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Molecular Weight Dependence and End-Group Effects on the Surface Tension of Poly(dimethylsiloxane)

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ABSTRACT: The surface tensions of amine-, hydroxyl-, and methyl-terminated poly(dimethylsiloxane) (PDMS) oligomers with molecular weights ranging from 1000 to 75 000 are measured by pendant drop tensiometry. The surface tension increases with molecular weight for the methyl-terminated polymers, decreases with molecular weight for the amine-terminated polymers, and is nearly independent of molecular weight for the hydroxyl-terminated polymers. This behavior is attributed to differences in surface tension of the end groups and the repeat unit of the chain ($\sigma_\infty - \sigma_e$); the methyl end group has a lower surface energy than the PDMS backbone whereas the surface energy of the amine group exceeds that of PDMS. The surface tension of the hydroxyl end group more closely matches that of the repeat unit of the chain. The surface tensions of the homologous series of materials extrapolate to the same value at infinite molecular weight when surface tension is assumed to follow an inverse dependence on molecular weight, indicating that this is the correct correlation for high molecular weight polymeric materials. Group contribution methods are used to predict the surface tensions for each group of materials. When compared to experimental results, these predictions suggest that the methyl end groups are preferentially attracted to the surface whereas amine end groups are depleted from the surface.

Introduction

It is well-known that many bulk properties of polymers are molecular weight dependent and can be expressed in a general form:[1,2]

$$X = X_\infty - k_0/M_n \qquad (1)$$

where X is a property (such as the glass transition temperature, coefficient of thermal expansion, bulk density, heat capacity, refractive index, specific volume, or modulus) for a number-average molecular weight M_n, and X_∞ is the same property evaluated at infinite molecular weight. This behavior has been attributed to the excess free volume associated with the end groups.

Similar empirical relationships have been proposed for the molecular weight dependence of polymer surface properties. The molecular weight dependence of polymer surface tension, for example, is often described by one of two equations:[3–5]

$$\sigma^{1/4} = \sigma_\infty^{1/4} - k_1/M_n \qquad (2a)$$

$$\sigma = \sigma_\infty - k_2/M_n^{2/3} \qquad (2b)$$

where k_1 and k_2 are semiempirical parameters. The applicability of these relationships has been discussed in some detail by Wu.[6] Experiments result in values for k_1 and k_2 that are much larger than the values of k_0 associated with bulk properties. In addition, k_0, k_1, and k_2 depend on the end-group type. Hata and Kasemura,[7] for example, showed that the surface tension and density of poly(ethylene glycol) and poly(propylene glycol) varied as the end group was changed from a hydroxyl group to a methyl group. Values for k_0 and k_2 changed dramatically as the end-group composition was varied.

Rigorous thermodynamic treatments of polymer surface properties have also been developed. Sanchez and Poser[8] developed a theory for the surface tension of polymer melts based upon the Cahn–Hilliard theory of inhomogeneous systems and lattice fluid theory. The theory does not furnish a direct molecular weight dependence of surface tension and, therefore, provides no means for assessing the validity of eq 2a,b. Off-lattice Monte Carlo simulations of polymer melts by Kumar et al.[9] predict that, in the limit of high molecular weight, surface tension follows eq 1. Lattice calculations by Theodorou[10] showed the power law dependence of surface tension on molecular weight varied continuously from M_n^{-1} behavior for high molecular weight to an approximate $M_n^{-2/3}$ dependence for low molecular weight. The latter behavior is consistent with the experimental findings of LeGrand and Gaines[5] for low molecular weight poly(dimethylsiloxane) (PDMS). In addition to these predictions, the theories suggest that end groups that are similar in composition to the repeat unit of the polymer backbone are not randomly distributed through the bulk of the material; rather, they are preferentially located at the surface.

When the end groups are different in composition than the polymer backbone, the segregation effects may be accentuated. A lattice analysis,[6] for example, proposed that the constant in eq 2b was

$$k_2 = (\sigma_\infty - \sigma_e)(2m_r)^{2/3} \qquad (3)$$

where σ_∞ represented the surface energy at infinite molecular weight, σ_e, the surface energy of the end group, and m_r, the molecular weight of the repeat unit. The relative magnitude of the surface energy of the chain backbone and end groups, that is, the sign of the term ($\sigma_\infty - \sigma_e$), dictates whether the surface tension increases or decreases with molecular weight.

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For end groups that are similar in constitution to the chain backbone (i.e., when $\sigma_e < \sigma_\infty$), eq 2a,b predicts that surface tension increases with molecular weight. Literature data for homopolymer surface tensions are generally consistent with this prediction.[6]

de Gennes[11] has theorized that the surface tension of polymeric materials should scale as:

$$X = X_\infty - k_3/(M_n)^x \qquad (4)$$

as a result of the interaction between the end group and the surface. If the interaction between the end group and the surface were repulsive, the exponent x would take on the value 1.0. If the interaction were attractive, x would equal 0.5. Further, he suggested that, in most practical cases, the value for x would be between these two limits.

A recent Monte Carlo lattice formulation developed by Kumar[12] suggests that the proportionality constant in eq 1 for polymer surface tension will be related to the affinity of the end group for the surface. The affinity is characterized by a parameter χ_s and is related to the difference in surface energy between the repeat unit and the end group. Changes in end-group composition change its surface energy relative to the repeat unit and could therefore lead to large charges in the polymer surface properties.

Although the data are limited, there are some examples in the literature where the end group is significantly different in chemical structure than that of the chain backbone. The surface tension of poly(ethylene glycol) and poly(propylene glycol), for example, has been found to be independent of molecular weight.[13,14] This effect has been attributed to hydrogen bonding leading to behavior equivalent to infinite molecular weight conditions. The surface tension of α,ω-alkanediols (where $\sigma_e > \sigma_\infty$) has been found to decrease as the molecular weight is increased;[15] this has been explained in terms of the dilution of the high-energy hydroxyl end groups as the chains become longer.

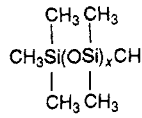
The purpose of this paper is 2-fold: first, to study the effects of molecular weight and end-group type on the surface tension of poly(dimethylsiloxane) and, second, to use this data to determine the molecular weight dependence of the surface tension. Poly(dimethylsiloxanes) are employed since they can be prepared with a variety of end groups with surface tensions that fall both above and below that of the PDMS backbone. Furthermore, the surface tension of methyl-terminated PDMS has been studied extensively[4,5,13] and is known to conform to eq 2b at low molecular weight.

Materials and Experimental Section

In selecting functionally terminated polymers for this study, there generally was a choice between two different types of materials: polydisperse materials with a functionality of exactly 2 or materials with a narrow molecular weight distribution (e.g., prepared anionically) with incomplete functionalization. Since the goal of this study was to examine end-group effects, poly(dimethylsiloxane), an example of the former type of system, was selected. Functionally terminated PDMS can be prepared by an equilibration procedure which ensures a functionality of 2, but it yields a polydisperse product.

Since the polymers used are polydisperse, it is important at the onset to investigate whether preferential surface segregation by molecular weight is occurring. Hariharan et al.[17] used a lattice model to estimate the extent of surface segregation of polymer chains due to the distribution of molecular weights. They found that the surface tension depends only on the number-average molecular weight; that is, surface tension is a simple weighted average of the values corresponding to the monodisperse systems. Several mixtures of materials with similar number-average molecular weights but with varying polydispersity indices were prepared in order to probe the possible effect on surface tension due to increased dispersion in the molecular weight distribution. The mixtures were made using two high molecular weight and three low molecular weight methyl-terminated PDMS indicated by an asterisk in Table I. The average molecular weight and polydispersity indices were confirmed by GPC.

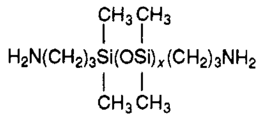
Table I. Number-Average Molecular Weight and Polydispersity Indices for Trimethylsiloxy-Terminated PDMS



$$\mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}(\mathrm{O}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}})_x\mathrm{CH_3}$$

M_n	PDI	M_n	PDI
162	1.02	3800	1.51
310	1.04	*4500	1.41
*415	1.07	5000	1.76
570	1.05	6500	1.69
1050	1.11	7000	2.01
1125	1.12	8800	3.24
1150	1.21	*8900	1.36
*2500	1.51	16800	2.47
3000	1.36	*24500	2.47

Table II. Number-Average Molecular Weight and Polydispersity Index for (Aminopropyl)dimethylsiloxy-Terminated PDMS



$$\mathrm{H_2N(CH_2)_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}(\mathrm{O}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}})_x\mathrm{(CH_2)_3NH_2}$$

M_n	PDI	M_n	PDI
218	1.04	2600	1.87
760	2.46	3700	2.67
860	2.49	5900	2.54
1200	1.91	6100	2.17
1300	2.28	7100	2.67
1400	2.79	10500	2.32
2000	1.87	18000	1.31
2100	3.33	37000	1.62
2500	2.46	79000	1.66

PDMS can be synthesized with a number of different end groups, allowing for the investigation of several interesting cases. PDMS has a low surface energy backbone. Trimethylsiloxy end groups are expected to have an attractive interaction with the surface. (Aminopropyl)dimethylsiloxy end groups should have a repulsive interaction, while hydroxydimethylsiloxy end groups are similar in structure to the polymer repeat unit. For simplicity, the end groups will be referred to as methyl, amine, and hydroxyl to represent the different functional groups.

Methyl-terminated PDMS oligomers were purchased from PolySciences and Petrarch Systems. α,ω-Dihydroxyl-terminated PDMS were purchased from Scientific Polymer Products. α,ω-Diamine-terminated oligomers of PDMS were synthesized using an equilibration polymerization process.[18] Materials were characterized by end-group titration methods, VPO, and GPC. Some of the functionalized materials were fractionated by supercritical fluid extraction.[19] Characteristics of the samples are given in Tables I–III.

Surface tension measurements were carried out using an automated pendant drop technique similar to that described in an earlier publication.[20] The pendant drop profile is analyzed by a robust shape comparison algorithm that has been modified to include a golden section optimization routine. The algorithm performs regression of the experimental pendant drop profile to the corresponding theoretical profiles predicted by the Bashforth–Adams relation.[21] The prediction interval for the measurements at 95% confidence is ±0.3 dyn/cm. Fluid densities required for the pendant drop analysis were measured using a Mettler Model DMA45 digital densitometer with an external DMA512 cell. Surface tension and density measurements were carried out at 30 ± 1 °C.

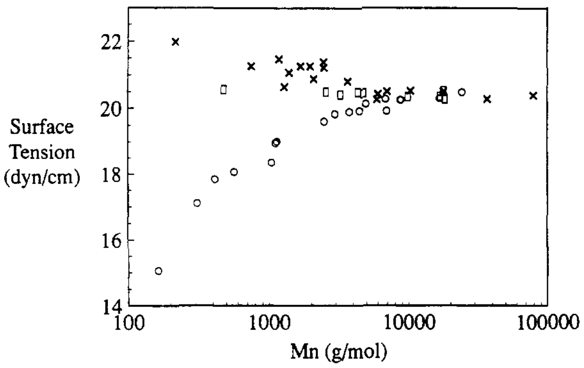
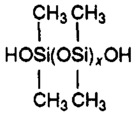


Figure 1. Surface tension as a function of number-average molecular weight of trimethylsiloxy-terminated PDMS (open circles), (aminopropyl)dimethylsiloxy-terminated PDMS (crosses), and hydroxydimethylsiloxy-terminated PDMS (open squares).

Table III. Number-Average Molecular Weight and Polydispersity Index for Hydroxydimethylsiloxy-Terminated PDMS



$$HOSi(OSi)_xOH \text{ with } CH_3\,CH_3 \text{ above and below}$$

M_n	PDI	M_n	PDI
480	2.71	10000	3.15
2600	1.93	17000	2.65
3300	1.75	18000	3.53
4400	1.81	18500	2.31
4900	1.63		

Table IV. Polydispersity Effects on the Surface Tension of Trimethylsiloxy-Terminated PDMS

M_n	PDI	density[a] (g/cm^3)	Surface Tension[a] (dyn/cm)
6500	1.69	0.9567	19.91
6500	1.94	0.9595	19.71
6300	3.27	0.9556	19.72
6100	3.42	0.9566	19.91
6100	5.65	0.9577	19.93
6100	7.63	0.9572	19.87
6300	8.71	0.9581	19.82

[a] Density and surface tension were measured at 30 °C.

Results and Discussion

The accuracy of the surface tensiometer was validated by measuring the surface tensions of methyl-terminated PDMS. The surface tension vs number-average molecular weight is shown in Figure 1. The values agree well with our own[27] and other previously reported data for PDMS.[13,16]

In order to investigate the effect of polydispersity on polymer surface tension, several mixtures of methyl-terminated PDMS with number-average molecular weight of approximately 6100 with polydispersity indices ranging from 1.69 to 8.71 were prepared. The mixture characteristics and results are presented in Table IV. The surface tensions and densities are not different within experimental error. This confirms the lattice model predictions[17] that surface tension will scale with number-average molecular weight and is not appreciably affected by the polydispersity index.

The data for surface tension as a function of molecular weight for the PDMS with the three different end groups (methyl, amine, and hydroxyl) are given in Figure 1. Clearly, both parameters affect the surface tension. For methyl-terminated PDMS, the surface tension increases as the molecular weight increases; the opposite trend is observed for the amine-terminated polymers. For the hydroxyl-terminated PDMS, surface tension appears to be only weakly dependent on molecular weight. As the molecular weight increases and approaches infinity, all of the functionally terminated materials seem to converge to the same surface tension. This is to be expected since, at infinite molecular weight, the end-group effect would vanish.

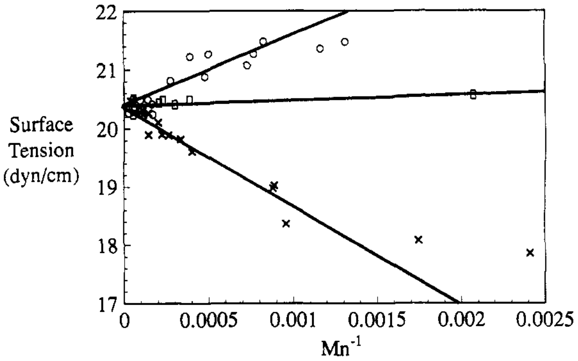


Figure 2. Surface tension as a function of M_n^{-1} for trimethylsiloxy-terminated PDMS (open circles), (aminopropyl)dimethylsiloxy-terminated PDMS (crosses), and hydroxydimethylsiloxy-terminated PDMS (open squares).

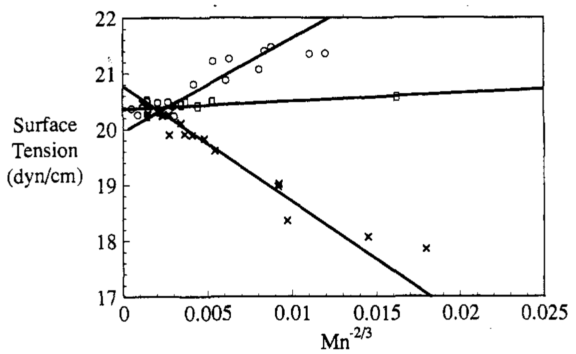


Figure 3. Surface tension as a function of $M_n^{-2/3}$ for trimethylsiloxy-terminated PDMS (open circles), (aminopropyl)dimethylsiloxy-terminated PDMS (crosses), and hydroxydimethylsiloxy-terminated PDMS (open squares).

The molecular weight dependence of PDMS is further examined in Figures 2 and 3 where the data are graphed as a function of M_n^{-1} according to eq 4 and $M_n^{-2/3}$ following eq 2b. Acceptable linear relationships are found for both cases; however, the surface tensions of these functionally terminated polymers must extrapolate to the same value as the molecular weight approaches infinity. The infinite molecular weight intercepts from Figures 2 and 3 (using 95% confidence intervals) are equal only for the case which conforms to eq 1. This provides strong evidence that surface tension scales as M_n^{-1} for high molecular weight homopolymers, in agreement with the molecular weight dependence recently reported by Sauer and Dee[13] for high molecular weight methyl-terminated PDMS and by Hata and Kasemura[7] for methyl- and hydroxyl-terminated poly(ethylene glycol).

Since the surface tension of a material is strongly influenced by its density (Bashforth–Adams relation), the density behavior of the PDMS materials as a function of molecular weight was also examined. The densities of the functionally terminated PDMS (Figure 4) show a linear relationship with inverse molecular weight as expected from eq 1. Both methyl- and amine-terminated materials exhibit the same trend; that is, the density of these materials increases with increasing molecular weight. The hydroxy-terminated PDMS density appears to be only a weak function of molecular weight similar to the trend in surface tension. These data appear to contradict the

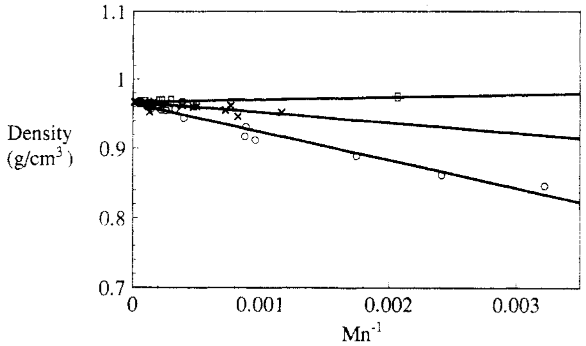


Figure 4. Density as a function of M_n^{-1} for trimethylsiloxy-terminated PDMS (open circles), (aminopropyl)dimethylsiloxy-terminated PDMS (crosses), and hydroxydimethylsiloxy-terminated PDMS (open squares).

Table V. Surface Entropy Estimated by $d\sigma/dT$ for End-Functionalized PDMS[22,23]

end group	$d\sigma/dT$ (dyn/cm °C)	end group	$d\sigma/dT$ (dyn/cm °C)
methyl	0.058	hydroxyl	0.055
amine	0.054		

conclusions of Sauer and Dee[13] that the dependence of surface tension on molecular weight is solely a result of the density dependence since, for the case of the amine-terminated PDMS, density still increases with molecular weight while the surface tension decreases as molecular weight increases. Some effect in addition to the influence of density is clearly required in order to explain these results.

It is possible that a change in the entropy of the system accounts for some of the observed end-group effect on surface tension. The magnitude of the entropic effect can be estimated by the change in surface tension with temperature at constant volume,[6] since the surface tension is the excess specific surface free energy and the change in surface tension with temperature is the entropy of surface formation per unit surface area. Experiments to determine $d\sigma/dT$ where T is the temperature have been carried out by Sauer and Dee[22] and Bhatia.[23] The results are given in Table V. The values for $d\sigma/dT$ for the different end groups are equivalent within experimental error. The entropy effect of the end groups, therefore, appears to be small and cannot by itself explain the observed effects of the end groups on the surface tension.

One effect that can provide a plausible explanation of data is the occurrence of preferential surface adsorption/depletion of the end groups. In the absence of surface segregation, the surface tension of a homogeneous two-constituent system follows a simple group additivity relationship. That is, the dilution of the end-group concentration as molecular weight increases might be expected to cause a commensurate change in the surface tension. Any deviation from this behavior would indicate surface segregation. If end groups are randomly distributed throughout the material, group additivity leads to the relation

$$\sigma = x_e\sigma_e + (1 - x_e)\sigma_r \qquad (5)$$

where x_e is the surface area fraction of end groups, σ_e is the surface tension of the end group, and σ_r is the surface tension of a repeat unit in the chain backbone. However, the relative surface fractions of the end group and repeat unit are not directly measurable.

Making the reasonable assumptions that the molecules pack on a cubic lattice and the end groups are randomly distributed, the surface fraction can be calculated according to the relation

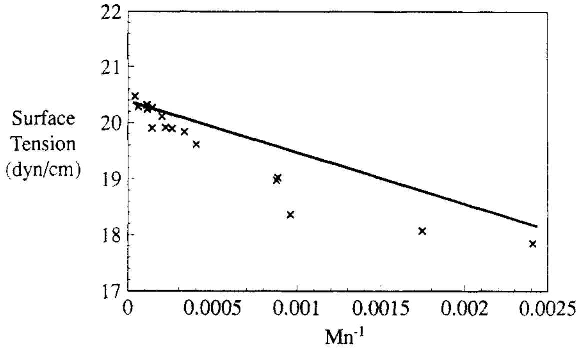


Figure 5. Experimental surface tension (crosses) and surface tension predicted by group contribution methods (line) for trimethylsiloxy-terminated PDMS.

$$x_e = 2v_e^{2/3}/(Nv_r^{2/3} + 2v_e^{2/3}) \qquad (6)$$

where v_e and v_r are the molar volumes of the end group and the repeat unit, respectively, and N is the number of repeat units. The molar volumes are determined experimentally from the slope and intercept of the line $1/\rho$ vs $1/M_n$ as follows:

$$1/\rho = v_r/m_r - 2(m_e v_r/m_r - v_e)/M_n \qquad (7)$$

where m_e and m_r are the molecular weights of the end group and repeat unit, respectively. It should be noted that the end groups are referred to by the functional group, i.e., methyl, amine, and hydroxyl. The chemical structures of the end groups are shown in Table I–III. These equations yield values of v_r equal to 76.3 cm^3/mol and values of v_e as follows: methyl, 117.0 cm^3/mol; amine, 130.2 cm^3/mol; hydroxy, 76.2 cm^3/mol.

Group additivity can also be applied to calculate the surface tension parameters required in eq 5. Koenhen and Smolders[24] have shown that the surface tension of nonpolar and slightly polar polymers can be related to the solubility parameter by

$$\sigma = (\delta^2/13.8)(n_s/v_s)^{-1/3} \qquad (8)$$

where n_s is the number of atoms in a segment and v_s is the molar volume of the segment. From tables of molar attraction constants of characteristic groups[25] it is possible to estimate the solubility parameter for the repeat unit and each of the end groups with the equation

$$\delta = \rho\sum F_i/M \qquad (9)$$

where F_i is the molar attraction constant of a specific group i and M is the molecular weight of the repeat unit or end group.

Using these equations, the surface tension of the repeat unit is calculated to be 20.1 dyn/cm, in reasonable agreement with the infinite molecular weight value of 20.37 ± 0.13 dyn/cm extrapolated from the experimental results. The group contribution predictions of surface tension for the methyl, amine, and hydroxyl end groups are 15.5, 32.8, and 26.9 dyn/cm, respectively. The calculations are illustrated in the appendix.

Figures 5–7 compare the group contribution predictions assuming a homogeneous distribution of end groups to the experimental surface tensions for methyl-, amine-, and hydroxyl-terminated PDMS. These comparisons suggest that the end groups are not randomly distributed throughout the material. In the case of the amine-terminated PDMS oligomers, the calculated value exceeds that of the experiment, suggesting a depletion of the high-energy

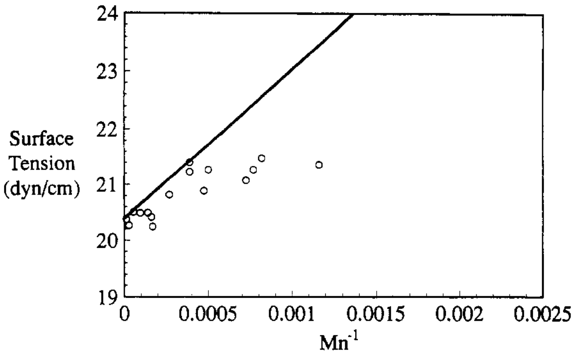


Figure 6. Experimental surface tension (circles) and surface tension predicted by group contribution methods (line) for (aminopropyl)dimethylsiloxy-terminated PDMS.

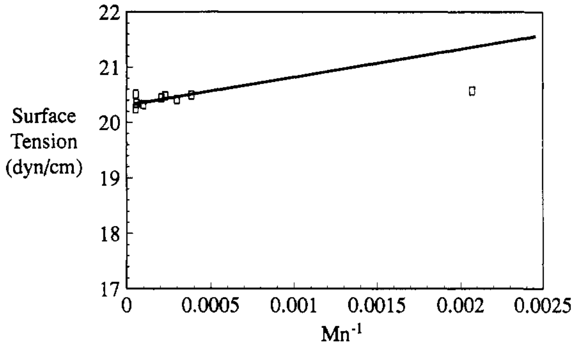


Figure 7. Experimental surface tension (squares) and surface tension predicted by group contribution methods (line) for hydroxydimethylsiloxy-terminated PDMS.

amine end groups from the surface. The low-energy methyl groups appear to be attracted to the surface as the experimental surface tensions for the methyl-terminated PDMS oligomers fall below the expected values. The hydroxyl group behaves as a neutral group, in that the predicted surface tensions agree closely with the experimental results.

Surface partitioning effects have been well documented in polymer solutions,[26] block copolymers,[27-33] and miscible homopolymer blends.[27,28,31] Theoretical treatment of these phenomena has also appeared.[32,34] The origin of this behavior can be clearly illustrated through classical thermodynamics. In the presence of an interface, a modified Gibbs–Duhem relation can be written for multicomponent systems[26] as

$$\sum \sigma_i \, dA_i = \sum n_i \, d\mu_i \qquad (10)$$

where σ_i is the surface tension of species i, dA_i is the change in the surface area due to the presence of species i, $d\mu_i$ is the change in the bulk chemical potential for species i, and n_i is the bulk mole fraction. Equation 10 shows that there will be a surface excess of the species i which has the lower surface tension. The increase in bulk free energy due to the change in chemical potential is balanced by the reduction in interfacial free energy. The surface tension will decrease due to this segregation, and thus surface tension measurements are a sensitive probe for the occurrence of preferential surface segregation.

Lattice and off-lattice model calculations[35] of melt surfaces also predict surface segregation of end groups; that is, low-energy end groups are attracted to the surface while high-energy (with respect to the backbone) end groups are repelled from the surface. The calculations predict that surface tension follows eq 1 where the sign and magnitude of k_0 are dependent on the relative interaction of the end group with the surface. The relative interaction can be modeled with an interaction parameter χ_s that is related to $(\sigma_\infty - \sigma_e)$ similar to the constant in eq 3. When χ_s is negative (i.e., $\sigma_e > \sigma_\infty$), end groups are depleted from the surface and surface tension decreases with molecular weight as observed for the amine-terminated PDMS. Positive χ_s (i.e., $\sigma_\infty > \sigma_e$) corresponds to the case of end-group attraction to the surface as expected for methyl-terminated PDMS. Recent simulations of polymer melts constrained between plates do predict an excess of chain ends at the surface consistent with our inference for methyl-terminated PDMS.[9]

The observed increase in surface tension with molecular weight for the methyl-terminated PDMS is thus consistent with the predictions of eq 3. Surface tension data for amine-terminated PDMS exhibit the opposite trend, showing a decrease in surface tension with an increase in molecular weight. This is again consistent with eq 3 since the surface tension of amine end group exceeds that of the polymer backbone. The surface tension data for the hydroxy-terminated PDMS falls between that of the methyl- and amine-terminated materials and appears to be independent of molecular weight. Hydrogen bonding between the terminal hydroxyl groups could account for this behavior as has been proposed in previous studies of hydroxy-terminated polymers. Alternatively, the molecular weight dependence predicted by eq 3 would vanish if the hydroxy groups were a so-called neutral end group, that is, if σ_e were equal to σ_∞ for this end group.

The group additivity approach presented herein provides at best qualitative support for the occurrence of end-group partitioning at surfaces. X-ray photoelectron spectroscopy (XPS) experiments,[36] however, substantiate the finding of an end-group depletion layer at the surface of amine-terminated PDMS. Publications describing XPS and neutron reflection investigations of end-group segregation in a number of functionalized polymers are forthcoming.

Conclusions

We have demonstrated that the surface tensions of poly(dimethylsiloxane) melts are strongly influenced by the precise chemical nature of the chain termini. The surface tension is found to be independent of the polydispersity index, indicating that surface segregation according to molecular weight is not significant. In all cases studied, the surface tension at high molecular weights is proportional to the inverse of the number-average molecular weight, with a value of the proportionality constant related to the difference in surface energies between the chain backbone and the end group. When the end group and backbone have similar surface energies (hydroxyl-terminated PDMS), the proportionality constant is effectively zero and surface tension is independent of molecular weight. The surface tension increases with molecular weight for end groups with surface energies lower than that of the backbone (methyl-terminated PDMS), but the increase is larger than that predicted by group additivity considerations, suggesting that lower-energy end groups are preferentially adsorbed at the free surface. The surface tension decreases with molecular weight for end groups with higher surface energies than that of the backbone (amine-terminated PDMS). In this case the decrease calculated by group additivity is larger than that observed experimentally, suggesting that high-energy end groups are depleted from the free surface. Supporting evidence for surface depletion of the amine end groups is provided by angle-dependent X-ray photoelectron spectroscopy results that will be described in future publications.

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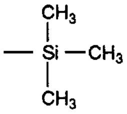
Appendix: Sample Group Contribution Calculation

methyl-terminated PDMS end-group structure



$$-\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$$

$m_e = 73$
$n_s = 16$
$1/\rho = a(1/M_n) + b$
$a = 83.1$
$b = 117.0$
$a = -2(m_e v_r/m_r - v_e)$
$m_r = 84$
$v_r = 76.4$ cm^3/mol
$v_e = 117.0$ cm^3/mol

group contribution to the cohesive energy density

group	F (MPa$^{1/2}$ cm^3/mol)
CH_3	437
Si	−77

$\rho_e = m_e/v_e = 0.624$ g/cm^3
$\sum F = 1234$
$\delta = \rho_e \sum F/m_e = 10.5$
$\sigma_e = (\delta^2/13.8)(n_s/v_e)^{-1/3} = 15.5$

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