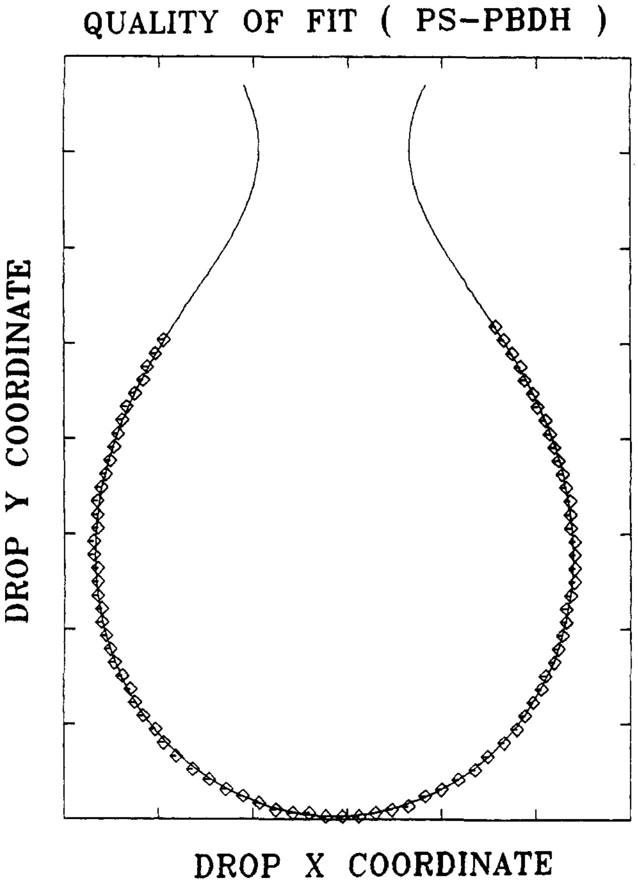

Figure 1. Quality of the fit obtained after the application of the algorithm to the experimental profile for a PS drop in PBDH. Solid line is the theoretical profile, and the data points denote the original segmented experimental drop profile.

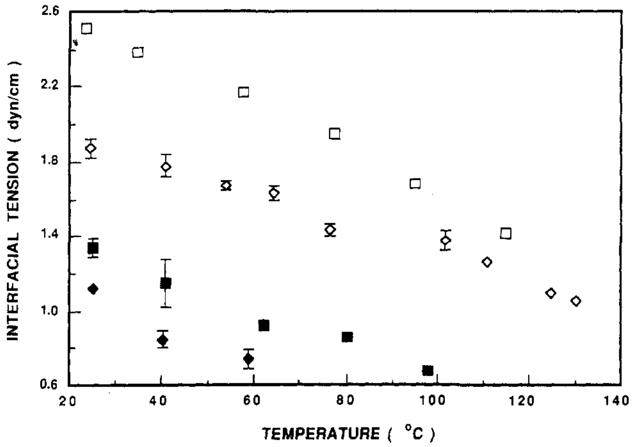

Figure 2. Experimental interfacial tension as a function of temperature for PBD/PDMS pairs. Open squares, PBD 1000/PDMS 3780; open diamonds, PBD 1000/PDMS 2000; filled squares, PBD 1000/PDMS 1250; filled diamonds, PBD 1000/PDMS 770.

1 shows the quality of the fit obtained for a PS drop in a matrix of PBDH.

Table II
Temperature Dependence of Interfacial Tension for PBD 1000/PDMS

	$\gamma = a - bt$	
polymer pair	a, dyn/cm	b, dyn/(cm °C)
PBD 1000/PDMS 770	1.34	1.06×10^{-2}
PBD 1000/PDMS 1250	1.54	9.38×10^{-3}
PBD 1000/PDMS 2000	2.06	7.54×10^{-3}
PBD 1000/PDMS 3780	2.82	1.19×10^{-2}

Table III
Temperature Dependence of Interfacial Tension for PS/PBDH 4080

	$\gamma = a - bt$	
polymer pair	a, dyn/cm	b, dyn/(cm °C)
PS 2200/PBDH 4080	3.71	1.48×10^{-2}
PS 4000/PBDH 4080	3.75	1.12×10^{-2}
PS 10200/PBPH 4080	3.83	8.82×10^{-3}

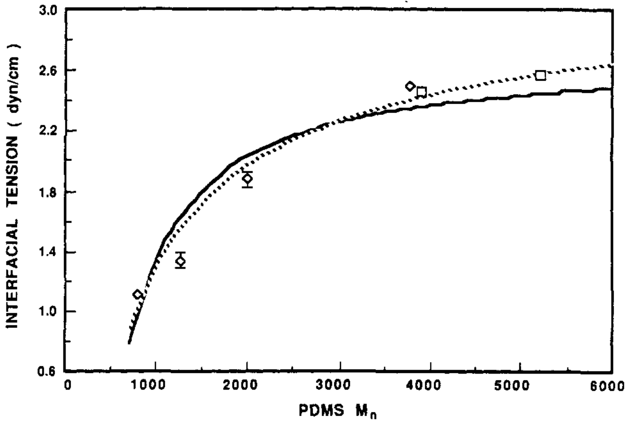

Figure 3. Experimental interfacial tension (25 °C) between PDMS and PBD 1000 as a function of PDMS M_n: open diamonds, these measurements; open squares, data taken from Anastasiadis et al.[23] Solid line represents the best fit to a M_n^{-1} dependence; dotted line is the fit for a $M_n^{-0.5}$ dependence.

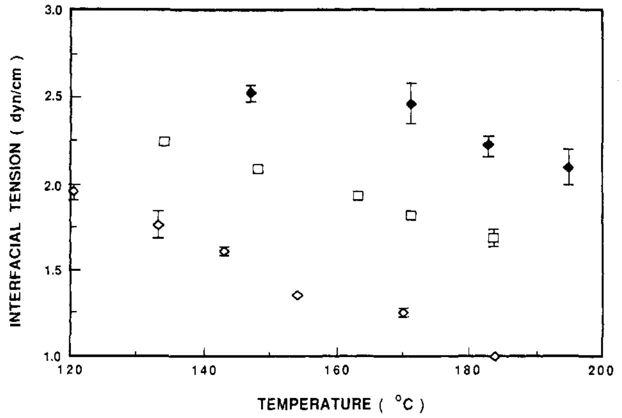

Figure 4. Experimental interfacial tension as a function of temperature for PS/PBDH pairs: filled diamonds, PS 10200/PBDH 4080; open squares, PS 4000/PBDH 4080; open diamonds, PS 2200/PBDH 4080.

Results and Discussion

Interfacial Tension Data. The interfacial tension data for the four PBD/PDMS pairs as a function of temperature are shown in Figure 2. In this figure and the figures that follow, the error bars indicate the standard deviations of the data. If no error bar is shown, the standard deviations is within the size of the symbol denoting the data point. Interfacial tension decreases almost linearly with temperature in the range 25–125 °C. The temperature coefficients (Table II) are of the same magnitude as those reported for other polymer pairs.[34] The data also exhibit an increase in interfacial tension as the molecular weight of the polymer increases. Figure 3 illustrates the effect of PDMS molecular weight on interfacial tension (at 25 °C) for constant molecular weight of PBD (M_n = 982).

The interfacial tension data for the PS/PBDH system appear in Figure 4. A linear decrease with temperature and an increase with M_n are also observed. The least squares linear fits of the data are given in Table III. In-

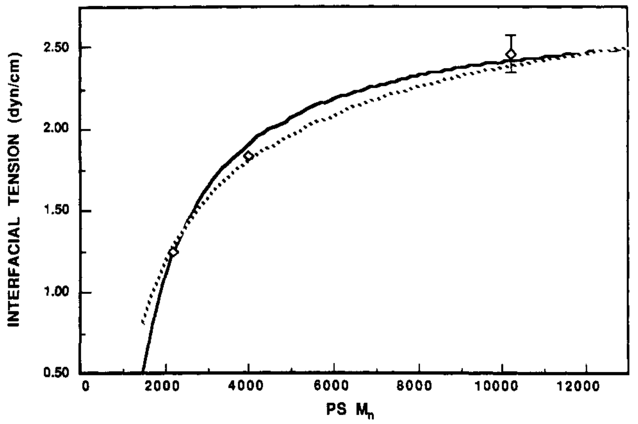

Figure 5. Experimental interfacial tension between PS and PBDH 4080 as a function of PS M_n at 171 °C. Solid line represents the best fit to a M_n^{-1} dependence; dotted line is the fit for a $M_n^{-0.5}$ dependence.

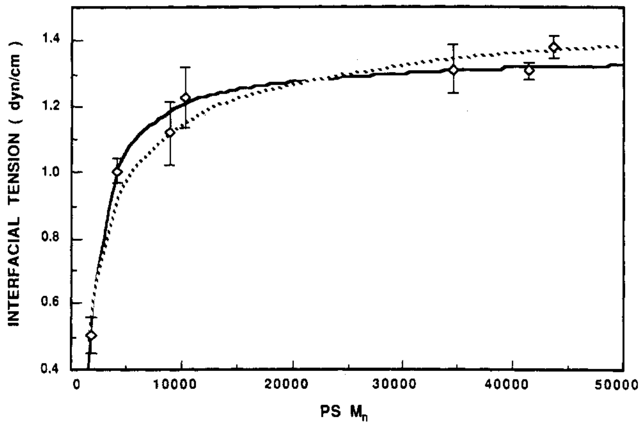

Figure 6. Experimental interfacial tension between PS and PMMA 10000 as a function of PS M_n at 199 °C. Solid line represents the best fit to a M_n^{-1} dependence; dotted line is the fit for a $M_n^{-0.5}$ dependence.

terfacial tensions at 171 °C for PS of various molecular weights and PBDH of a fixed molecular weight are given in Figure 5. Similar behavior is observed for other temperatures. Interfacial tensions for the PS/PMMA system (Figure 6) cover the broadest range of molecular weight. The precision in these measurements (standard deviation is ca. 6%) is the lowest of the three systems due to the high viscosities.

The interfacial tension data for all three systems appear to correspond well to the empirical $M_n^{-2/3}$ expression proposed by Gaines and co-workers,[9,10] at least based upon the criteron of apparent linearity in plots of γ vs $M_n^{-2/3}$. A more rigorous estimation of the power law of the molecular weight dependence was obtained by performing nonlinear least-squares regression of the data upon an expression of form $\gamma = C_1 - C_2/M_n^z$. This analysis yielded the following values for the exponent z: 0.54 for PDMS/PBD at 25 °C; 0.68 for PS/PBDH at 171 °C; and 0.90 for PS/PMMA at 199 °C. A smaller exponent for PDMS/PBD could be explained by the occurrence of surface fractionation of the polydisperse PDMS according to molecular weight. Surface tension data for mixtures of PDMS oligomers suggest that the lower molecular weight species are concentrated at the surface.[35] The other materials, on the other hand, are relatively monodisperse. In addition, surface analyses of bimodal molecular weight blends of polystyrene failed to document surface fractionation of the low molecular weight species.[36,37] Alternatively, the PDMS/PBD system is closest to its critical point, and in proximity to the critical point an $M_n^{-0.5}$ dependence of interfacial tension has been predicted.[19,22] The PS/PBDH system shows good correspondence with the $M_n^{-2/3}$ dependence. A similar dependence for the surface tension has been explained by using a simple lattice analysis[38] that incorporates the contribution of the end groups at the interface. For these moderate molecular weights, the end-group effects are important and an $M_n^{-2/3}$ dependence might be expected.[39] The PS/PMMA blends, on the other hand, contain the highest molecular weight constituents and should thus conform best to the limit of infinite molecular weight. In this limit, the exponent z is predicted to be unity.[40]

The nonlinear regression results, therefore, suggest that the exponent z of the molecular weight dependence of polymer–polymer interfacial tension increases as the molecular weight of the constituents increases. There is theoretical support for this trend; however, we should emphasize that the precisions of the present data are not sufficient to quantitatively substantiate the trend. This is illustrated in Figures 3, 5, and 6 where we have plotted the best fits to the data assuming either $z = 0.5$ (dotted lines) or $z = 1.0$ (solid lines). Both relations yield predictions that fall within the experimental errors.

Comparison with Theory. Helfand and Tagmi[13] derived an expression for polymer–polymer interfacial tensions by performing a self-consistent mean field solution of a segmental diffusion equation across the interface. In the limit of infinite molecular weight they obtained the following closed form expression valid for symmetric polymers

$$\gamma = (\chi/6)^{1/2}\rho_0\, bkT \tag{3}$$

where χ is the Flory-Huggins interaction parameter, ρ_0 the number average monomer density, b the Kuhn statistical segment length, k Boltzmann's constant, and T the temperature in K. Helfand and Sapse[14] removed the restriction of property symmetry and obtained

$$\gamma = kT(\rho_0\chi)^{1/2}\left[\frac{\beta_A + \beta_B}{2} + \frac{1}{6}\left(\frac{\beta_A - \beta_B}{\beta_A + \beta_B}\right)^2\right] \tag{4}$$

with $\beta_i = \rho_i b_i$ for species i equal to A or B. Helfand[15] and Roe[16] have separately developed interfacial tension theories that are based on lattice models in the spirit of the Flory–Huggins approach.[41] Experimental verification of the lattice theories are difficult however, since the parameters of the lattice are unknown a priori.

Comparison of our experimental data with the predictions of the Helfand theories requires knowledge of ρ_0, b, and χ. ρ_0 is obtained from the experimental density data, while Kuhn statistical segment lengths are calculated from tabulated characteristic ratios.[42]

There are no literature data on the Flory–Huggins interaction parameter for the PBD/PDMS blend, and our previous attempts to model this system, employing the regular solution theory estimation of χ using literature values of the solubility parameter, were not successful.[23] The Flory–Huggins interaction parameter and its temperature dependence for the PS/PBDH system was previously calculated[43] by small-angle X-ray scattering analysis of homogeneous poly(styrene-*b*-(hydrogenated 1,2-butadiene)) diblock copolymers, using the theory of Leibler.[44] The interaction parameter obtained from the analysis is given by

$$\chi = \chi_S + \chi_H/T \tag{5}$$

where $\chi_S = 0.0057$, $\chi_H = 21.0$, and T is the absolute temperature. This functional form of the interaction parameter is consistent with the notion that χ may be written

Table IV
Literature Interaction Parameter Data

system	diene microstructure			$10^3\alpha$, mol/cm^3 [g]	χ	ref
	1,2	1,4	3,4			
PS/PI[a]		90	10	$-0.9 + 750/T$		50
P(S-*b*-I)[b]		93	7	$0.1055 + 293/T$[h]	$0.0090 + 25/T$	43
P(S-*b*-I)[b]	38	3	59		$-0.0937 + 66/T$	48
PS/PBD[c]	23	77		$-0.9 + 750/T$		50
PS/PBD[c]	6	94		$-1.05 + 537/T$		49
P(S-*b*-BD)[d]	95	5			$-0.021 + 25/T$	43
P(S-*b*-BD)[d]	unspecified				$-0.027 + 28/T$	51
PS/PBD[c]	14	81			$-0.2024 + 116/T$	18
P(S-*b*-BDH)[e]	95	5			$0.0057 + 21/T$	43
PS/PBDH[f]	95	5		$-1.61 + 894/T$[i]	$-0.1296 + 73/T$[j]	

[a] PS = polystyrene; PI = polyisoprene. [b] P(S-*b*-I) = poly(styrene-*b*-isoprene) diblock copolymer. [c] PBD = polybutadiene. [d] P(S-*b*-BD) = poly(styrene-*b*-butadiene) diblock copolymer. [e] P(S-*b*-BDH) = polystyrene-*b*-(hydrogenated 1,2-butadiene)) diblock copolymer. [f] PBDH = hydrogenated 1,2-polybutadiene. [g] $\alpha = \chi\rho_M$ with ρ_M is the average molar density in mol/cm^3. [h] Calculated from the measured χ with ρ_M = 0.01172 mol/cm^3. [i] Calculated by using the experimental densities and χ. [j] Calculated by using Helfand–Tagami theory with experimental interfacial tension data.

as the sum of an enthalpic and an entropic contribution. Refinements of the original Flory–Huggins equation[41] suggest that χ embraces all the changes in the enthalpy and the noncombinational entropy upon mixing.[45–47] Noncombinatorial contributions to the entropy of mixing arise, for example, from positive or negative volumes of mixing and changes in coil expansion/chain rigidity in the mixture. Also the changes of order that accompany the contact energy effect lead to a noncombinatorial entropy of mixing contribution. Expressions of the above form have already been reported for polystyrene–polydiene systems.[48–51]

A comparison of the predictions of the theories by Helfand et al. with our experimental data appears in Figure 7. Since the theory explicity assumes infinite molecular weight, we show only the comparison for the blend with highest constituent molecular weights (PS 10200/PBDH 4080). The experimental interaction parameters represented by (5) were used in this calculation. The magnitude of the theoretical predictions corresponds well with the experimental data. The theoretical interfacial tensions are found to increase with increase in temperature, however, opposite to the behavior of the experimental data.

Two of the possible causes of the observed discrepancy between the experimental and the predicted interfacial tensions involve assumptions inherent to the calculation. First of all, we have previously stated that the theory explicitly assumes infinite molecular weight. Therefore, application of the theory to our data of relatively low molecular weight materials may not be appropriate. Secondly, we have assumed that the interaction parameter determined for diblock copolymers properly describes the interactions between the corresponding two homopolymers in an immiscible blend.

Examination of literature expressions for experimental interaction parameters suggests that the latter assumption may not be valid. Although experimental interaction parameters for binary homopolymer blends and diblock copolymers both seem to correspond to the relationship described in eq 5, there appears to be a discernible difference in the behavior of the temperature independent term for the two types of systems. The origin of this term is generally ascribed to noncombinatorial entropy effects which are not accounted for in Flory–Huggins theory, as discussed earlier in this communication. There are not many data currently available in the literature that can permit detailed comparison between interaction parameters calculated from diblock copolymers and from the respective homopolymer blends. To our knowledge all χ_S values that have been reported for block copolymers have been found to be much smaller in magnitude than the corresponding values for binary homopolymer blends.

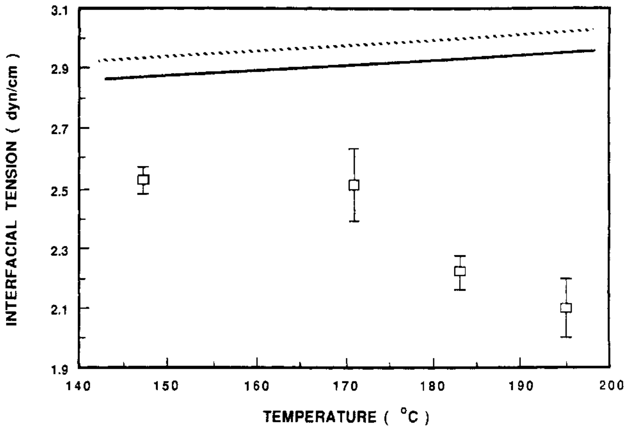

Figure 7. Comparison of experimental interfacial tension (points) for PS 10200/PBDH 4080 with Helfand theories: solid line, Helfand–Tagami,[13] eq 4; dashed line, Helfand–Sapse,[14] eq 5.

A compilation of some of the available data is shown in Table IV. For the polystyrene–polyisoprene system, for example, the α_S term varies from -0.9×10^{-3} for the binary blend[50] to $+0.1 \times 10^{-3}$ for a similar diblock copolymer.[43] As pointed out by Rounds,[50] the parameter α_S represents an excess entropy of mixing over the combinatorial entropy alone. A negative value specifies that the mixture has greater excess entropy than the pure components. From Table IV, it appears that this excess entropy is lower for diblock copolymers than for binary polymer blends. This result may be attributed to the additional entropy constraints intrinsic to block copolymers that are associated with the covalent bond between unlike sequences.

As an alternative to using our experimental expression for χ from the P(S-*b*-BDH) diblocks in the Helfand–Tagami theory, we have applied the theory directly to our data to extract apparent χ values that would make these data meet the theoretical prediction.

The apparent χ values (Figure 8) do correspond qualitatively to the form of expression 5 but differ substantially from the diblock copolymer χ data. Regression of the apparent χ parameter data, however, gives an expression which is in good agreement with data for the other binary blends (Table IV). For the range of temperatures accessible to most experiments, these apparent χ values are larger than those found for PS/PBD, consistent with the observation that in diblock copolymers, a hydrogenated diene sequence (PBDH) is less miscible with polystyrene than the original PBD sequence.[43]

As we have previously discussed, a thorough comparison of our results with the Helfand theories is not possible, due to the assumption of infinite molecular weight inherent to the calculation. The effect of molecular weight on interfacial tension can be calculated however by applying an approach[23] based upon an extension of the square gradient approach of van der Waals[52] as modified by Cahn and Hilliard.[24]

Such an approach has been used to model the surface tensions of liquids[53] and polymer melts,[54-56] polymers at the liquid–liquid interfaces in biphasic regular binary solutions,[57] interfacial tensions of low and high molecular weight liquid mixtures[17] and demixed polymer solutions,[58] and spinodal decomposition in polymer blends.[18,59] Sanchez[60] has shown that the gradient theory is "in harmony with the microscopic theory of Helfand and co-workers although the latter treats polymer interfaces from a completely different point of view".

The basis of the theory is the assumption that the free energy per unit volume in a region of nonuniform composition is a function of both the local composition ϕ and the composition of the immediate environment. The total free energy for the mixture of volume V is

$$G = \int_V [G_0(\phi) + \kappa(\nabla\phi)^2 + ...]\,\mathrm{d}V \tag{6}$$

where $G_0(\phi)$ is the free energy density of a uniform system of composition ϕ and $\kappa(\nabla\phi)^2$ is the additional positive contribution to the free energy arising from the local concentration gradient.

Following the development by Cahn–Hilliard,[24] the interfacial tension for the case of an one-dimensional composition change across a flat interface separating two coexisting phases α and β is given as

$$\gamma = 2\int_{\phi_\alpha}^{\phi_\beta} (\kappa\Delta g(\phi))^{1/2}\,\mathrm{d}\phi \tag{7}$$

where ϕ_α and ϕ_β are the volume fractions of the two coexisting phases and $\Delta g(\phi)$ is the excess free energy density of the uniform system with respect to a standard state of an equilibrium mixture of α and β, i.e.

$$\Delta g(\phi) = \Delta G_0(\phi) - [n_\mathrm{A}\Delta\mu_\mathrm{A}(\phi_\mathrm{e}) + n_\mathrm{B}\,\Delta\mu_\mathrm{B}(\phi_\mathrm{e})] \tag{8}$$

where n_A and n_B are the number density of molecules of type A and B, respectively, ϕ_e is the equilibrium composition of either of the coexisting phases, and $\Delta\mu_\mathrm{A}$ and $\Delta\mu_\mathrm{B}$ are the changes in chemical potentials of A and B. From the Flory–Huggins lattice model[41] for the free energy, it follows that

$$\Delta G_0/kT = n_\mathrm{A}\ln\phi + n_\mathrm{B}\ln(1-\phi) + \chi n_\mathrm{A}N_\mathrm{A}(1-\phi) \tag{9}$$

$$\Delta\mu_\mathrm{A}/kT = \ln\phi + (1-\phi)\left(1 - \frac{N_\mathrm{A}u_\mathrm{A}}{N_\mathrm{B}u_\mathrm{B}}\right) + \chi N_\mathrm{A}(1-\phi)^2 \tag{10}$$

$$\Delta\mu_\mathrm{B}/kT = \ln(1-\phi) + \phi\left(1 - \frac{N_\mathrm{B}u_\mathrm{B}}{N_\mathrm{A}u_\mathrm{A}}\right) + \chi N_\mathrm{B}\frac{u_\mathrm{B}}{u_\mathrm{A}}\phi^2 \tag{11}$$

with

$$\phi = \frac{n_\mathrm{A}N_\mathrm{A}u_\mathrm{A}}{n_\mathrm{A}N_\mathrm{A}u_\mathrm{A} + n_\mathrm{B}N_\mathrm{B}u_\mathrm{B}} \tag{12}$$

N_A and N_B are the respective degrees of polymerization and u_A and u_B the specific monomer volumes. The composition ϕ_α and ϕ_β of the coexisting phase α and β at equilibrium are found by equating the chemical potentials, such that

$$(\Delta\mu_\mathrm{A})_\alpha = (\Delta\mu_\mathrm{A})_\beta \qquad (\Delta\mu_\mathrm{B})_\alpha = (\Delta\mu_\mathrm{B})_\beta \tag{13}$$

The coefficient of the square gradient form can be derived by using linear response theory within the framework of the random phase approximation.[61-63] de Gennes[63] suggested that the coil remains ideal on the scale of one coil, even in the case of a dense mixture of interacting chains. Therefore, an ideal single chain approximation can be employed in the calculation of the scattering function, $S(q)$, where q is the scattering vector. The scattering function is related to the volume fractions and the chain length by[63-66]

$$\frac{1}{S(q)} = \frac{1}{\phi u_\mathrm{A}N_\mathrm{A}f_\mathrm{D}(N_\mathrm{A},q)} + \frac{1}{(1-\phi)u_\mathrm{B}N_\mathrm{B}f_\mathrm{D}(N_\mathrm{B},q)} - \frac{2\chi}{u_\mathrm{A}} \tag{14}$$

where $f_\mathrm{D}(N,q)$ is the Debye function,[67] defined as

$$f_\mathrm{D}(N,q) = \frac{2}{U^2}(U + \exp(-U) - 1) \tag{15}$$

with

$$U = N^2q^2b^2/6 = q^2\langle r_0^{\,2}\rangle/6 = q^2R_\mathrm{G}^{\,2} \tag{16}$$

where b is the Kuhn statistical segment length, $\langle r_0^{\,2}\rangle$ is the mean-squared end-to-end distance, and R_G is the radius of gyration.

Two limiting expressions for $S(q)$ can be calculated for $qR_\mathrm{G} \gg 1$ and $qR_\mathrm{G} \ll 1$. The first corresponds to a sharp interface, while the second corresponds to a relatively diffuse one. For $qR_\mathrm{G} \gg 1$, $f_\mathrm{D} \approx 12/Nq^2b^2 = 12/q\langle r_0^{\,2}\rangle$, and

$$\frac{1}{S(q)} = \frac{q^2}{12}\,\frac{\langle r_0^{\,2}\rangle_\mathrm{A}}{\phi u_\mathrm{A}N_\mathrm{A}} + \frac{\langle r_0^{\,2}\rangle_\mathrm{B}}{(1-\phi)u_\mathrm{B}N_\mathrm{B}} - \frac{2\chi}{u_\mathrm{A}} \tag{17}$$

whereas, for $qR_\mathrm{G} \ll 1$, $f_\mathrm{D} \approx N(1 - q^2\langle r_0^{\,2}\rangle/18)$, and using the equation for the spinodal curve

$$\frac{2\chi_\mathrm{S}(\phi)}{u_\mathrm{A}} = \frac{1}{N_\mathrm{A}u_\mathrm{A}\phi} + \frac{1}{N_\mathrm{B}u_\mathrm{B}(1-\phi)} \tag{18}$$

the scattering function is given by

$$\frac{1}{S(q)} = \frac{2(\chi_\mathrm{S}(\phi) - \chi)}{u_\mathrm{A}} + \frac{q^2}{18}\,\frac{\langle r_0^{\,2}\rangle_\mathrm{A}}{\phi u_\mathrm{A}N_\mathrm{A}} + \frac{\langle r_0^{\,2}\rangle_\mathrm{B}}{\phi u_\mathrm{B}N_\mathrm{B}} \tag{19}$$

Therefore the square gradient coefficient, $\kappa^{(\mathrm{i})}$, for the narrow interphase is

$$\frac{\kappa^{(\mathrm{i})}}{kT} = \frac{\langle r_0^{\,2}\rangle_\mathrm{A}}{24\phi u_\mathrm{A}N_\mathrm{A}} + \frac{\langle r_0^{\,2}\rangle_\mathrm{B}}{24(1-\phi)u_\mathrm{B}N_\mathrm{B}} \tag{20}$$

and the coefficient, $\kappa^{(\mathrm{ii})}$, applicable to the broad interphase case is

$$\frac{\kappa^{(\mathrm{ii})}}{kT} = \frac{\langle r_0^{\,2}\rangle_\mathrm{A}}{36\phi u_\mathrm{A}N_\mathrm{A}} + \frac{\langle r_0^{\,2}\rangle_\mathrm{B}}{36(1-\phi)u_\mathrm{B}N_\mathrm{B}} \tag{21}$$

Equation 21 and its equivalent for a symmetric system have been widely used[18,59,62,64,66] to model the dynamics of concentration fluctuations in binary polymer blends near the critical point, whereas eq 20 has been used to study micelle formation in homopolymer copolymer mixtures.[65]

A comparison between the predictions of the square gradient theory approach and our experimental interfacial tensions for the PS 10200/PBDH 4080 system is shown in Figure 9. The experimental values of χ given by eq 5 were used in the calculations. The predicted interfacial tensions compare remarkably well with our data for the coefficient of the square gradient term, κ, given by eq 20 and are within 20% of the experimental data for the coefficient κ given by eq 21. Note that, no adjustable

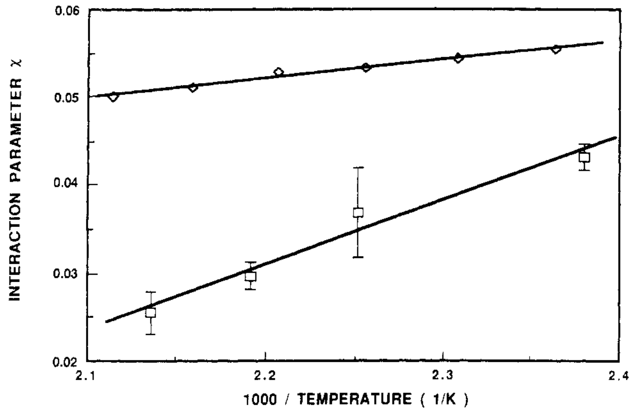

Figure 8. Comparison of interaction parameter data of Owens[43] (diamonds) with values obtained from Helfand–Tagami theory[13] (squares) using experimental interfacial tension data.

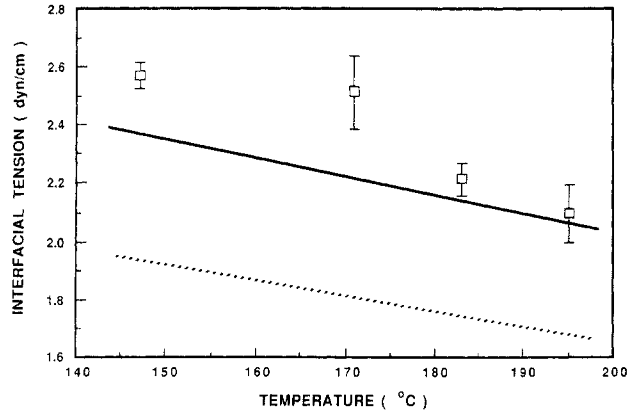

Figure 9. Comparison of experimental interfacial tension (data points) for PS 10200/PBDH 4080 with the square gradient theory. The square gradient coefficient is given by eq 20 (solid line) and eq 21 (dotted line).

parameters were allowed in this comparison.

The theory was also examined with respect to its ability to predict the molecular weight dependence of interfacial tension. In Figure 10 the predictions of the theory are compared to our PS/PBDH 4080 systems at a temperature of 171 °C. The representation in terms of the $M_n^{-2/3}$ dependence was adopted because it conforms closely with the result from nonlinear regression. At high molecular weights, with use of eq 21 for the coefficient κ, the theoretical curve corresponds well with the extrapolated empirical relationship for the experimental data, while use of eq 20 leads to an overestimation of interfacial tension by ca. 20%. Adjustable parameters were *not* allowed in this comparison. The theory does predict an apparent dependence of interfacial tension on $M_n^{-2/3}$, where M_n is the number average molecular weight, however, it deviates considerably from the experimental data for low molecular weights. The predictions of the theory are physically unrealistic for low molecular weights, since they erroneously indicate complete miscibility (i.e., $\gamma = 0$) for a PS molecular weight of ca. 2400. During our experiments, however, two phases were always present under these conditions, and appreciable mixing was not observed. Similarly, when the theory was applied to a PS 2200/polybutadiene ($M_n = 7800$, $M_w/M_n = 1.02$, 95% 1,2) blend, with interaction parameter values measured by Owens[43] from the respective copolymer, misibility was erroneously predicted at 145 °C; two phases were present however, during our interfacial tension measurements.[68]

The inability of the theory to predict the proper critical molecular weight does not necessarily indicate inadequacy of the square gradient approach but implies failure of the Flory–Huggins free energy expression. Therefore, within the framework of Flory–Huggins theory, it again appears that the use of χ values determined for diblock copolymers is inappropriate in describing the interactions in polymer blends.

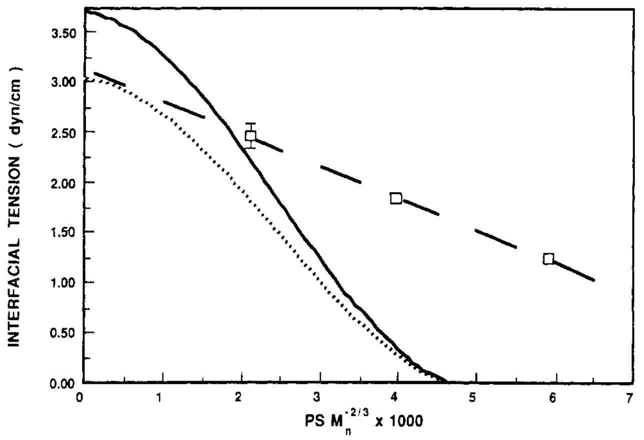

Figure 10. Comparison of experimental interfacial tension (data points) for PS/PBDH 4080 at 171 °C with the square gradient theory. The square gradient coefficient is given by eq 20 (solid line) and eq 21 (dotted line). The dashed line is the linear fit of the data.

There may also be deficiencies associated with the use of the square gradient theory itself. Halperin and Pincus[57] pointed out that because the Cahn–Hilliard theory is a mean-field theory, its validity near the critical point is only qualitative. On the other hand, the theory assumes weak composition gradients that may be realized only close to the critical region. Binder[64] suggested that for the $qR_G \gg 1$ case, an additional correction term should be included in the gradient term, which arises from the finite range of interactions, and is proportional to $\chi\psi^2(\Delta\phi)^2$ where ψ is the range of interactions. For $\chi < 1$, however, this correction term is negligible as suggested by de Gennes.[62] He also argues that eq 21 describes well the additional positive contribution to the free energy from the local concentration gradients, even in the case $\chi \gg \chi_c$ (χ_c is the value of the interaction parameter at the critical point), i.e., in the strong segregation limit. Additionally, polymer molecules in the interfacial region are limited in their allowable configurations and subsequently suffer a loss of configurational entropy.[69] If the interface is broad relatively to the molecular size, these effects are minimal and the square gradient coefficient represented by eq 21 or a slightly modified form of eq 21 is appropriate. In the narrow interface limit, however, both entropic and energetic contributions should be included in the gradient term. For low molecular weights, both these contributions are important, since nonlocal entropic contributions are comparable in magnitude to the nonlocal enthalpic contributions.[39,40,70] Meier[39] suggested that more explicit interfacial constraints should be included to describe the loss of configurations at the narrow interface limit.

Even with these uncertainities, however, we are encouraged by our present results. To our knowledge, the square gradient theory is the first thermodynamic theory to predict an apparent $M_n^{-2/3}$ dependence of interfacial tension, and the first to successfully reproduce the temperature dependence of interfacial tension.

Concluding Remarks

The preceding discussion points out several problems associated with the establishment of a fundamental understanding of interfacial tensions in immiscible binary homopolymer blends. A number of further developments, both theoretical and experimental, are required to overcome these problems.

The most essential experimental requirement is the knowledge of the interaction parameter, χ, for the actual system being studied. Procedures for the determination of χ parameters in binary homopolymer blends have been discussed by Riedl and Prud'homme.[71] Most methods developed to date require either knowledge of the binodal curve of the phase diagram or accessibility to the miscible state. Attainment of these conditions for most polymer pairs restricts the materials to be of rather low molecular weight. As mentioned earlier, the interfacial tension measurements are subject to this same constraint.

Statistical thermodynamic theories, on the other hand, have been solved primarily for the case of infinite molecular weight. The theories based upon the square gradient framework can be applied to low molecular weight mixtures but do not appropriately consider the loss of configurations available to the chains in the interphase region. Thus in order to compare theoretical predictions to *accessible* experimental data, one must either solve the statistical thermodynamic theories for finite molecular weight or develop a more rigorous square gradient theory which considers all of the appropriate constraints of the chains in the interphase. These refined theories could be compared directly to accessible experimental data on polymer–polymer interfacial tension.

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