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# Molecular Weight and Temperature Dependence of Polymer Surface Tension: Comparison of Experiment with Theory

It has been observed that the surface tensions of liquids are strongly correlated with the bulk thermodynamic properties.[1,2] Since there is an abundance of pressure-volume-temperature ($P$-$V$-$T$) data for materials, it is desirable to develop a strategy for the prediction of surface tensions from bulk polymer properties. The predictions of lattice fluid[3] and mean-field models[4] combined with density gradient theories have been compared with experimental surface tensions for polymers and low molecular weight liquids. The coefficient of the square gradient term used in the density gradient formalism to predict surface tensions was shown to be different for polymer and low-MW liquids.[3] It is not known whether this difference is due to an inadequacy of the theory over a wide MW range, inaccurate bulk liquid properties, which are used as input parameters for the theory, or other factors related to chemical structure. In an attempt to resolve some of these issues, we have made very precise surface tension measurements covering a wide range of PDMS molecular weights and temperatures and have also used extensive $P$-$V$-$T$ data obtained for the same samples to predict surface tensions. Good agreement is found for all molecular weights and temperatures. The same reduced square gradient coefficient ($\bar{\kappa} = 0.50$) with an error of less than 2% is used to describe the data for number-average molecular weights from 770 to 76 000 at all temperatures. This is an important step in attaining the goal of predicting accurately the surface tension of a variety of polymers at any temperature at which bulk properties can be measured.

The Cahn-Hilliard[5] theory is used in combination with an equation of state theory. Here the Flory, Orwoll, and Vrij[6] (FOV) theory is used. Cahn and Hilliard showed that in a system with an interface the free energy of the system can be written in the form:

$$A = \int_v [a_0(\rho) + \kappa(\nabla\rho)^2]\, \mathrm{d}\rho \qquad (1)$$

$a_0(\rho)$ is the free energy density of the uniform fluid of density $\rho$, $\kappa$ is the square gradient coefficient, and the second term describes the energy associated with the presence of an interface in the system with $\nabla\rho$ the gradient in $\rho$. The theory predicts that the surface tension of a planar interface is given by the expression

$$\gamma = 2\int [\kappa\Delta a]^{1/2}\, \mathrm{d}\rho \qquad (2)$$

where $\Delta a$ is the difference between the Helmholtz free energy density of a homogeneous fluid of density $\rho$ and a two-phase equilibrium mixture of the same density. The range of integration is from the low density state at $\rho_g$ to the high density state at $\rho_l$ where g and l refer to vapor and liquid, respectively. If $\kappa$ and $\Delta a$ are known, then we can compute the surface tension and density profile for a given system.

To evaluate eq 2, we need to compute $\kappa$ and $\Delta a$. To compute $\kappa$, we must assume an interaction potential. In practice $\kappa$ is treated as an adjustable parameter. The quantity $\Delta a$ is computed by using the equation of state. The equation of state used to describe the polymer liquid state must describe both the density of the liquid and the vapor state to within the experimental accuracy. The equations are first fit to pressure-volume-temperature ($P$-$V$-$T$) data for the polymer sample. Three fitting parameters ($P^*$, $T^*$, $V^*_{sp}$) were obtained for blocks of liquid data, which ranged from 0 to 30 MPa and 50 °C temperature increments. At the mean temperature of each block we computed the densities $\rho_l$ and $\rho_g$, which describe the liquid-vapor equilibrium, and hence compute $\Delta a$. For cell models like the FOV model it is necessary to introduce the $c$ parameter where $3c$ is the average number of degrees of freedom per mer unit. The value of $c$ sets the length scale for the problem. If the value of $c$ is set equal to 0.1111, then the value of the hard-core mer volume is given by the expression $ckP^*/T^*$ ($k$ is the Boltzmann constant), and the reduced $\bar{\kappa}$ needed to model the surface tension data is close to 0.5.

The advantages and limitations of the Wilhelmy technique using a vertical plate as a surface tension probe have been reviewed.[7] We have extended the technique by using small-diameter fibers to overcome the slow rate of viscous relaxation of the wetting meniscus. There are several advantages over the more common pendant drop technique. The main ones are that equilibration is faster and that, for temperature-dependent studies, density data are not needed because the Wilhelmy technique is an absolute technique. The Wilhelmy apparatus was described previously.[8,9] Briefly, smooth glass fibers (7 $\mu$m $\leq d \leq$ 300 $\mu$m) were drawn from molten glass and used as vertical Wilhelmy surface tension probes. The polymer surface tension $\gamma$ is related to the measured wetting force ($F = g\Delta m$, $g$ is the gravitational constant and $\Delta m$ is the change in mass for the fiber in contact with the liquid subtracted from the dry fiber mass) divided by the fiber diameter $d$ times $\pi$.

$$\gamma \cos\theta = g\Delta m/(\pi d) \qquad (3)$$

The contact angle ($\theta$) on the glass fiber is zero for these systems and a buoyancy correction is not needed for small-diameter fibers.[9] The sample temperature is determined by placing a microthermocouple in the liquid polymer (~1 g total) near where the fiber is immersed.

Properties of the PDMS samples used are given in Table I. The surface tensions were determined by the Wilhelmy method. The 1700, 71 000, 103 000, and 1 010 000 MW PDMS samples were supplied by Scientific Polymer Products. The other PDMS samples were obtained from Polysciences, Inc. Molecular weights were determined by GPC, viscosity, and light scattering. The open symbols in Figure 1 are experimental data determined by the fiber method as a function of $T$, and the filled symbols are calculated from the $P$-$V$-$T$ data taken from ref 10. Each theoretical point is a result of analyzing $P$-$V$-$T$ data over 50 °C temperature blocks as was discussed above using $\bar{\kappa} = 0.50$, and the results are plotted as the filled symbols in Figure 1. The solid curves are second-order polynomial fits to guide the eye. Good agreement is seen with the experimental data for the three molecular weights. The fourth is shown just to indicate the trend. The slope of the curves ($-\partial\gamma/\partial T$) is the surface entropy ($S$). Considering a narrow temperature range and neglecting curvature, a least-squares fit of the data in the range 20 °C < $T$ < 140 °C gives $S = 0.051$, $S = 0.055$, and $S = 0.065$ for $M_n$ = 32 000, 2600, and 770, respectively. The theoretically determined surface tensions follow this trend closely. The experimental values are consistent with those published earlier for 75 000 and 3900 MW samples over a more narrow temperature range.[11] $S$ is larger for low molecular weight oligomers because polymers have lower coefficients of thermal expansion than oligomers.[3] This leads to a more slowly changing interfacial density gradient with $T$, and thus the surface tension varies slower with $T$. It is also evident that both experiments and theory show curvature

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**Table I**
**Surface Tension and Molecular Weight of PDMS, 20 °C**

| $M_w$[a] | $M_n$[a] | γ, mN/m |
|---|---|---|
| | 770 | 19.35 ± 0.02 |
| | 1 700 | 20.13 ± 0.02 |
| 3 900 | 2 600 | 20.35 ± 0.02 |
| 17 000 | 7 830 | 20.62 ± 0.02 |
| 71 000 | 32 000 | 20.82 ± 0.02 |
| 103 000 | 43 900 | 20.84 ± 0.03 |
| 250 000 | 76 000 | 20.92 ± 0.04 |

[a] $M_w$ and $M_n$ are the weight-average and number-average molecular weights, respectively.

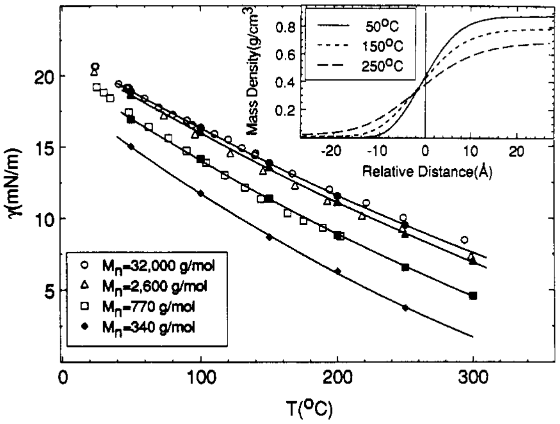

**Figure 1.** Temperature dependence of PDMS surface tension. Experiment is represented by the open symbols. The theoretically calculated values (filled symbols) are fitted by a second-order polynomial (solid curves). Note the strong variation in the absolute value of surface tension as one approaches the lower molecular weights. No experiments were reported for 340 MW PDMS. The inset gives the polymer density profile normal to the interface. These profiles are calculated by theory and when integrated, give accurate values of the surface tension at the three different temperatures.

in γ as a function of $T$ (Figure 1). This is caused by the rapid increase in the thermal expansivity with increasing temperature in the vicinity of the critical temperature. The critical temperature where γ approaches zero is ~513 °C for high-MW PDMS and 426 °C for 770 MW PDMS; the former is in agreement with tabulated values.[12]

It has been suggested that the discrepancy between density gradient theory and experiment is due to inaccurate values of the bulk liquid properties such as the densities calculated using the equation of state.[11] Using an equation of state that accurately represents the liquid density, we now show close agreement between theory and experiment. This also implies that the surface entropy depends principally on the local density and is independent of the density gradient and that the contributions due to conformational entropy are negligibly small in comparison. In contrast, for the polymer/polymer interface the conformational entropic contributions are quite important because of the finite segmental interactions between two immiscible polymers.[13,14]

The density profiles are directly determined by theory. Representative profiles are given in the inset of Figure 1 for 770 MW PDMS at three different temperatures. The surface tension is determined from these density profiles via eq 2 with the broader interfaces corresponding to the lower surface tensions. Note that the bulk density decreases with increasing temperature and that there is a small but significant vapor phase density of PDMS at 250 °C for this low-MW species. Any inaccuracies in the vapor densities predicted by the equation of state will result in increasing error near the critical point.

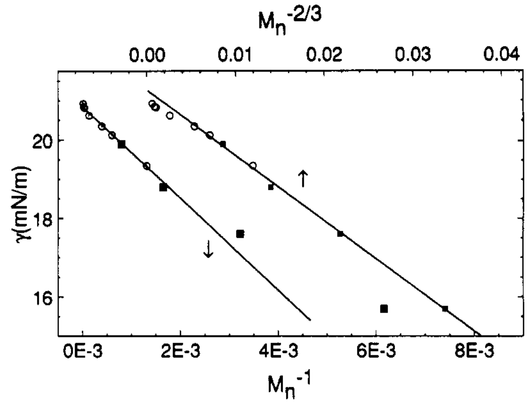

**Figure 2.** Measured surface tension γ versus $M_n^{-1}$ (lower line) and $M_n^{-2/3}$ (upper line) for PDMS at 20 °C. The open circles (error <0.04 mN/m) are from this work, and the squares are from the literature.[12,16] The solid lines are drawn through the data and indicate that at $M_n > \sim 3000$ the data deviate from the $M_n^{-2/3}$ dependence. The higher molecular weight data are well fit by the $M_n^{-1}$ dependence.

It is known that the surface tension of low molecular weight oligomers follows an inverse two-thirds molecular weight dependence[12,15,16]

$$\gamma = \gamma_\infty - K_e/M_n^{2/3} \qquad (4)$$

where $\gamma_\infty$ and $K_e$ are constants. Since extensive literature data for high-MW PDMS are not available, we have measured the surface tensions of a series of well-characterized high-MW PDMS samples (Table I; Figure 2). Some literature values[12,16] for the trimers, pentamers, etc., are also plotted in Figure 2 as the filled squares. Systematic deviation from the $M_n^{-2/3}$ dependence is seen in the top curve starting at $M_n > 3000$. In fact, the plot of γ vs $M_n^{-1}$ (bottom line) indicates that the data scale with $M_n^{-1}$ for molecular weights above 770. The same trend is seen with monodisperse polystyrene samples.[17] The reason for the $M_n^{-1}$ dependence is related to the rather complicated interrelationship of bulk density to surface tension and will be discussed in more detail at a later date. There is significant deviation from the $M_n^{-1}$ dependence in the bottom curve for the two lowest molecular weights (solid squares) as expected since the $M_n^{-2/3}$ dependence is well verified for oligomers.

We have established that the Cahn–Hilliard density gradient theory in conjunction with equation of state theories predicts surface tensions in good agreement with experiment from high-MW polymers to oligomers over a wide temperature range using a single value of $\bar{\kappa} = 0.50 \pm 0.01$. The agreement of the theory, which takes into consideration only bulk liquid properties, indicates that the contributions due to conformational entropy at the polymer/air surface are negligibly small. A similar strategy will be applied in the future to check the universality of the value of $\bar{\kappa}$ for a variety of polymer and oligomer systems.

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## References and Notes

(1) Siow, K. S.; Patterson, D. *Macromolecules* **1971**, *4*, 26.
(2) Patterson, D.; Rastogi, A. K. *J. Phys. Chem.* **1979**, *74*, 1067.
(3) Poser, C. I.; Sanchez, I. C. *J. Colloid Interface Sci.* **1979**, *69*, 539.
(4) Theodorou, D. N. *Macromolecules* **1989**, *22*, 4578.
(5) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258.
(6) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.

(7) Dettre, R. H.; Johnson, R. E. *J. Colloid Interface Sci.* **1966**, *21*, 367.
(8) Sauer, B. B.; Carney, T. E. *Langmuir* **1990**, *6*, 1002.
(9) Sauer, B. B.; DiPaolo, N. V., submitted for publication in *J. Colloid Interface Sci.*
(10) Ougizawa, T.; Walsh, D. J., to be submitted for publication.
(11) Bhatia, Q. S.; Chen, J.-K.; Koberstein, J. T.; Sohn, J. E.; Emerson, J. A. *J. Colloid Interface Sci.* **1985**, *106*, 353.
(12) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
(13) Poser, C. I.; Sanchez, I. C. *Macromolecules* **1981**, *14*, 361.
(14) Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 1223. Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 1229.
(15) Rossini, F. D. Selected Values of Properties of Hydrocarbons and Related Compounds. Research Project 44; American Petroleum Research Institute, Carnegie Press: Pittsburgh, PA, 1953.
(16) Gaines, G. L. *J. Phys. Chem.* **1969**, *73*, 3143. LeGrand, D. G.; Gaines, G. L. *J. Polym. Sci.* **1971**, *C34*, 45.
(17) Dee, G. T.; Sauer, B. B., unpublished data.

**Bryan B. Sauer* and Gregory T. Dee**

*E. I. du Pont de Nemours and Company, Inc.*
*Central Research and Development*
*Experimental Station*
*Wilmington, Delaware 19880-0356*

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