Macromolecules **1994,** *27,* 6112-6116

Molecular Weight Dependence of Surface Tension of Linear Perfluorinated Alkane Melts Including High Molecular Weight Poly(tetrafluoroethylenes)

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

Central Research and Development, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19880-0356

Received May 12, 1994; Revised Manuscript Received July 29, 1994[⊗]

ABSTRACT: Surface tensions (γ) and bulk pressure-volume-temperature (PVT) properties were measured for linear perfluorinated alkanes. The Cahn-Hilliard density gradient theory combined with an equation of state modeling of bulk properties was used to describe the temperature and MW dependence of γ for the perfluorinated alkanes. It is implicitly assumed in the theory that the surface has the same composition as the bulk, so it is known that the theory should fail in cases where significant orientation occurs at the free surface. Surface excesses of CF_3 chain ends were found to contribute negligibly to the measured surface tensions for perfluorinated oligomeric $CF_3(CF_2)_nCF_3$ to high molecular weight (MW) poly(tetrafluoroethylene) (PTFE). The surface tension of a high MW PTFE (MW ca. 70 000 g/mol) sample was measured for the first time using the modified Wilhelmy method. Theory could adequately reproduce the experimental γ and furthermore show that essentially the same results are predicted for an ultrahigh MW PTFE sample for which experimental values of γ could not be obtained because of the high melt viscosity. All of the perfluorinated alkane data were combined on a universal plot scaled by the PVT fitting parameters. The utility of the universal curve is that, for homopolymers for which PVT data are available, γ can be predicted at any temperature and MW to within 2%, with minimal computation.

Introduction

Fluoropolymers such as poly(tetrafluoroethylene) (PTFE) are widely used because of their surface properties and chemical and temperature resistance. The melt surface tensions of these materials are generally difficult to measure because of their high viscosities and high melting points. In many cases it is important to have the value of γ at the actual elevated temperature at which the materials are processed. Literature data are available for many standard polymers and other liquids.[1-4] For other polymers, especially high melting or less conventional polymers, data are extrapolated and may not be accurate or available. Very little PTFE surface tension data exist. Preliminary data for one medium MW sample were obtained recently in this laboratory.[5] It was a PTFE sample with carboxylic acid chain ends and a MW roughly between 10 000 and 30 000 g/mol. Because of the high MW of this sample, chain end effects could not be detected.[6] The values of γ for this sample[5] are consistent with those reported here for other even higher MW PTFE samples with perfluorinated chain ends. Data for a fluoropolymer "oil" with a MW of 1070 g/mol have also been reported.[7] The oil was a viscous fluid at room temperature because of chain branching and unsaturation,[7] whereas a pure perfluorinated linear alkane of this MW would have a relatively high melting point (T_m) of 185 °C.[8] The results presented below for "pure" linear materials indicate that values of γ for this oil are about 10% higher than those for linear PTFE of the same MW.

Surface tension data are also scarce for PTFE oligomers between C20 and C40 because of the high melting points, high vapor pressures, and difficulties in determining densities. Dettre and Johnson[7] summarized data for perfluorinated chain lengths between C5 and C12 at 20 °C. They compared the results with polyethylene and its oligomers and found similarities in the surface tension dependence with MW. We have attempted to obtain a more complete perfluorinated homologous series by including measurements on perfluorinated C20, C31, and C1400.

In the preceding paper,[9] extensive bulk property data in the form of PVT properties were reported for perfluorinated oligomer to polymer (PTFE) homologous series. In the present work, these PVT data are fitted with the equation of state theory of Flory, Orwoll, and Vrij (FOV)[10] and this information is incorporated into the Cahn-Hilliard[11,12] density gradient theory for the prediction of γ. The PVT data fitting method described previously was used to insure precise representation of the bulk liquid properties.[13]

Theoretical Background

The surface tension (γ) of a planar interface is derived by Cahn-Hilliard theory as[11,12]

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

where κ is the square gradient parameter and Δa is the difference between the Helmholtz free energy density of a homogeneous fluid of density ρ and a two phase equilibrium mixture of the same density.

Three fitting parameters are obtained from analyzing a given block of PVT data[13] with the FOV equation of state,[10] the reduced temperature T^*, specific volume V_{sp}^*, and pressure P^*. The scaled surface tension ($\tilde{\gamma}$) is given by

$$\tilde{\gamma} = 2\int_{\tilde{\rho}_v}^{\tilde{\rho}_l} [\tilde{\kappa} \Delta \tilde{a}]^{1/2}\, d\tilde{\rho} \qquad (2)$$

where $\tilde{\rho}_l$ and $\tilde{\rho}_v$ are the scaled densities of the liquid and vapor phases, respectively, and $\tilde{\kappa}$ is the reduced square gradient parameter. The scaled quantities are defined by[13]

$$\tilde{\gamma} = \gamma/\gamma^* \quad \text{and} \quad \tilde{\kappa} = \kappa/\kappa^* \quad \text{with } \kappa^* = (ckT^*)^{8/3}/P^{*5/3},\ \Delta\tilde{a} = \Delta a/P^* \qquad (3)$$

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

0024-9297/94/2227-6112$04.50/0

where

$$\gamma^* = (P^*)^{2/3}(T^*)^{1/3}(ck)^{1/3} \tag{4}$$

and k is Boltzmann's constant. The value of c is fixed to 0.111 to give a physically reasonable length scale in the FOV model.[13] The actual choice of c was shown not to be important in the calculation of γ^* because it is compensated by the value of the reduced square gradient coefficient $\tilde{\kappa}$ which is generally fixed to a constant value to normalize theory to the experimental data.[13] The value of c in the FOV model has been assumed to be unity by past workers.[14,15]

We have found that the most important aspect of the calculation of γ is the method used to obtain an accurate representation of the bulk properties. We have shown that the only way to accurately describe the data is by fitting small blocks of PVT data. This leads to a minor complication of having different fitted parameters (P^*, v_{sp}^*, and T^*) for each block of PVT data.[13] These blocks of PVT data are limited to a range of ca. 30 °C and a pressure variation from 10 to 50 MPa. If one attempts to use global values of P^*, v_{sp}^*, and T^* to fit entire PVT data sets, then serious systematic errors are observed because it is impossible to obtain a precise fit of the PVT data with only three parameters. As was shown previously, these errors are readily seen in the predicted temperature dependence of γ.[13]

Experimental Section

Materials. The molecular weights and melting points of the samples studied are listed in Table 1 and details of their characterization were given previously.[9] Perfluorohexane (C_6F_{14}, abbreviated C6) and perfluorododecane ($C_{12}F_{26}$) were gifts from Walter Mahler of DuPont. PTFE samples with weight average molecular weights of M_w = 1588 g/mol, M_w = 70 × 10^3 g/mol, and M_w = 27 × 10^4 g/mol were gifts of William Tuminello from DuPont. Perfluorononane (C_9F_{20}, lot 910840) and perfluoroeicosane ($C_{20}F_{42}$, lot 923053) were obtained from PCR Inc., Gainesville, FL. A commercial grade PTFE sample with very high MW (M_w estimated to be between 10 and 30 × 10^6 g/mol, ca. C400000) was taken from a block of Teflon.

Methods. The molten polymer surface tensions (γ) were measured using a modified Wilhelmy method.[5] Zero contact angle of the PTFE melt on the glass fiber is required for this measurement. Due to the high energy of the bare fiber and the low energy of the PTFE melt, this condition is satisfied. No densities are needed for the determination of γ. Approximately 0.5 mL of each polymer or oligomer were needed. No special precautions were taken to expose the molten sample to an inert atmosphere.

PVT melt properties were obtained using the method described previously[16] and were reported in the previous paper.[9] The instrument was obtained from Gnomix Research, Boulder, CO. Densities of PTFE and oligomers at 25 °C were measured using density bottles for liquids, and an autopycnometer (Micrometrics) for solids. For accurate results the room temperature sample density must be measured very carefully and solid samples must be prepared free of voids. Room temperature densities are required as input to calculate the absolute values of the specific volume, V_{sp} (=$1/\rho$), determined as a function of T and P using the PVT machine.

Results

Surface Tension. Experimental surface tensions are shown in Figure 1. The C20 and C31 samples began to vaporize very rapidly at their melting points so only one value of γ was obtained for each sample within a few degrees of their respective melting points. Even under these conditions, the Wilhelmy technique was not an optimum method for high vapor pressure melts such as C20 and C31, because the vapor solidifies and precipitates onto the hangdown wire and other parts of the equipment. The single points shown were reproduced very carefully, but no further attempts were made to take data at higher temperatures. Unlike the linear alkanes, which have rather low melting points and low vapor pressures, the perfluorinated linear alkanes have high melting points (Table 1). The high vapor pressures for these PTFE oligomers arise because of the close proximity of the melting points to the boiling points (i.e., $T_{bp} - T_m$ = ca. 100 °C).

Table 1. Perfluorinated Linear Alkanes[a]

	M_n[b]	M_w[b]	T_m (°C)
C6	338	338	−90[c]
C9	488	488	–
C12	638	638	77
C20	1038	1038	164
C31	1588		219
C1400		70 × 10^3	332
C5400[d]		27 × 10^4	331
C400000[d]		20 × 10^6	334

[a] C*n* is the abbreviated name where *n* is the number of carbons per chain. [b] M_n and M_w are the number and weight average molecular weights, respectively. [c] Taken from ref 8. [d] Surface tensions were not experimentally measured for these samples.

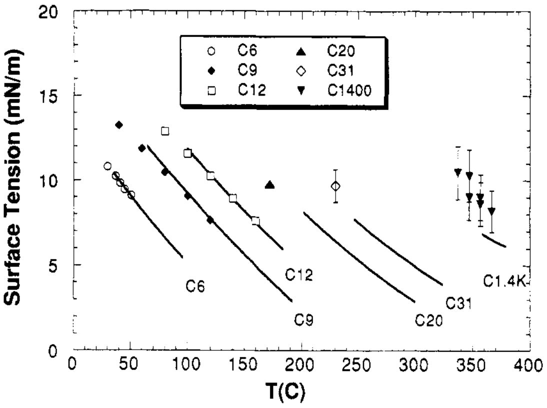

Figure 1. Experimental and theoretical melt surface tensions vs temperature are shown for perfluorinated linear alkanes including high MW PTFE. The predictions are represented by the solid curves and were calculated using a constant value of the reduced square gradient coefficient of $\tilde{\kappa}$ = 0.47 independent of temperature and MW. The experimental data for C9 and C12 were taken from ref 27.

The modified Wilhelmy method is the best method for the determination of γ for high MW (C1400) sample because C1400 has negligible vapor pressure. This sample was also too viscous for the determination by the standard pendant drop technique. The error bars on the experimental points (Figure 1) are due to the high temperatures and viscosities. The accuracy is high compared to other methods. The values for a previously studied PTFE sample[5] of slightly lower MW are consistent with those for C1400 in Figure 1.

The predictions in Figure 1 are represented by the solid curves and were calculated using a constant value of the reduced square gradient coefficient of $\tilde{\kappa}$ = 0.47 independent of temperature and MW. This value of $\tilde{\kappa}$ was fixed by normalizing the experiment to one temperature and one MW (i.e., C6 at 30 °C). Calculations give rise to discrete points (not shown) with some random scatter which depends on the noise in the blocks of PVT data. The scatter here is less than the thickness of the curves. The slight curvature in the theoretical predictions is real and has been seen in previous studies.[13,17] The changes in the calculated values (Figure 1) are entirely due to changes in bulk properties as they are determined by analysis of small

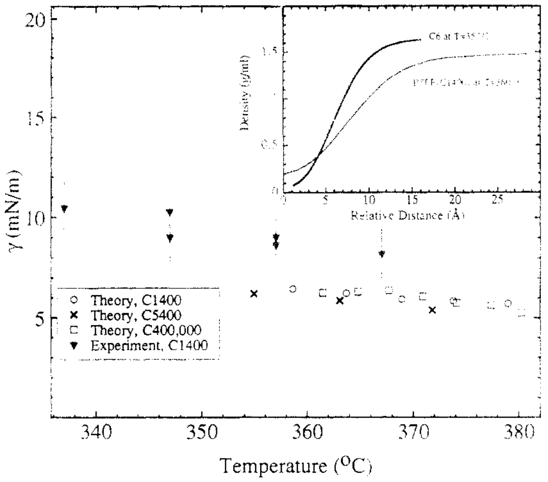

Figure 2. Experimental surface tensions for C1400 and predictions for C1400, C5400, and C400000. All of these MWs are high enough to reach the high MW limit of γ. The similarity of the data for the three samples indicates that the precision is high for each of the three PVT data sets. There is likely a slight inaccuracy of the PVT data to cause the systematic deviation from experiment (see the text). (inset) Density versus relative distance showing the concentration profile normal to vapor/liquid interface calculated by the Cahn–Hilliard theory for C6 at 35 °C (thick solid curve) and C1400 at 360 °C (thin solid curve).

temperature–pressure blocks of PVT data. The analysis of small blocks was shown to be necessary in order to obtain a precise representation of the bulk properties as was shown earlier.[13]

The Cahn–Hilliard theory also allows one to calculate the interfacial density profiles with no adjustable parameters. While the exact shape of the density profile is not specified by theory, the overall dimensions are expected to be accurate. The inset of Figure 2 shows that the typical dimensions are on the order of 15 Å for materials with low surface tensions. The similarity of the interface widths of low and high MW samples under these conditions is expected because the bulk (PVT) properties are similar at the respective MWs and temperatures. These interface widths are slightly broader than those presented earlier for higher surface tension melts.[13]

The agreement of experiment and theory in Figure 1 for C6, C9, and C12 is excellent. For the three higher MW samples, experiment agrees with theory to within experimental error. The theoretical data do not extend to temperatures as low as the experiment because the melting transition at higher pressures interferes with the analysis of liquid PVT data. For example, T_m = 330 °C at P = 0.1 MPa but increases to ca. 355 °C at 50 MPa for C1400.[9,18] The upper limit of our PVT instrument is 400 °C, leaving only a small block of data above the melting point from which one can obtain values of P^*, V_{sp}^*, and T^* for PTFE (i.e., C1400, C5400, and C400000). Although the precision is high for the C1400 predictions, there is possibly a small but systematic error due to inaccuracies in the measured PVT bulk liquid properties at $T > T_m$. The calibration of the PVT cell is not well verified at high temperatures, due in part to a lack of extensive data to compare with. This could also be due to small errors in our measured density at room temperature of the semicrystalline solid. These densities are necessary for the determination of absolute values of V_{sp} from the PVT output. Any errors in the room temperature density are magnified in the high temperature liquid properties due to the large volume expansion in the melting of PTFE.[18]

To further address the issue of the accuracy and precision of PVT data in the Cahn–Hilliard theory, three "high" MW PTFE samples of widely varying crystallinities and MWs were studied. Carefully measured room temperature densities were obtained for each sample. Figure 2 shows that the predictions of γ are almost identical for these samples. This indirectly verifies our room temperature density determinations which are the key input used to determine the absolute values of V_{sp} in the PVT data. In general, we have found that density determinations at 25 °C can be difficult because of voids and weak cohesive strengths for high crystallinity fluoropolymers.[9]

The molecular weight dependence of γ at constant temperature is typically represented in a M_n^{-1} or $M_n^{-2/3}$ plot.[1,19] Examples of both plots are given for perfluoroalkanes at 100 °C in Figure 3A. The plot indicates that the $M_n^{-2/3}$ dependence is valid for the oligomers, as has been shown in the literature at 20 °C for many materials.[1,19] A slight deviation from the $M_n^{-2/3}$ dependence can be seen for the highest MW in the plot similar to that seen for high MWs in $M_n^{-2/3}$ plots for linear alkanes including polyethylene.[20] It is also seen that the M_n^{-1} dependence holds for all but the lowest molecular weights as was shown earlier.[6,17,20] One drawback of this analysis for PTFE and oligomers is that temperature extrapolations were needed for the points at 100 °C for C20, C31, and C1400 because of their high melting points. The extrapolations for C20 and C31 were done with the aid of the theoretical slopes shown in Figure 1. Since the temperature dependence of C1400 is not well-defined by either experiment or theory because of the narrow range of accessible temperatures, a line was drawn from the experimental melt data to the accepted 20 °C value of ca. 23 mN/m for the surface free energy of PTFE, determined by various empirical methods in Table 5.1 in ref 2. Using this crude extrapolation, we obtain the value at 100 °C shown in Figure 3 for C1400. The trend at 100 °C can also be seen for plots compiled at other temperatures such as 160 °C (Figure 3C). Compiling a plot at 20 °C is ill advised because of the very long temperature extrapolations required for chain lengths greater than ca. C12.

The data for PTFE is compared to those for the linear alkane homologous series in Figure 3B. This plot suggests that a stronger MW dependence occurs for the perfluorinated series. Actually, if one plots the data in terms of chain length,[7] it is seen that the slopes of the MW dependence for alkanes and perfluoro alkanes (Figure 3C) are actually very similar, as is the case with bulk density.[9] Bulk densities are well-represented by a M_n^{-1} dependence over the entire range as is well-known for other materials.[21]

Cahn–Hilliard theory reproduces all of these experimental features with MW (Figure 1), as was the case with the linear alkane series.[13] Thus, both the $M^{-2/3}$ to M^{-1} dependence of γ are well-described by theory and must be due to the variation in bulk properties such as density, compressibility, and expansivity with MW. It is known that surface tension is mainly governed by short range forces and that chain connectivity is of minor importance. The bulk property variations depend mainly on short range forces and for a given chemical repeat unit they are governed by the variation in the number of chain ends per unit volume.[13,22] The lowest MW samples have the highest number of chain ends per unit volume and this lowers the bulk density because each chain end has a larger molar volume (mol/cm^3).

Because CF_3 groups are known to be more surface active relative to CF_2 groups,[23,24] there is a significant enthalpic driving force for chain end segregation. On the basis of the comparison of experimental and theoretical surface tensions, we see no evidence of a surface excess of chain

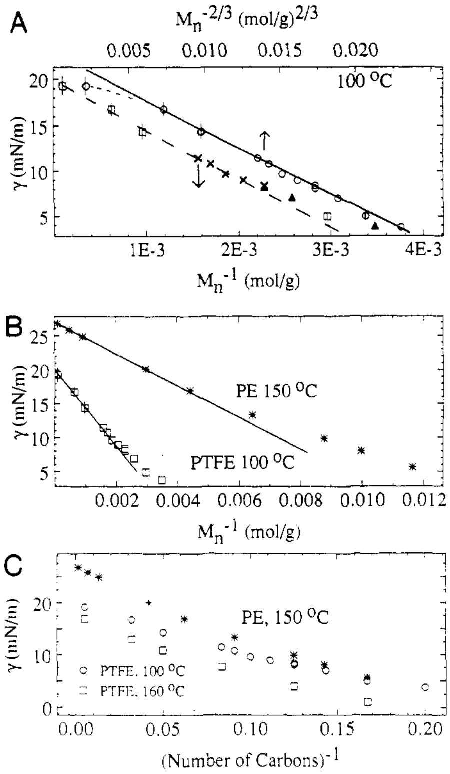

Figure 3. (A) Surface tension versus M_n^{-1} and $M_n^{-2/3}$ for PTFE and oligomers at 100 °C compiled using data shown in Figure 1 and from refs 27 and 28. The $M_n^{-2/3}$ dependence is valid for oligomers but fails at the highest M_n. Conversely, the M_n^{-1} dependence seems to hold for all but the lowest molecular weights (see the text). (B) Comparison of M_n^{-1} dependence for linear alkane[20] and linear perfluoroalkane homologous series. (C) Comparison of the same data from Figure 3B except the x-axis is plotted as the reciprocal number of carbons to facilitate a more direct comparison of γ as a function of chain length.

ends. It's likely that there is a slight surface excess of chain ends at high MW's because of entropic[25,26] and enthalpic advantages, but because the number of chain ends per unit volume is so low,[6] we cannot observe any contributions to the measured surface tensions. At the low MWs there is a significant chain end density but the enthalpic advantage of chain end segregation may be balanced by entropic penalties. Also, the interfaces are relatively broad for all MWs (i.e., 15 Å, inset of Figure 2), but especially for the low MWs, molecular dimensions become comparable to the interface width and this "diffuse" interphase region may diminish any orientation effects to a level where we cannot detect them by surface tension measurements. The ramifications of this diffuse interface will be addressed in future work.

Discussion

The strong temperature and MW dependence of γ illustrates the importance of careful liquid bulk property characterization. Without accounting for the bulk property changes, one cannot adequately describe surface tension. For the perfluorinated linear alkanes, there are moderate changes in density with temperature and MW.[9] For a 20% change in density, the surface tension can easily change by a 100% or more. Incorporating the variation in density and other bulk properties into the Cahn–Hilliard theory allows one to quantitatively describe the temperature and MW dependence with no adjustable parameters. It is implicitly assumed in the theory that the surface has the same composition as the bulk, so it is known that the theory should fail in cases where orientation occurs at the free surface. For example, depletion or excesses of end groups or side groups, or preferential block adsorption in copolymers,[20] will lead to deviations from theory as was shown previously. In the case of perfluorinated alkanes, any affects of surface excesses of CF_3 groups are too small to be detected by our methods as was discussed above.

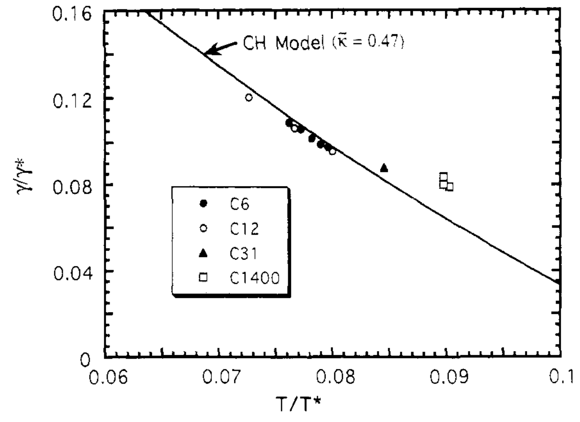

Figure 4. A plot of the scaled surface tension, γ/γ^*, as a function of the reduced temperature, T/T^*, for a series of linear perfluorinated alkanes including high molecular weight PTFE (see the text). The curve is generated using density gradient theory using a fixed value of the reduced square gradient parameter of $\tilde{\kappa}$ = 0.47.

A standard way of normalizing the data to account for differences in bulk properties is to scale the variables. The temperature is scaled with T^* and the surface tension is scaled by dividing by the reduced surface tension (γ^*) which is directly calculated from the PVT fitting parameters (eq 4). Figure 4 shows the reduced experimental data for PTFE and oligomers. The universal theoretical curve is obtained using a value of $\tilde{\kappa}$ = 0.47 for PTFE, i.e., the same value as was used for all the predictions in Figure 1. The different MWs of the perfluoro alkanes are specified in the figure caption. There is a slight deviation of the data points for C1400 from the universal curve. The reason for this was given in the Results section regarding the data in Figure 1. This is an example of the strong corresponding states principle[15] for γ and reinforces the idea that the short range forces are dominant, and the chain like contributions such as configurational entropic restrictions or end group excesses of polymers at free surfaces contribute negligibly. It was pointed out previously by Patterson and Rastogi that the existence of theories which predict these types of universal curves does not impart deep physical significance to the assumptions on which those theories are based.[15]

The results for polyethylene and oligomers (linear alkanes) for several chain lengths from C7 to higher MW samples[13] are compared with the perfluorinated linear alkanes in Figure 5. Theoretical curves calculated using two different values of $\tilde{\kappa}$ are also shown. Figure 5 indicates that species with the same chemical repeat unit can be described to within a few percent independent of MW. The same type of universal plot has been compiled by Patterson and Rastogi.[15] An approximate corresponding states theory was shown to exist[15] and the data for linear alkane homologous series (chain length greater than propane) including polyethylene could be collapsed onto a single curve. Their data had slightly more scatter because of the various sources from which the values of γ and the bulk properties were obtained. Systematic oligomer to polymer homologous series were only available for linear alkanes in their study. With more extensive data we can now observe the type of grouping as a function of different

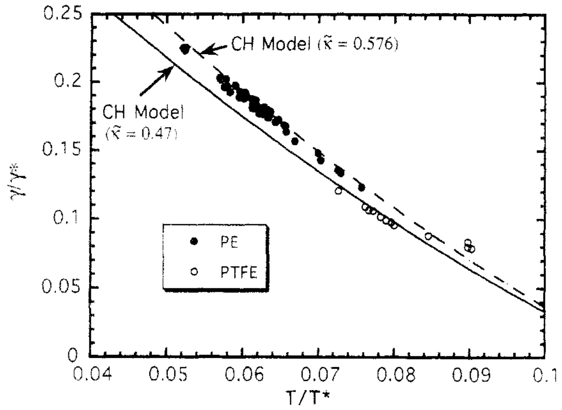

Figure 5. A plot of the scaled surface tension, γ/γ^*, as a function of the reduced temperature, T/T^*, for series of linear alkanes (PE) and perfluorinated alkanes (PTFE). The curves are generated using density gradient theory using fixed values of $\tilde{\kappa}$ = 0.576 (dashed line) and $\tilde{\kappa}$ = 0.47 (dashed line) (see the text for polynomial fits to the curves).

chemical repeats such as perfluorinated and hydrogenated linear alkanes, as is shown in Figure 5. Several other homologous series have been characterized in a similar way by different values of $\tilde{\kappa}$, as was discussed previously.[13,20]

There is a significant practical advantage of having a universal curve which describes the data. One can simply fit the universal curve to a polynomial, and after obtaining P^*, V_{sp}^*, and T^* for a given fluid, only simple algebra is necessary for the calculation of γ to an accuracy better than 2% for a given chemical species. For an unknown composition, the universal curve gives predictions accurate to ±6% for most polymers and oligomers based only on PVT properties. For the range of T/T^* shown in Figures 4 and 5, the curves can be reproduced by the empirically determined polynomial given by

$$\gamma/\gamma^* = \tilde{\kappa}\,(1.01585 - 12.6708T/T^* + 32.2042T^2/(T^*)^2) \tag{5}$$

Thus, the more extensive calculations of γ using the Cahn–Hilliard formalism are not necessary.

Other practical aspects of the theory are illustrated by the study of improcessable fluoropolymers such as C400000 in Table 1. The MW for this sample is so high that the material does not flow in the melt. Although the melt surface tension cannot be measured for a system which does not flow, with the PVT characterization of the melt, accurate values of γ can be predicted. Figure 2 shows these predictions for the C400000 sample compared to those for two moderate MW PTFEs. Many commercial fluoropolymers and fluorocopolymers require very high MWs (i.e., greater than ~300 000 g/mol) for mechanical integrity, and this may be the only way to determine the surface tension of these melts with a high degree of accuracy.

Conclusions

Surface tensions and bulk PVT properties were measured for linear perfluorinated alkanes including high MW PTFE. The Cahn–Hilliard density gradient theory combined with an equation of state modeling of bulk properties were used to describe the temperature and MW dependence of γ for the perfluorinated alkanes. It is implicitly assumed in the theory that the surface has the same composition as the bulk, so it is known that the theory should fail in cases where significant orientation occurs at the free surface. No evidence of an surface excess of chain ends (CF_3 groups) was seen from perfluorinated C6 to high MW PTFE from the comparison of experiment with theory. The surface tension of a high MW PTFE (M_n = 70 000) sample was measured for the first time. Theory could adequately reproduce these values and furthermore show that essentially the same results are predicted for an ultrahigh MW PTFE (MW ~20 000 000) sample for which experimental values of γ could not be obtained. All the perfluorinated alkane data were combined on a universal plot scaled by the PVT fitting parameters. The utility of the universal curve is that, for any sample for which PVT data can be obtained, γ can be predicted at any temperature and MW to within 2%, with minimal computation.

Acknowledgment. The authors would like to thank their DuPont colleagues W. Mahler, W. Tuminello, B. Haley, and N. V. DiPaolo for their contributions.

References and Notes

(1) Wu, S. *J. Macromol. Sci.-Rev. Macromol. Chem.* **1974**, *C10*, 1.
(2) Wu, S. In *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
(3) Koberstein, J. T. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1987; Vol. 8.
(4) Wu, S. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989.
(5) Sauer, B. B.; DiPaolo, N. V. *J. Colloid Interface Sci.* **1991**, *144*, 527.
(6) Jalbert, C.; Koberstein, J. T.; Yilgor, I.; Gallagher, P.; Krukonis, V. *Macromolecules* **1993**, *26*, 3069.
(7) Dettre, R. H.; Johnson, R. E. *J. Phys. Chem.* **1967**, *71*, 1529.
(8) Starkweather, H. W., Jr. *Macromolecules* **1986**, *19*, 1131.
(9) Dee, G. T.; Sauer, B. B.; Haley, B. J. *Macromolecules*, preceding paper in this issue.
(10) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
(11) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258.
(12) Poser, C. I.; Sanchez, I. C. *J. Colloid Interface Sci.* **1979**, *69*, 539.
(13) Dee, G. T.; Sauer, B. B. *J. Colloid Interface Sci.* **1992**, *152*, 85.
(14) Roe, R.-J. *Proc. Natl. Acad. Sci.* **1966**, *56*, 819.
(15) Patterson, D.; Rastogi, A. K. *J. Phys. Chem.* **1970**, *74*, 1067.
(16) Zoller, P.; Bolli, B.; Pahud, V.; Ackermann, H. *Rev. Sci. Instrum.* **1976**, *47*, 948.
(17) Sauer, B. B.; Dee, G. T. *Macromolecules* **1991**, *24*, 2124.
(18) Starkweather, H. W., Jr.; Zoller, P.; Jones, G. A.; Vega, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 751.
(19) Legrand, D. G.; Gaines, G. L., Jr. *J. Colloid Interface Sci.* **1969**, *31*, 162.
(20) Sauer, B. B.; Dee, G. T. *J. Colloid Interface Sci.* **1994**, *162*, 25.
(21) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581.
(22) Carré, A.; Vial, J. *J. Adhesion* **1993**, *42*, 265.
(23) Zisman, W. A. In *Advances in Chemistry Series 43*; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1964; p 1.
(24) Johnson, R. E.; Dettre, R. H. *Surf. Colloid Sci.* **1969**, *2*, 132.
(25) Kumar, S. K.; Vacatello, M.; Yoon, D. Y. *Macromolecules* **1990**, *23*, 2189.
(26) Zhao, W.; Zhao, X.; Rafailovich, M. H.; Sokolov, J.; Composto, R. J.; Smith, S. D.; Satkowski, M.; Russell, T. P.; Dozier, W. D.; Mansfield, T. *Macromolecules* **1993**, *26*, 561.
(27) Haszeldine, R. N.; Smith, F. *J. Chem. Soc.* **1951**, 603.
(28) Rohrback, G. H.; Cady, G. H. *J. Am. Chem. Soc.* **1949**, *71*, 1938.