The Effect of End Groups on Thermodynamics of Immiscible Polymer Blends. 1. Interfacial Tension

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ABSTRACT: Interfacial tension is measured for immiscible blends of poly(butadiene) (PBD) and poly(dimethylsiloxane) (PDMS) as a function of molecular weight and end group type of the siloxane. Blends containing amine-terminated PDMS (PDMS-NH_2) show reduction in interfacial tension by as much as 30% compared to blends containing methyl-terminated PDMS (PDMS-CH_3). Interfacial tensions for blends of PBD against mixtures of PDMS-CH_3 and PDMS-NH_2 are linearly dependent on the amine content, indicating an absence of any significant surfactant effect for the lower interfacial energy aminated component. The interfacial tension reduction observed for the amine-terminated systems is therefore attributed to changes in the bulk interactions resulting from end group substitution. These changes are qualitatively explained through binary interaction theory by considering the PDMS as a copolymer of chain backbone and end group units. Interfacial tensions for blends of fixed molecular weight PBD against high molecular weight PDMS (both methyl and amine terminated) are found to follow the relationship: $\gamma = \gamma_0 - k/M_n$, where M_n is the number-average molecular weight of the PDMS and γ_0 is a parameter related to the interfacial tension for infinite molecular weight PDMS, which is independent of end group type, while k is a parameter that is found to depend strongly on the end group type, but is a constant for a particular end group. The observed experimental scaling behavior compares favorably with quantitative theoretical predictions proposed by Anastasiadis, Gancarz, and Koberstein, and by Broseta, Fredrickson, Helfand, and Leibler.

Introduction

Interfacial modification in immiscible polymer blends is an area of intense research and rapid growth. Control of the interfacial tension between two immiscible polymers is important because it governs the dispersed phase size and the adhesion between the two phases. It is well-known that addition of a block copolymer to an immiscible polymer blend results in reduction of interfacial tension and, therefore, a reduction in dispersed phase size.[1-4]

The purpose of this paper is to explore the concept of end group control to modify polymer/polymer interfaces. There are many advantages to this concept. The effect of end groups on the bulk properties of the polymer are small, whereas their effect on the interfacial properties may be much greater. The end group effect on bulk physical properties, such as density and yield strength, typically follows the relationship:[5,6]

$$P = P_\infty - k_b/M_n \tag{1}$$

where P is a bulk property, P_∞ is the bulk property at infinite molecular weight, and k_b is a constant which is typically small, in the range of 5-50 for density, for example.

Similar scaling relations for polymer-air melt surface tension have been proposed to be of the form:

$$\sigma = \sigma_\infty - k_\sigma M_n^{-z} \tag{2}$$

where σ_∞ is the infinite molecular weight surface tension, k_σ is a constant for a particular end group type, and z is a scaling exponent found to lie in the range of 2/3 to 1.0.[7-9] Recently, surface tension for high molecular weight polymers has been shown to scale with M_n^{-1} for PDMS and other polymeric materials.[8-10] Experimental work of Jalbert et al.[10] demonstrates that the value of k_σ depends strongly on the end group type and, therefore, that polymer surface tension can be controlled to a certain extent through end group modification. The purpose of this paper is to determine if end groups have similar effects on polymer-polymer melt interfacial tension.

Interfacial tension has been found to scale with molecular weight according to expressions of the form:

$$\gamma = \gamma_\infty - k_{\gamma A}(M_n)_A^{-x} - k_{\gamma B}(M_n)_B^{-x} \tag{3}$$

where γ_∞ is the interfacial tension at infinite molecular weight and $(M_n)_A$ and $(M_n)_B$ are the molecular weights of polymers A and B, respectively. The magnitude of the constants $k_{\gamma A}$ and $k_{\gamma B}$ for polymer A and B, respectively, are typically large, in the range of 100-400. Values for the scaling exponent, x, ranging from 0.5 for blends near their consolute temperature to 1.0 for high molecular immiscible blends have been observed experimentally or predicted from theory.[11-15] If the magnitudes of these constants depend on the end group type, it should be possible to manipulate end groups in order to modify interfacial properties, while changing bulk properties only slightly.

Experimental measurements provide preliminary evidence that end groups do influence polymer-polymer melt interfacial tension values. End group substitution was found to influence the interfacial tensions of n-alkanes against water.[15] Addition of carboxyl end groups or side groups and amine side groups to a poly(dimethylsiloxane) (PDMS) chain resulted in a reduction of the interfacial tension between PDMS and poly(ethylene oxide).[1] Similar interfacial tension reduction was observed upon addition of amine end groups to PDMS in a PBD/PDMS immiscible blend.[16]

In this first paper, the effect of aminopropyl end groups of α,ω-functionally terminated PDMS on the interfacial tension between PDMS and poly(butadiene) (PBD) is

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Table I. Molecular Weight Characteristics of PDMS Materials[a]

PDMS-CH_3: absolute M_n	size exclusion chromatography[b] M_n	size exclusion chromatography[b] M_w/M_n	vapor-phase[a] osmometry M_n
890[c]		1.10	890 ± 156
1120[c]	1270	2.22	1120 ± 37
1270[c]	1310	1.17	1270 ● 110
2200[c]		1.51	2200
4580[c]	3410	1.39	4580 ± 140
3630[d]	2700	1.91	3630
10K[d]	5870	1.78	10000
19.6K[d]		3.24	19600

[a] Errors are half the measurement range ($R/2$) for two or three measurements. [b] Based on polystyrene standards. [c] Source: Petrarch. [d] Source: Virginia Polytechnic Institute.

investigated. The PBD/PDMS system can be considered to be immiscible, as a result of the large solubility parameter difference. This is supported by measurements of the cloud point curves for low molecular weight PDMS materials (M_n of 890–1310) with poly(isoprene) (M_n of 1250), as will be discussed in the second paper[17] in this series. Interfacial tension is measured using pendant drop tensiometry, as a function of PDMS molecular weight for amine- and methyl- (standard) terminated PDMS. In addition, interfacial tension is measured using different amounts of amine-terminated PDMS (PDMS-NH_2) in the standard methyl-terminated PDMS (PDMS-CH_3) phase to determine whether end group-modified PDMS exhibits surfactant activity. Interaction parameters, estimated in the paper that follows,[17] are used to predict the interfacial tension using current theories.[13,14]

Experimental Section

Materials. PBD from Polysciences, Inc. (M_n of 1000, M_w/M_n of 1.07), PBD from Nissho Iwai (M_n of 3000, M_w/M_n of 1.27), PDMS-CH_3 from Professor Judy Riffle at the Virginia Polytechnic Institute, and PDMS-CH_3 from Petrarch were used as received. PDMS-NH_2 materials were obtained from Goldschmidt Chemical Corp. PDMS-NH_2 is synthesized by an equilibration reaction, in which the cyclic siloxane material is inserted into the difunctionally terminated starting material, resulting in a functionality of exactly two.[18] Although the resulting polydispersity is high (ca. 2), these materials are preferable to anionically polymerized materials of lower polydispersity in which the functionality is difficult to control precisely and is usually less than two. Any material which has not been end-functionalized could act as a strong surfactant and influence our results. We have thus chosen materials with controlled functionality, but with a broader molecular weight distribution. At completion of the equilibration reaction, a small percentage of siloxane cyclics remain. PDMS-NH_2 materials were fractionated by super critical fluid fractionation[19] to obtain fractions of relatively narrow molecular weight distribution which are free of siloxane cyclics and other low molecular weight impurities.

PDMS-CH_3 and PDMS-NH_2 materials were characterized by size exclusion chromatography (SEC), vapor-phase osmometry (VPO), and end group titration. SEC was carried out using a Waters/Millipore system with a Model 510 pump, Model 410 differential refractometer, Model 840 data station, and five Ultrastyragel columns with pore sizes of 10,000, 1000, 500, 100, and 100 Å, with toluene as the solvent. PDMS-NH_2 materials were derivatized prior to SEC characterization to avoid retention in the columns, by reacting excess phenol isocyanate with the amine end groups. VPO was conducted on a Wescan Model 233 VPO at 50 °C using toluene as the solvent. PDMS-NH_2 end group titrations were carried out using a measured amount of PDMS in 2-propanol. Bromophenol blue was used as an indicator, and titration to a yellow end point was carried out using 0.1 N HCl. It was assumed that the PDMS-NH_2 had exactly two end groups per chain. Characterization results for PDMS-CH_3 and PDMS-NH_2 are presented in Tables I and II, respectively.

Table II. Molecular Weight Characteristics of PDMS-NH_2 Materials[a]

PDMS-NH_2: absolute M_n	size exclusion chromatography M_n	size exclusion chromatography M_w/M_n	vapor-phase osmometry M_n	end group titration M_n
1310[c]	410	2.28		1310 ● 16
1625[c]	550	2.05	1580	1670 ± 25
2440[c]	500	2.12		2440 ± 40
2920[c]	1130	1.76		
4600[c]	2740	2.04	5020	4100 ± 900
5750[c]	2820	1.63		
9790[c]	5780	1.49		
10.6K[d]	10800	2.32	11000 ± 2800	10100 ± 300
18.1K[c]	10530	1.56		18100 ± 900
30.1K[c]	26400	1.62		

[a] Errors are $R/2$ for two or three measurements. [b] Based upon polystyrene standards. [c] Source: Goldschmidt Chemical Co., samples fractionated by Phasex Corp. [d] Source: Virginia Polytechnic Institute.

Absolute molecular weights obtained by VPO, end group titration, or interpolation from absolute molecular weight–SEC molecular weight calibration curves were used for all the analysis.

Methods. Interfacial tension measurements were made by pendant drop tensiometry using a system for digital analysis of pendant drop images similar to that described previously.[20,21] The experimental profile is compared to the theoretical profile as predicted by the equations of Bashforth and Adams.[22] A robust shape comparison algorithm, that has been modified to include a golden section optimization, is used to determine the shape parameter and the magnification factor for the resulting drop profile, which is used to calculate the interfacial tension.

A drop of the higher density polymer (PDMS) is suspended from the tip of a glass capillary of a Drummond positive displacement syringe. The drop is suspended in a matrix of the lower density polymer (PBD) which is contained in a glass cuvette. A clean cuvette containing fresh PBD was used for each experiment. Pure PBD and PDMS materials were used for the two phases, which is consistent with cloud point curve results.[17] In addition, a sedimentation experiment was conducted using PBD and the lowest molecular weight PDMS material. The resulting interfacial tension was the same, within experimental error, as the pure component measurement. Therefore, it is reasonable to use the pure components for interfacial tension measurements. The cuvette is placed in a chamber controlled to 30 ± 1 °C in air. Wetting of the outside of the capillary was minimized by pretreating the glass capillaries with trimethoxymethylsilane. The observed image was digitized and thresholded to obtain the drop profile using an AT&T TARGA image capture board. A 0.5 mm × 0.5 mm grid was analyzed for calibration of the magnification factor. Images were obtained and analyzed at regular intervals until a constant, equilibrium result was obtained. The drop volume was then increased, and the same procedure repeated. In a second set of experiments probing surfactant behavior, mixed PDMS phases were prepared by adding differing amounts of PDMS-NH_2 to the PDMS-CH_3 phase. The measured interfacial tensions of the mixed samples are employed to determine whether interfacial tension reduction is due to a surfactant effect. The PDMS-CH_3/PDMS-NH_2 blends were mixed prior to the experiment for a minimum of 30 min in the melt state.

Density measurements, necessary for interfacial tension calculations, were conducted at 30 °C using an Anton Paar K.G., Model DMA 60 digital density meter, with external cell, Model DMA 602. Temperature precision of ±0.1 °C was obtained with a water bath.

Results

Interfacial tension results for PBD (1K)/PDMS-CH_3 and PBD (1K)/PDMS-NH_2 are presented in Table III. Results obtained for the former system by Anastasiadis[13] are also included. The results show that interfacial tension increases with PDMS molecular weight and that the interfacial tension is lower for the aminopropyl-terminated

Table III. Interfacial Tension Results for Amine- and Methyl-Terminat. d PDMS against PBD (1K)[a]

PDMS sample (M_n absolute)	interfacial tension (dyn/cm) methyl end group	methyl end group[13]	amine end group
PDMS-CH_3 (890)	0.99 ± 0.01	1.01	
PDMS-CH_3 (1120)	0.98 ± 0.03		
PDMS-CH_3 (1270)	1.24 ● 0.05	1.27	
PDMS-NH_2 (1310)			1.04 ± 0.02
PDMS-NH_2 (1625)			1.42 ± 0.07
PDMS-CH_3 (2200)		1.85	
PDMS-NH_2 (2440)			1.60 ± 0.02
PDMS-NH_2 (2920)			2.00 ± 0.06
PDMS-CH_3 (3630)	2.50 ± 0.08		
PDMS-CH_3 (4580)		2.44	
PDMS-NH_2 (5750)			2.20 ● 0.04
PDMS-NH_2 (9790)			2.46 ± 0.02
PDMS-CH_3 (10K)	2.77 ± 0.09		
PDMS-NH_2 (18.1K)			2.77 ± 0.05
PDMS-CH_3 (19.6K)	2.86 ± 0.06		
PDMS-NH_2 (30.1K)			2.82 ± 0.09

[a] Standard deviations were calculated on the basis of four or five measurements of two or three different equilibrated drops.

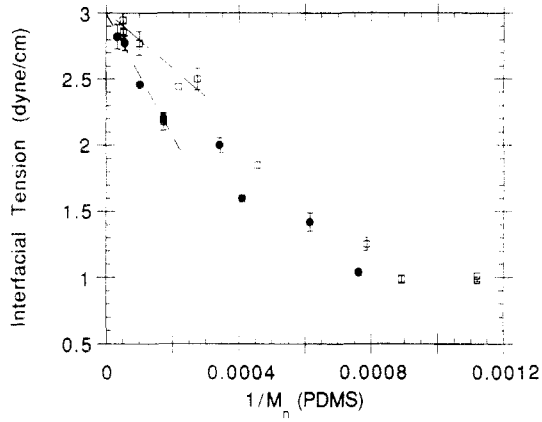

Figure 1. PBD (1K)/PDMS interfacial tension vs $1/M_n$: (□, solid line) PDMS-CH_3; (●, dashed line) PDMS-NH_2.

PDMS as compared to the standard methyl-terminated PDMS. Good agreement with the results of Anastasiadis et al.[13] is observed for the PDMS-CH_3 measurements. The end group effect is clearly illustrated in Figure 1. For example, the interfacial tension between PBD (1K) and PDMS-CH_3 (1270) is 1.27 dyn/cm, compared to 1.04 dyn/cm for PDMS-NH_2 (1310). For a PDMS molecular weight of 10 000 the interfacial tension is reduced from 2.77 to 2.46 dyn/cm (11% reduction) by changing from methyl to amine end groups.

The interfacial tension reduction was further investigated by varying the amount of amine-terminal groups in the PDMS phase. This is accomplished by mixing methyl- and amine-terminated PDMS in the PDMS phase. If the amine end groups are surface active, only a small amount of aminated PDMS added to methyl-terminated PDMS should act as a surfactant and decrease the interfacial tension substantially. The signature of surfactant behavior is therefore a departure from a linearity in the relationship between interfacial tension and composition.[3] The results for the PBD (3K)/[PDMS-CH_3 (10K)/PDMS-NH_2 (4.6K)] and PBD (3K)/[PDMS-CH_3 (19.6K)/PDMS-NH_2 (10.6K)] systems are shown in Figures 2 and 3. For both PDMS-CH_3 molecular weights there is a linear relationship between interfacial tension and PDMS-NH_2 concentration up to 75% PDMS-NH_2. This behavior indicates somewhat surprisingly that PDMS-NH_2 does not act like a surfactant, even though it leads to a lower interfacial tension value. The observed interfacial tension reduction is augmented

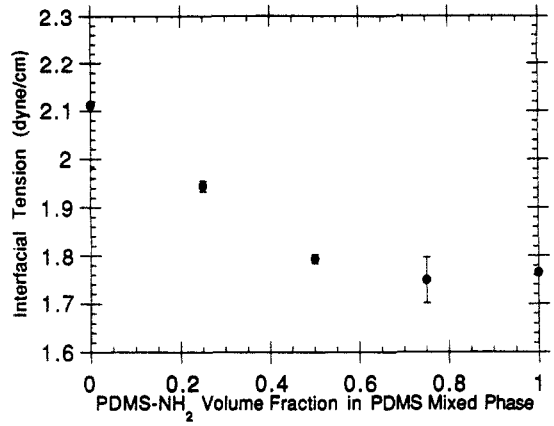

Figure 2. PBD (3K)/[PDMS (10K), PDMS-NH_2 (4K)] interfacial tension vs volume fraction PDMS-NH_2 in the PDMS-NH_2/PDMS-CH_3 mixed phase.

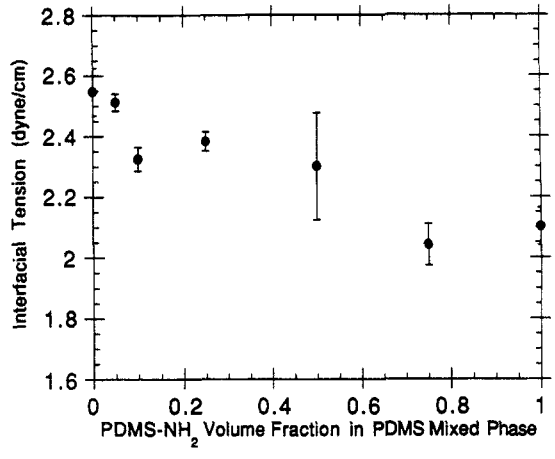

Figure 3. PDB (3K)/[PDMS (20K), PDMS-NH_2 (10K)] interfacial tension vs volume fraction PDMS-NH_2 in the PDMS-NH_2/PDMS-CH_3 mixed phase.

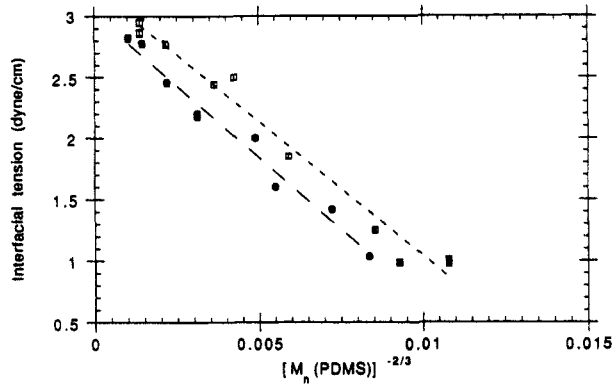

Figure 4. PBD (1K)/PDMS interfacial tension vs $M_n^{-2/3}$: (□, - - -) PDMS-CH_3; (●, – –) PDMS-NH_2.

by the use of PDMS-NH_2 of lower molecular weight than that of PDMS-CH_3. The observed linear reduction, in fact, indicates that neither the amine end groups nor the lower molecular weight of the aminated PDMS leads to significant interfacial activity of this material.

Discussion

The scaling exponent for the molecular weight dependence of interfacial tension, x, can be determined from inspection of the data in Table III. In Figure 4 the interfacial tension data are plotted as a function of $M_n^{-2/3}$ as has been observed by Gaines and LeGrand[11,12,15] and Anastasiadis et al.[13] The results of linear regression of

the data in Table III to this functional form are, for PBD/PDMS-CH_3 interfacial tension and PBD/PDMS-NH_2 interfacial tension, respectively:

$$\gamma = 3.230\ (\pm 0.086) - [218.8\ (\pm 37.6)]M_n^{-2/3} \quad R = 0.9879 \quad (4)$$

$$\gamma = 3.014\ (\pm 0.179) - [234.2\ (\pm 37.6)]M_n^{-2/3} \quad R = 0.9871 \quad (5)$$

where M_n is the PDMS molecular mass in daltons and γ is in dyn/cm. If the $M_n^{-2/3}$ dependence assumed in these relationships were correct, the y-intercept would be the same for the two lines, as at infinite molecular weight there should be no end group effect. The y-intercept values obtained differ by 0.216 dyn/cm, which is greater than the standard error for the intercepts (see eqs 4 and 5). This suggests that, although the correlation coefficients (R) are quite high, the $M_n^{-2/3}$ relationship may not be correct for this system.

The M_n^{-1} dependence of interfacial tension predicted by Broseta et al.[14] is expected to hold for w_i greater than $\sim$10, where $w_i = \chi_{AB} r_i$ and r_i is the relative chain length of component i. This corresponds to molecular masses of greater than 3000 and 4000 daltons for PDMS-CH_3 and PDMS-NH_2, respectively. The interfacial tensions for molecular weights within this predicted range yield the following regression relationships for PDMS-CH_3 and PDMS-NH_2, respectively:

$$\gamma_{\text{PDMS-CH}_3/\text{PBD}} = 3.014\ (\pm 0.238) - [2081\ (\pm 1430)]M_n^{-1} \quad R = 0.945 \quad (6)$$

$$\gamma_{\text{PDMS-NH}_2/\text{PBD}} = 2.984\ (\pm 0.063) - [4621\ (\pm 514)]M_n^{-1} \quad R = 0.989 \quad (7)$$

These regressions, based on six data points for PDMS-CH_3 and five data points for PDMS-NH_2, are depicted as the two lines in Figure 1. The intercepts are within 0.4% (±0.01 dyn/cm) of each other, which is clearly within experimental error, suggesting that the M_n^{-1} dependence is correct for high molecular weights. The drop in slope (i.e., $x < 1$) predicted by Broseta et al. at higher values of w_i[14] is also qualitatively supported by the data.

The results of the Cahn–Hilliard/Flory–Huggins treatment of Anastasiadis et al.[13] and Broseta et al.[14] show that the scaling exponent, x, changes with molecular weight, with a value of 1.0 at high molecular weight and a value of 0.5 as the critical point is approached.[14] In between the two extremes the slope gradually drops, so that a $M_n^{-2/3}$ relationship would be expected in the intermediate range, as is observed for the PBD/PDMS system.

The $M_n^{-2/3}$ relationship observed by Gaines and LeGrand[11,12] is also consistent with the Cahn–Hilliard/Flory–Huggins treatment of Anastasiadis et al.[13] and Broseta et al.[14] Gaines and LeGrand measured interfacial tension for oligomers with low molecular weights (100–1000), so that the values for w_i would be below the predicted range for M_n^{-1} behavior. Close inspection of the data of Gaines and LeGrand[11,12] reveals a drop in slope at low molecular weights, which is consistent with this theory as well.

It is interesting to compare the effect of the end groups on a bulk property, such as density, to that of the interfacial tension. The change in bulk density with M_n is as follows for PDMS-CH_3:

$$\rho = 0.9684\ (\pm 0.0015) - [47.5\ (\pm 6.1)]M_n^{-1} \quad (8)$$

and for PDMS-NH_2 it is

$$\rho = 0.969\ (\pm 0.0015) - [16.2\ (\pm 6.7)]M_n^{-1} \quad (9)$$

It is useful to rescale eqs 4, 5, 8, and 9 by dividing the equations by the PDMS infinite molecular weight value, as shown:

$$\frac{\rho_{\text{PDMS}} - \rho_{\text{PBD}}}{\rho_{\infty\text{PDMS}} - \rho_{\text{PBD}}} = 1 - \frac{k}{(\rho_{\infty\text{PDMS}} - \rho_{\text{PBD}})M_n} \quad (10)$$

$$\gamma/\gamma_\infty = 1 - k_\gamma/\gamma_\infty M_n \quad (11)$$

The values of $k/(\rho_\infty - \rho_{\text{PBD}})$ and k_γ/γ_0 define the percent reduction in the property which is observed as molecular weight is reduced and end group effects become more important. The values for $k/(\rho_\infty - \rho_{\text{PBD}})$ are 493 and 167 for methyl and amine end groups, respectively, compared to values for k_γ/γ_∞ of 695 and 1550 for methyl and amine end groups, respectively. Clearly, the end groups have a much greater effect on interfacial tension than on density.

The methyl end group results in a greater density reduction as compared to the amine end group, whereas the amine end group results in a greater interfacial tension reduction, as compared to the methyl end group. Density arguments, therefore, cannot explain the reduced interfacial tension for amine end groups. Surface tension measurements of PDMS-CH_3 and PDMS-NH_2 materials (identical to the ones used in this study) by Jalbert et al.[10] suggested that end group segregation can control the surface tension in certain cases. However, the gradual linear decrease in PDMS/PBD interfacial tension as PDMS-NH_2 is added (Figures 2 and 3) shows that the amine end group does not act as a surfactant. If surfactant activity was occurring, the maximum interfacial tension reduction would occur upon small additions of PDMS-NH_2 to the PDMS phase. Therefore, we can rule out end group segregation as the cause for the interfacial tension reduction.

The behavior of mixed methyl and amine-terminated systems is similar to that observed for random copolymers, as was noted by Rastogi and St. Pierre for the poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO) system.[23] In their work, surfactant behavior was noted for PEO/PPO homopolymer mixtures, whereas a linear decrease in surface tension was observed for random copolymers of PEO and PPO up to a PEO concentration of 75%. The random copolymer segments are constrained by their covalent bonds so that the lower energy component cannot migrate toward the surface to reduce the surface tension. Our data are consistent with the random copolymer system; segregation of either end group is not observed.

It is also interesting to note that the PDMS-NH_2 molecular weight is lower than that of the PDMS-CH_3 by a factor of 2. One might expect the lower molecular weight (i.e., lowest surface energy) component to migrate to the interface in this case in order to lower the interfacial tension. The absence of surfactant activity confirms that molecular weight segregation is not occurring at the PBD/PDMS interface. Therefore, the effect of PDMS polydispersity on the PDMS/PBD interfacial tension results is small.

The fact that reduced interfacial tensions arising from amine end groups are not related to any surface activity of the material is not surprising. To our knowledge there are no known specific interactions between amine groups and poly(dienes). On the basis of group additivity arguments, the methyl-terminated PDMS has a lower surface energy than amine-terminated PDMS and might be expected to segregate preferentially at the interface. In

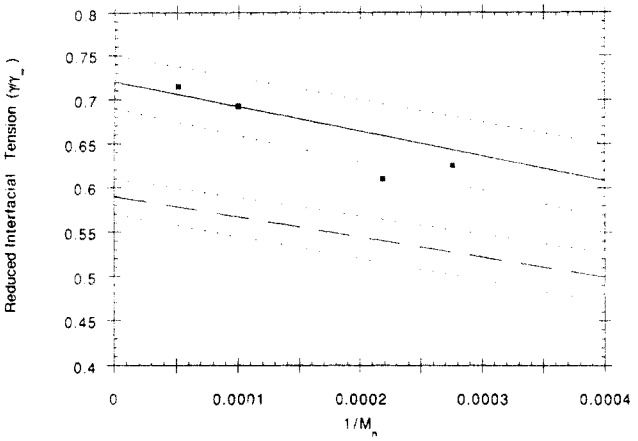

Figure 5. Reduced PBD/PDMS-CH_3 interfacial tension (γ/γ_∞) vs $1/M_n$ PDMS-CH_3: (■) experimental (dashed line) theory, weak segregation limit; (solid line) theory, strong segregation limit. Dotted lines define a region for a ±10% variation of the interaction parameter.

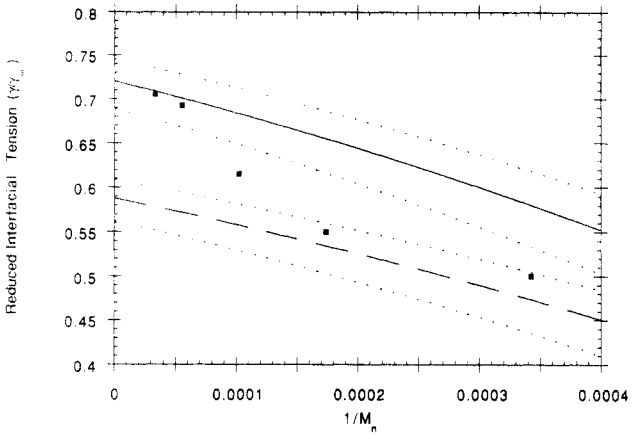

Figure 6. Reduced PBD/PDMS-NH_2 interfacial tension (γ/γ_∞) vs $1/M_n$ PDMS-NH_2: (■) experimental; (dashed line) theory, weak segregation limit; (solid line) theory, strong segregation limit. Dotted lines define a region for a ±10% variation of the interaction parameter.

fact, a slight tendency for the methyl-terminated PDMS acting as a surfactant is observable in Figure 2 at high amine contents. The question remains then as to why the interfacial tension is reduced for the aminated PDMS even though it is not surface active. In the paper that follows, we demonstrate that the interfacial tension reduction is a bulk effect rather than an interfacial effect. Cloud point measurements and subsequent estimations of interaction parameters show that aminated PDMS blends with polyisoprene have lower critical temperatures and smaller interaction parameters than their methyl-terminated counterparts.[17]

A self-consistency check of these results can be made by using these data to calculate interfacial tensions for our PDMS/PBD blends (assuming the interaction parameters for PDMS/PBD and analogous PDMS/PI systems are equal). Interfacial tensions were calculated using the combined Cahn–Hilliard/Flory–Huggins theories of Anastasiadis et al.[13] and Broseta et al.[14] using eq 19 (see Appendix for equation and derivation). Interaction parameters were estimated from cloud point curves for the similar polyisoprene (PIP)/PDMS system, which resulted in a value of 0.157 for PIP (1K)/PDMS-CH_3 (1270) and 0.119 for PIP (1K)/PDMS-NH_2 (1310).[17] Details of the calculations are found in the Appendix. γ_∞ refers to the interfacial tension where both polymers have infinite length and is estimated by applying the theory of Helfand et al.[24] The calculated value for γ_∞ is 4.66 dyn/cm. The analytical expression of Broseta et al.[14] is a reasonable approximation for w_i greater than 5, which corresponds to molecular weights larger than 1700 and 2300 for PDMS-CH_3 and PDMS-NH_2, respectively. Figures 5 and 6 present the theoretical and experimental reduced interfacial tension (γ/γ_∞) vs $1/M_n$ for the weak and strong exclusion limit case for PDMS-CH_3 and PDMS-NH_2, respectively. The dotted lines define ranges assuming a variation of ±10% for the interaction parameter. The results for PBD/PDMS-CH_3 show good agreement with theory for the strong segregation limit, which is reasonable for such a system. However, the PBD/PDMS-NH_2 results do not agree with the theory. The data do not fall within the strong segregation limit, as would be expected for such a system. The slope of approximately −400 (actually the curve is not linear, due to the variation of the interaction parameter) for the theoretical curve is much smaller than the slope of −990 for the experimental results. The experimental results suggest that the amine end groups, at least in this system, have a more dramatic effect on the interfacial tension than is predicted by the Cahn–Hilliard/Flory–Huggins treatment. This might be expected since these theories do not explicitly consider effects of a thermodynamically distinct end group. The theoretical curves for the amine and methyl end group should extrapolate to the same interfacial tension value at infinite molecular weight. This does not occur because average interaction parameters were used. Measurements of the interaction parameters in the following paper show that the interaction parameter increases as the molecular weight increases as a result of a reduction in the end group effects.[17] This could explain the sharper reduction observed in experimental interfacial tension measurements. Clearly, more detailed information on the exact molecular weight dependence of the interaction parameter would be needed to confirm this.

The reduction in interfacial tension observed can be understood qualitatively within the framework of the binary interaction theory, which was first referred to by Simha[25] and Stockmayer[26] for a copolymer solvent system and later developed by ten Brinke, Karasz, and MacKnight;[27] Kambour, Bendler and Bopp;[28] and Paul and Barlow[29] as it applies to copolymer blends. The theory states that increased miscibility in copolymer–copolymer systems can occur without specific interactions, as a result of intrachain repulsion between the different covalent bonded monomers within the polymer chain. In the case of end groups, this theory may be applied to our system, if functionally terminated PDMS is considered as a random copolymer of PDMS denoted as B and the end group identified by C. A combined Flory–Huggins interaction parameter for the homopolymer/"copolymer" functional PDMS system would be

$$\chi_{blend} = y\chi_{AB} + (1-y)\chi_{AC} - (1-y)y\chi_{BC} \qquad (12)$$

where y denotes the PDMS volume fraction in the "copolymer" (B_yC_{1-y}) and A denotes the polydiene. The definition of each interaction parameter is evident from the subscripts. From this expression it is clear that a large interaction parameter between PDMS and its end group (χ_{BC}), resulting from a large solubility parameter difference, would act to reduce the overall interaction parameter, χ_{blend}. As the PDMS-NH_2 molecular weight increases, the end group effect decreases, resulting in an increase in the interaction parameter and a corresponding increase in the interfacial tension. This theory is explored further in the

following paper using interaction parameters determined from cloud point curves.

Conclusions

Interfacial tension measurements on binary homopolymer blends of poly(butadiene) and poly(dimethyl siloxane) (PDMS) show that interfacial tension can be modified by changing the end groups of the PDMS homopolymer. Blends with amine-terminated PDMS show interfacial tension reduction of as much as 30% from the values for blends with methyl-terminated PDMS. The interfacial tensions scale with M_n^{-1} at moderate to high molecular weights, consistent with the prediction of Brosetta et al.[14] The results indicate that the end group phenomena do not correlate with density changes, and the absence of significant surfactant activity suggests that the end groups do not migrate to the interface. The observed interfacial tension reduction is attributed to changes in the bulk thermodynamics caused by the different end groups. Changes in the bulk interactions are explained qualitatively by considering the end-modified PDMS as a random copolymer of PDMS and end groups, and subsequently applying binary interaction theory to model the overall interaction parameters (discussed in the second paper in this series).[17] Theoretical predictions of the interfacial tensions based upon these estimated χ parameters agree well with the experimental data.

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Appendix

The interfacial tension for both polymers of infinite molecular weight, γ_∞, is calculated using the self-consistent mean field approach of Helfand et al. using the following equation for asymmetric polymers:[24]

$$\gamma_\infty = kT\alpha_{AB}^{1/2}\left[\frac{\beta_A+\beta_B}{2}+\frac{(\beta_A-\beta_B)^2}{6(\beta_A+\beta_B)}\right] \tag{13}$$

where $\alpha_{AB} = \chi_{AB}(\rho_{0A}\rho_{0B})^{1/2}$ and $\beta_i^2 = (1/6)\rho_{0i}b_i^2$, χ_{AB} is the Flory–Huggins interaction parameter, ρ_0 is the density defined as $\rho_0 = \rho/M$, and b is the statistical segment length, defined such that the mean-square end-to-end distance is Nb^2, where N is the degree of polymerization. The statistical segment length, b, was determined from the following equation:

$$b_i = m_i^{1/2}\left(\frac{\langle r_0^2\rangle}{M}\right)^{1/2} \tag{14}$$

using published values for the characteristic ratio, $(r_0/M)^{1/2}$.[30] Characteristic ratios of 0.61 and 1.03 Å were used to estimate statistical segment lengths of 5.3 and 7.6 Å for PDMS and PBD, respectively. The number-average molecular weight was used to calculate r_i, using the monomer molecular weight of PBD as the reference. The interaction parameter used for the calculation of w_i as obtained from the analysis of cloud point curve for a similar PIP/PDMS-CH_3 blend is detailed in the paper that follows.[17]

Anastasiadis, Gancarz, and Koberstein[13] used the Flory–Huggins rigid lattice theory[31] in conjunction with the Cahn–Hilliard square gradient approximation[32] to model temperature and molecular weight dependencies of the interfacial tension. The Cahn–Hillard expression for interfacial tension is as follows:

$$\gamma = 2N_v\int_{\phi_A}^{\phi_B}[K\Delta G(\phi)]^{1/2}\,d\phi \tag{15}$$

where ϕ_A and ϕ_B are the compositions of phases A and B, N_v is the number of molecules per unit volume, and ΔG is the free energy of mixing, defined by the Flory–Huggins free energy expression.[31] The square gradient coefficients, $\kappa^{(i)}$ and $\kappa^{(ii)}$, were derived from linear response theory with the random-phase approximation of de Gennes,[33] resulting in the following equations for the strong segregation limit (narrow interface) and weak segregation limit (broad interface), respectively:

$$\kappa^{(i)} = \frac{m_A\langle r_0^2\rangle_A}{24\phi_A^2}+\frac{m_B\langle r_0^2\rangle_B}{24\phi_B^2} \tag{16}$$

$$\kappa^{(ii)} = \frac{m_A\langle r_0^2\rangle_A}{36\phi_A^2}+\frac{m_B\langle r_0^2\rangle_B}{36\phi_B^2} \tag{17}$$

Broseta, Fredrickson, Helfand, and Leibler, using the same approach, derived the following analytical expression for the interfacial tension for incompatibility degree, w_i, in the range of 5–10 for the strong segregation limit:[14]

$$\gamma = \gamma_\infty\left[1-\frac{\pi^2}{12}\left(\frac{1}{w_A}+\frac{1}{w_B}\right)+\dots\right] \tag{18}$$

where $w_i = \chi_{AB}r_i$, r_i is the relative chain length of component i, and χ_{AB} is the interaction parameter between polymers A and B. In terms of PDMS molecular weight $(M_n)_B$, the resulting equation is

$$\frac{\gamma}{\gamma_\infty} = 1-\frac{\pi^2 m_A}{12\chi_{AB}(M_n)_A}-\frac{\pi^2 m_A}{12\chi_{AB}(M_n)_B} \tag{19}$$

where m_A is the monomer molecular weight of PBD and $(M_n)_A$ is the PDB molecular weight (1000). Interfacial tension was calculated using the analytical expression resulting from the theory of Broseta et al.,[14] which is applicable to the strong segregation limit, where R_g is larger than the interfacial width. The γ/γ_∞ value for the weak segregation limit, using eq 17 in the Cahn–Hilliard square gradient expression for interfacial tension, requires a multiplier of 0.816 for eq 19. Interfacial tension values were calculated for both cases using the square gradient coefficients given by eqs 16 and 17. The reduced interfacial tension was calculated for moderate to high molecular weights using eq 19.

Interaction parameters were estimated from cloud point curves for the similar polyisoprene (PIP)/PDMS system using the Flory–Huggins treatment.[17] The interaction parameter for PIP/PDMS-CH_3 (1270) of 0.157 was assumed to be constant for all molecular weights. The interaction parameter for PBD/PDMS-NH_2 was estimated from the PIP/PDMS (1310) interaction parameter (0.119) and the infinite molecular weight interaction parameter, i.e., that of PIP/PDMS-CH_3. The resulting equation is as follows:

$$\chi = 0.16 - 52/M_n \tag{20}$$

Such a form for the interaction parameter is consistent with the binary interaction theory, with the blend inter-

action parameter defined as follows:

$$\chi_{blend} = y\chi_{AB} + (1-y)\chi_{AC} - (1-y)y\chi_{BC} \quad (21)$$

where y denotes the PDMS volume fraction in the PDMS-NH_2 "copolymer" (B_yC_{1-y}), where B is the PDMS "block", C is the aminopropyl "block", and A denotes the poly(diene). The definitions of the interaction parameters are clear from the subscripts. The definition of y is as follows:

$$rV_B/(rV_B + V_C) \quad (22)$$

where r is the PDMS-NH_2 degree of polymerization and V_B and V_C are the molar volumes of the PDMS monomer unit and the end group, respectively. Assuming that $V_B \sim V_C$, one gets

$$\chi_{blend} = \left(\frac{r}{r+1}\right)\chi_{AB} + \left(\frac{1}{r+1}\right)\chi_{AC} + \frac{r}{(r+1)^2}\chi_{BC} \quad (23)$$

For $r \gg 1$ this reduces to

$$\chi_{blend} = \chi_{AB} + \frac{1}{r}(\chi_{AC} + \chi_{BC}) \quad (24)$$

or

$$\chi_{blend} = \chi_{AB} + \frac{m}{M_n}(\chi_{AC} + \chi_{BC}) \quad (25)$$

where m is the monomer molecular weight. Therefore, χ_{blend} should scale as $1/M_n$.

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