Surface Tension and Melt Cohesive Energy Density of Polymer Melts Including High Melting and High Glass Transition Polymers

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Received February 14, 2002; Revised Manuscript Received May 29, 2002

ABSTRACT: Melt surface tensions and pressure−volume−temperature (*PVT*) data were obtained for many hydrophobic and hydrophilic polymers including high melting polyesters and polyamides such as poly(ethylene terephthalate) and nylon 66. A model is developed that uses surface tension to convert *PVT* data (from which the thermodynamic quantity "internal pressure" is calculated) into another thermodynamic bulk property, the cohesive energy density (CED). The errors inherent in assuming that the CED has the same proportionality factor to internal pressure independent of chemical structure are discussed. The results emphasize the difference between internal pressure and CED, where only internal pressure can be directly obtained from *PVT* data. The CED is the quantity that must be used for calculations of surface tension, and examples of the determination of melt surface tension are given for several polar or hydrogen-bonding polymers and semicrystalline or amorphous polymers of different molecular weights. Poly(2-vinyl pyridine) is contrasted with poly(4-vinyl pyridine), where the strong hydrogen bonding of the latter contributes to a large deviation of the proportionality factor between CED and internal pressure compared to that of the typical weakly interacting polymer. The results indicate that thermodynamic quantities, such as CED as a function of temperature in the melt, can be calculated for almost any molten liquid using these new models. The calculation of the CED for nylon 66 using structure/property relationships also provides a method for the determination of surface tensions for that polymer that cannot be directly measured.

Introduction

Vapor/liquid surface tensions are important for understanding various aspects of polymer melt processing, including the modeling of film extrusion, fiber spinning, and blend mixing. Accurate literature data are unavailable for many commercial polymers that have high melting temperatures. Bulk thermodynamic properties are inherently coupled to surface tension.[1,2] This paper proposes advances in the quantification of surface tension in terms of bulk cohesive properties and illustrates their application mainly to polymers, although the methods are also applicable to small molecule liquids. The measurement of surface tension in polymer liquids is difficult for several reasons. Polymer liquids have high viscosities and, hence, long relaxation times.[1] Many polymers become fluid only at high temperatures. This combination of long relaxation times and high temperatures makes conventional experimental methods[1,2] difficult, if not impossible. Pendant drop[1] or Wilhelmely plate[1,3] methods require long times for equilibration. The stability of polymer liquids at high temperatures has also restricted surface tension measurements on many polymer liquids.[1] Recently, we developed a method for the rapid measurement of the surface tension of very viscous liquids.[4] This new approach employs a modified Wilhelmey method in which a very narrow glass fiber is used as a probe. Very rapid and accurate measurements can be made. This has allowed us to gather a large body of data for polymer liquids,[2,5−8] but there are still experimental difficulties with some polymers such as the polyamides discussed at the end of this paper.

Polymer thermodynamic data are needed for many applications, but cohesive energy density (CED) data are available only in limited cases.[9−12] Up to now, the CED could not be directly measured for polymer liquids because of their negligible vapor pressures, although for oligomers and solvents, the CED can be measured using heats of vaporization.[10] The temperature dependence of the CED is almost always ignored because elevated temperature data are difficult to obtain and are simply not available. Even for small molecules, the CED is sometimes difficult to obtain experimentally with high precision.[13] This work reports a novel method for converting *PVT* data into CED data for polymers that allows one to determine the CED, including its temperature dependence, possibly for the first time. Accurate CED values are important when solubility parameters are used to model blend miscibility[12] at high temperatures based on the CEDs of the components.

Background

The cohesive energy density is equal to U/V and is "related" to the quantity obtained from *PVT* data called the internal pressure, P_i

$$P_i = (\partial U/\partial V|_T) \tag{1a}$$

$$= T\,(\partial S/\partial V|_T) - P \tag{1b}$$

$$= T(\alpha/\beta) - P \tag{1c}$$

with

$$\mathrm{CED} = U/V \tag{1d}$$

where U is the internal energy, V is the molar volume, α is the volumetric thermal expansion coefficient, S is the molar entropy, β is the isothermal compressibility, and P is the pressure.[13] We emphasize that the values of P_i as a function of temperature are determined from *PVT* data. Even though reliable *PVT* data have been established for many materials over the past few

10.1021/ma0202437 CCC: $22.00

Table 1. Summary of Parameters Extracted from Surface Tension and *PVT* Measurements on Each Material

	$\tilde{\kappa}$	n	CED (temp) (MPa (°C))	T_m (°C)
hexadecane (C16)	0.57	1.21	197 (150)	18
polyethylene (C2000)	0.57	1.21	220 (200)	134
PS	0.49	1.35	230 (200)	amorph
PPO	0.53	1.25	190 (200)	amorph
PEO	0.59	1.17	340 (200)	60
PCAP	0.58	1.18	325 (200)	60
PBT, poly(butylene terephthalate)	0.67	0.95	420 (260)	223
poly(trimethylene terephthalate)	0.70	1.05	400 (260)	223
PET	0.78	0.95	474 (300)	255
PEKK	0.71	0.88	440 (340)	305
P-2VP, poly(2-vinyl pyridine)	0.62	1.15	269 (250)	amorph
P-4VP, poly(4-vinyl pyridine)	0.87	0.90	600 (250)	amorph
poly(amide ester) copolymer	0.72	1.05	470 (200)	160
nylon 66[a]	0.72	1.05[a]	420 (290)	260
polyamide MPMD-12	0.7	1.05	319 (290)	190

[a] Nylon 66 was very difficult to measure experimentally, and no values of γ are available from the Wilhelmy method. Thus, we assumed that it has the a value of $\tilde{\kappa}$ identical to that of the polyamide ester because the two polymers are similar in composition.

years,[14,15] the thermodynamic parameters extracted from such data have inherent limitations. In particular, P_i has been wrongly assumed to be equivalent to the CED for lack of any better measure of the CED. Hildebrand[10] introduced the quantity n ($n = P_i$/CED) and observed that, for a large number of low-molecular-weight liquids, n is about equal to 1. Allen, Gee, and Wilson[13] discussed the discrepancies between CED and P_i for low-molecular-weight materials, which provided an important lead into what was needed for the correct modeling of thermodynamic properties. They used eq 1b, which relates the internal pressure to the change in entropy with volume. They speculated that, for systems with polar or hydrogen-bonding components, the change in entropy with the thermal expansion coefficient is reduced by the presence of these strong interactions while the CED remains high. This would give rise to the values of n less than 1 that are observed for alcohols and other hydrogen-bonding liquids. In this work, we show that the internal pressure can be related to the CED using experimental surface tension data. Using only P_i obtained from *PVT* data (or from thermal expansion and compressibility data) to model surface tension will contribute to errors, especially for melts of polar polymers as was recognized previously.[2,7]

In our laboratory over the past several years, a puzzling question has been recognized in the analysis of melt surface tension (γ) and *PVT* data for "polar" polymers such as poly(ethylene terephthalate) (PET). When the standard thermodynamic analysis was applied to compare measured surface tensions and the internal pressure of PET was analyzed in a precise way,[2,5] a large discrepancy was found between the values of γ calculated using internal pressure and the measured values. Such modeling of γ using thermodynamic properties required a rather large value of the reduced square gradient parameter ($\tilde{\kappa}$) (Table 1) to "fit" the data. Because the understanding was somewhat empirical, the problem remained unsolved until the relationship of P_i to CED was determined. We now realize that the discrepancies are a result of the relationship between CED and P_i and the dependence of this relationship on the nature of the interactions in the system of interest. These issues will be discussed here with the appropriate solutions.

The standard model typically used for the past several years[2] considers that the surface tension (γ) of a planar interface is described by Cahn–Hilliard density gradient theory[16]

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

where 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. The integration is in the direction normal to the interface and from the low-density vapor state with density ρ_v to the high-density liquid state ρ_l. The value of Δa is determined from precisely analyzed *PVT* data as was discussed previously.[5] This theory is referred to as the Cahn–Hilliard equation-of-state theory,[17] and the importance of the choice of the particular equation of state has been discussed recently,[2] as has the mathematical methodology for precise representation of the thermodynamic quantities as a function of temperature.[18]

For practical applications, it is sometimes convenient to write the equations in terms of reduced variables. The reduced equation for surface tension is[5]

$$\tilde{\gamma} = 2\int_{\tilde{\rho}_l}^{\tilde{\rho}_v} (\tilde{\kappa}\Delta\tilde{a})^{1/2}\, \mathrm{d}\tilde{\rho} \tag{3}$$

where $\tilde{\kappa}$ is the square gradient parameter and is essentially a constant multiplicative factor, so it can be taken outside the integral to give

$$\tilde{\gamma} = 2(\tilde{\kappa})^{1/2}\int_{\tilde{\rho}_l}^{\tilde{\rho}_v} (\Delta\tilde{a})^{1/2}\, \mathrm{d}\tilde{\rho} \tag{4}$$

Thus, we can use $\tilde{\kappa}$ to vertically shift the theoretical predictions on the plot of surface tension versus temperature. It is known that $\tilde{\kappa}$ is independent of molecular weight (MW) and temperature when the internal pressure is being used to calculate Δa,[5,6] making this theory very useful for surface tension predictions. Other scaled parameters are defined as follows

$$\Delta\tilde{a} = \Delta a/P^*$$

$$\tilde{\gamma} = \gamma/\gamma^* \tag{5}$$

with

$$\gamma^* = \epsilon^*/v^{*2/3}$$

and

$$\tilde{\kappa} = \kappa/\kappa^*$$

with

$$\kappa^* = \epsilon^* v^{*5/3} \tag{6}$$

where it was shown that[5]

$$\gamma^* = P^{*2/3} T^{*1/3} (ck)^{1/3} \tag{7}$$

P^* and T^* are parameters obtained by fitting *PVT* data[5] based on the application of the Flory–Orwoll–Vrij (FOV)[19] equation of state, which is derived from a microscopic model that models the molecules as being made up of segments or "mers" of volume v^*. The characteristic interaction energy per mer is ϵ^*. The other microscopic parameters that enter into the model are n_{mer}, the number of mers per molecule, and c, where $3c$ is the number of degrees of freedom per mer. The reduced temperature T^*, specific volume v^*_{sp}, and pressure P^* (all determined from PVT data) are used to scale the equation of state and are related to the microscopic parameters as follows: $P^* = \epsilon^*/v^*$; $T^* = \epsilon^*/ck$, where k is Boltzmann's constant, and $Nn_{\mathrm{mer}}v^* = M_{\mathrm{w}}v^*_{\mathrm{sp}}$, where N is Avogadro's number and M_{w} is the weight-average molecular weight of the molecule. Molecular weight actually does not affect the theoretical predictions because it is compensated mathematically by n_{mer}. In the FOV model, the relationship between the macroscopic parameters (P^*,T^*, v^*_{sp}) and the microscopic parameters (ϵ^*, v^*, n_{mer}, c) is ill-defined. To relate the two sets of parameters, a choice must be made for one of the microscopic parameters. The scaled surface tension, eq 7, depends explicitly on c. The choice of c merely determines the size of the mer used to define the polymer segment. If one makes a poor choice of the value of c, it can be compensated by the value of $\tilde{\kappa}$, as these are just offsetting multiplicative constants. Choosing c to be on the order of 0.11 results in values of v^* that are similar to the van der Waals volume for a typical polymer repeat unit and gives a value of $\tilde{\kappa}$ similar to that used for lattice models such as the Sanchez−Lacombe model.[17]

In the FOV model, the CED is equal to the internal pressure (CED $= P_{\mathrm{i}} = P^*\tilde{\rho}^2$). This is a consequence of the fact that a van der Waals potential is used to describe the interactions between the mers. Thus, the parameter P^* could be obtained by fitting to either CED or P_{i} data as a function of temperature. The values of P^* thus obtained would not be the same because the van der Waals potential is not an exact description of the nature of the interactions between molecules with diverse chemical structures. If one wished to use this model to describe properties that are related to the internal energy of the liquid, such as mixture thermodynamics or the surface tension, one would choose to use the CED to fit the scaling parameters. If one wanted to describe the thermal expansivity and the compressibility accurately, then one would use the internal pressure to fit the parameters. Clearly, the model as formulated cannot do both. For the modeling of surface properties, one should use the CED to define the parameters of the model, but in the case of most liquids, this is not possible because of the lack of CED data.

The main premise of the new analysis[7] is that a universal curve exists for the reduced surface tension as a function of reduced temperature of the liquid when scaled with the CED of the liquid. Once this curve is established for one liquid, it can be used for other liquids. In particular, in cases where the internal pressure is used to scale the surface tension, the differences between the scaled surface tension curves reflect the relationship between the CED and the internal pressure for that liquid. In ref 7, we established the nature of the universal scaled surface tension curve for polyethylene using the CEDs for a number of linear alkane oligomers. We assume that this curve will be the same for all polymer liquids where no gross surface segregation occurs at the liquid/vapor interface. With this assumption, we can construct a function $n(T)$ for any polymer using the following relationship

$$\gamma/\gamma^*(\mathrm{CED})|_{\alpha T} = n^{2/3}\gamma/\gamma^*(P_{\mathrm{i}})|_{\alpha T} \tag{8}$$

where $\gamma^*(\mathrm{CED})|_{\alpha T}$ indicates a reduction parameter calculated using the CED for that liquid state and $\gamma^*(P_{\mathrm{i}})|_{\alpha T}$ indicates a reduction parameter calculated using the internal pressure (P_{i}) for a polymer liquid state. The quantity n equals the ratio P_{i}/CED. The first function in eq 8 is assumed to be fixed for all polymers and was determined using linear alkane data, where data were available up to higher-molecular-weight alkanes.[7] In that study, two universal curves for surface tension scaled using the CED were identified.[7] One was for small molecules, and the other was for polymer molecules. The reason for the existence of two curves comes from the fact that polymer molecules have conformational constraints at liquid/vapor interfaces.[20] This entropic contribution to the surface tension results in a 5−10% displacement between the universal curve describing small molecules that do not suffer any conformational constraints at the surface and and the curve describing polymer molecules, which are defined to be any molecule large enough to have conformational restrictions at the interface.[20] One must consider that the interfacial full width is typically 10−15 Å (1.0−1.5 nm). The previous work showed that intermediate chain lengths such as a $C_{24}H_{50}$ linear alkane had intermediate surface entropy contributions.[7]

In our previous work,[5,6] we used PVT data (P_{i}) to model surface tension data. The observation that different values of the parameter $\tilde{\kappa}$ were necessary for data from polymers with different chemical structures was a consequence of using P_{i} as a measure of the cohesive energy. The values of n presented in Table 1 for a number of polymers were determined using eq 8 where the input information was the measured surface tension and the PVT data for that polymer liquid. Further verification of the true universality of the function on the left-hand side of eq 8 will require studies of the surface tension and PVT properties of oligomer series of other polymer species for which heats of vaporization are available for determinations of the CEDs of these liquids.

Experimental Section

PVT data were obtained using methods and equipment described previously.[14,15] The most important feature of the analysis of the PVT data is the method required to obtain a precise representation of the thermodynamic properties. This was done by fitting separate small temperature and pressure blocks of PVT data as described previously.[5,18] Even though this entails a temperature dependence of the PVT or other fitting parameters, it is the only way to obtain a precise representation of the data. Without such a method, a global three-parameter fit to the entire temperature range is imprecise and causes systematic deviations of the calculated bulk properties from the true ones.

Hexadecane ($C_{16}H_{34}$), 150-carbon linear polyethylene (C_{150}), polystyrene (PS, M_{n} = 60 000), poly(propylene oxide) (PPO, M_{n} = 2000), and poly(ethylene oxide) (PEO, M_{n} = 4000) samples were described earlier.[6] Polycaprolactone (PCAP, M_{n} ≈ 20 000, cat. 7039) was obtained from Polyscience, Inc. Poly(4-vinylpyridine) (P4VP, M_{n} ≈ 25 000, cat. 700) and P2VP (M_{n} ≈ 20 000, cat. 813) were from Scientific Polymer Products. PET was from Aldrich (M_{n} ≈ 20 000, cat. 138). Nylon 66 was additive-free Zytel 101 from DuPont. Poly(trimethylene terephthalate), poly(tetramethylene terephthalate) (PBT), and poly(aryl ether ketone ketone) (PEKK) were from DuPont. The

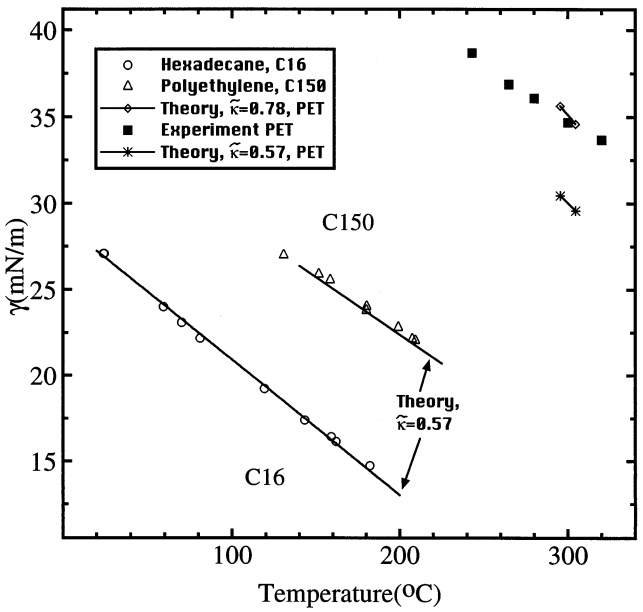

Figure 1. Surface tensions measured by Wilmelmy technique for PET, hexadecane (C16), and low-molecular-weight polyethylene with 150 carbons (C150) compared to *PVT*-based theoretical predictions (see text).

poly(amide ester) copolymer was made by Dr. G. Zahr of DuPont with 0.216 mol fraction of hexamethylenediamine, 0.6 mol fraction of adipic acid, and 0.184 mol fraction of ethylene glycol to give a copolymer with approximately 36 mol % nylon 66 blocks and the rest aliphatic polyester groups. This polymer had a broad melting point of ~160 °C, which is lower than the normal nylon 66 homopolymer melting point 260 °C because of the short nylon 66 blocks in the copolymer. This sample was important because we failed to obtain experimental surface tensions for all of the other polyamides. The polyamide made from 2-methyl pentamethylenediamine and $HOOC(CH_2)_{10}COOH$ is called polyamide MPMD-12 and is an isomer of nylon 6−12.

Results and Discussion

Previous work[5,6] has shown that the Cahn−Hilliard equation-of-state theory gives accurate predictions for nonpolar to moderately polar polymers such as poly(ethylene oxide) and many others using $\tilde{\kappa}$ values of around 0.55 ± 0.05. For a given polymer series such as the alkanes or almost any other series, $\tilde{\kappa}$ is independent of molecular weight and temperature to within about ±0.01,[5,6] except for poly(tetrafluoroethylene) (PTFE), where some discrepancies could not be resolved.[2] The calculations are based on the variation of the *PVT* properties (P_i) with temperature and molecular weight. For example, Figure 1 shows a good fit of experimental data for C16 and C150 linear alkanes with essentially no adjustable parameters. If the correct analysis were applied to C16 and C150 using CED instead of internal pressure, then the agreement would actually be slightly worse[7] because of surface entropic contributions.[20] This can actually be done for the alkanes because both P_i and independent CED values are available for different MWs and at different temperatures.[7,13]

Although the alkanes[5,6] and other polymers can be modeled with *PVT* data and values of $\tilde{\kappa}$ close to 0.57, for PET, the same value of $\tilde{\kappa}$ (0.57) gave excessively low predictions of surface tension relative to experiment (Figure 1). For example, a value of $\tilde{\kappa} = 0.57$, (remember, $\tilde{\kappa}^{1/2}$ is simply a multiplicative constant in eq 4) gives the lower curve in Figure 1 for PET, whereas it fits the alkanes almost perfectly. To adjust the data to experiment for PET, a larger prefactor of $\tilde{\kappa} = 0.78$ must be used to shift the prediction (Figure 1). Either the experimental *PVT* data or the Wilhelmy surface tension data are wrong, or something about the polar and/or high melt temperature of PET causes the theory to require a large value of $\tilde{\kappa}$. Either way, the predictive power of the equation-of-state method would be reduced because $\tilde{\kappa}$ cannot be easily predetermined. PET is very well behaved as far as Wilhelmy surface tension measurement is concerned,[21] and degradation at ~290 °C and higher causes only minor inaccuracies of the *PVT* results.[22] Thus, we conclude that some aspect of the theory or bulk thermodynamic information must be at fault for this material. The next step is to correct this situation.

For the solution, one must consider the subtle discrepancies between CED and P_i (eq 1) that are sometimes ignored in the literature. The CED is the correct quantity for modeling surface tension, and because the theoretical values in Figure 1 were derived from P_i and not CED, it suggests a large deviation between the ratio of P_i and CED for polyethylene relative to that for PET. Such a deviation could be explained by the strong specific polar or hydrogen-bonding interactions. They would have a different influence on P_i than CED, because CED is a direct measure of the interaction energy between molecules and P_i is simply the response of the internal energy to a change in volume. A more detailed discussion on the physical differences between the two quantities has been given previously.[13] Data for several other hydrogen-bonding or polar polymers show a consistent trend, all being characterized by larger values of $\tilde{\kappa}$ in Table 1.

After Hildebrand,[10] the ratio n is defined as

$$n = (\partial U/\partial V)/\mathrm{CED} = P_i/\mathrm{CED} \tag{9}$$

The value of n becomes as low as 0.9 for highly polar polymers and reaches almost 2.0 for nonpolar fluoropolymers[7] (Table 1). As for $\tilde{\kappa}$, n is slightly temperature-dependent,[7,13] although the reduced $\tilde{\kappa}$ is essentially independent of temperature.[5,18] Much of the discussion below will be in terms of $\tilde{\kappa}$, but this parameter has a close (inverse) relationship to n (Table 1). The value of n is related to $\tilde{\kappa}$ at 150 °C by an empirical fit to experimental data for many polymers studied here

$$n = 0.803\tilde{\kappa}^{-0.927} \tag{10}$$

We were not able to derive this relationship mathematically, but it is possible to determine this approximate inverse relationship empirically once n and $\tilde{\kappa}$ are measured for a few polymers. Because the values of n are slightly temperature-dependent, the relationship will change slightly depending on the temperature as will be discussed later. Furthermore, it is the CED that governs γ, so this strong variation in n with structure explains the large degree of error encountered when assuming that P_i is equal to CED.

Returning to the modeling of surface tension data, Figure 2 shows that a rather large value of $\tilde{\kappa} = 0.70$ is needed to shift the *PVT*-based surface tension prediction to experiment for poly(trimethylene terephthalate). Poly(butylene terephthalate) (PBT) also has a relatively high value of $\tilde{\kappa}$ (Table 1), although the polar groups are slightly "diluted" relative to those in PET, possibly explaining its slightly lower value compared to PET.

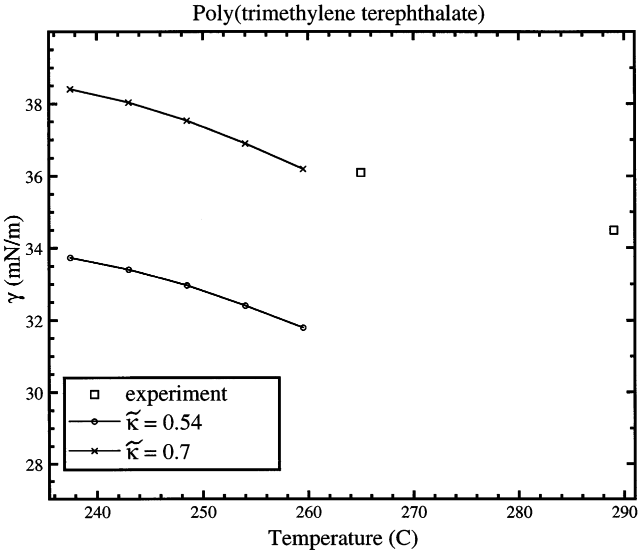

Figure 2. Measured surface tension for poly(trimethylene terephthalate) compared to theory based on *PVT* data determined using the two different values of $\tilde{\kappa}$ indicated.

Note the expanded scale of the data in Figure 2. Such comparisons require very accurate *PVT* and surface tension data.

Poly(aryl ether ketone ketone) (PEKK) is a higher melting polymer (Table 1) that is typically more stable in the melt than the aromatic polyesters, which makes the *PVT* results more accurate over a wider range of melt data.[22] PEKK might exhibit aromatic stacking interactions in the melt, which also facilitate better polar interactions of the carbonyl groups. It also has a large value of $\tilde{\kappa}$ relative to materials such as poly(propylene oxide) (PPO) and polystyrene, which have κ values typical of nonpolar polymers without strong specific interactions (Table 1) around 0.5. Although polar and even water-soluble, PEO and poly(caprolactone) $[-((\mathrm{CH_2})5\mathrm{CO_2})-]$ presumably have weaker polar interactions than PET or PEKK, as indicated by their relatively moderate values of $\tilde{\kappa}$ (Table 1). The aliphatic polar polymers [PEO and poly(caprolactone)] also have low melting points (T_{m}) of around 60 °C, which could be a partial indication that the crystals are also stabilized by weaker interactions.[23]

It might be somewhat surprising that the interactions in poly(caprolactone) are weaker than those in PET. It is known that there are aromatic stacking interactions in PET, which also must cause the polar groups to be more localized to each other. The ester groups are also more closely spaced along the PET chain, which could contribute to its higher polar interactions and higher $\tilde{\kappa}$ relative to that of poly(caprolactone).

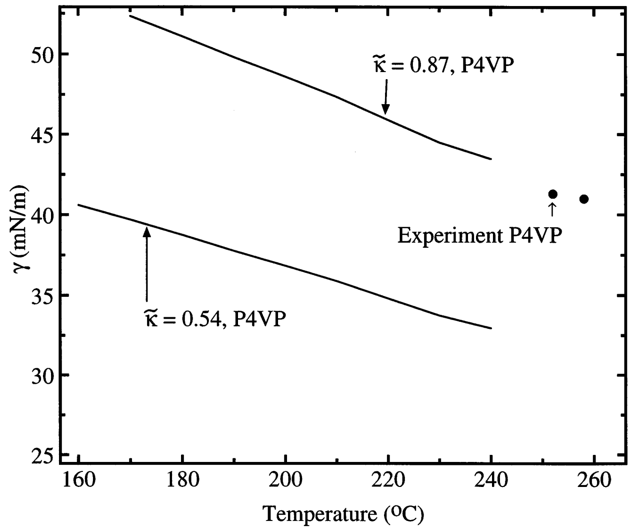

Figure 3. Measured values (filled circles) and theoretical *PVT*-based predictions (solid curves) of P4VP surface tension at two different values of $\tilde{\kappa}$. The theoretical surface tensions are terminated at high temperatures because sample degradation influences the *PVT* data.

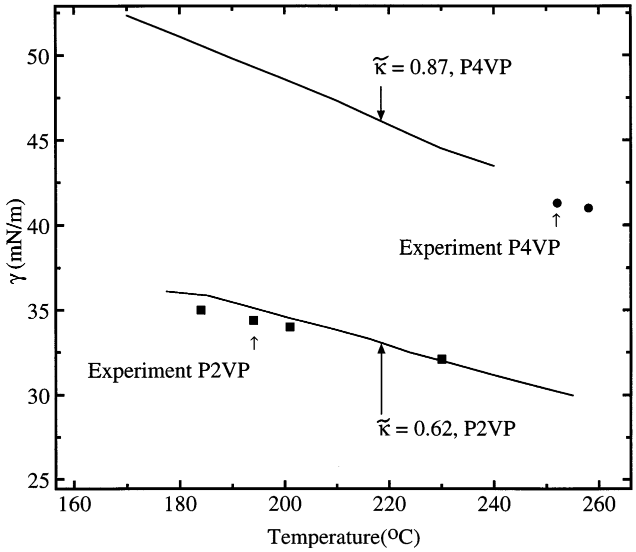

Figure 4. Measured surface tensions for P2VP and P4VP compared to theory with both theoretical curves adjusted to their respective best fits using the indicated values of $\tilde{\kappa}$.

Especially interesting comparisons include the well-studied amorphous polymers poly(2 vinyl pyridine) (P2VP) and P4VP. Although these polymers are isomers of each other, the huge value of $\tilde{\kappa}$ for P4VP relative to those P2VP and the other samples studied (Table 1) indicates an extremely strong specific polar interaction (hydrogen bond) in P4VP. The large difference between experiment and the *PVT*-based calculations using a value of $\tilde{\kappa} = 0.54$ characterizes the magnitude of the strong interactions in P4VP (Figure 3). Again, the *PVT*-based predictions do not quite overlap in temperature with the experimental surface tensions because of a slight degradation of the polymer in the *PVT* cell at elevated temperatures,[22] and our experimental surface tensions are limited by viscosity on the low-temperature side. P2VP has a slightly high but relatively typical value of $\tilde{\kappa}$ of 0.62. Directly measurable differences between P4VP and P2VP include a higher surface tension (Figure 4) but only a slightly higher density for P4VP. Because the densities are comparable and the surface tension is so high for P4VP, the value of the CED for P4VP must also be much higher (Table 1), as discussed below.

P4VP and P2VP are widely studied in the literature in terms of X-ray reflection and various interface and blend properties, mainly with PS in the form of homopolymers and copolymers.[24] The Flory–Huggins interaction parameter is $\chi = 0.1$ for P2VP/PS and falls in the range $\chi \approx 0.4-7.5$ for P4VP/PS.[24] The range is rather broad for P4VP/PS because of the various techniques applied to obtain these values, and a range of $\chi \approx 1.4-7.5$ is obtained from the possibly more reliable methods. The value of χ for P2VP is quite typical for a completely incompatible blend, but the value for P4VP is an order of magnitude higher than ever before measured for a nonionic polymer pair, which indicates a so-called “super-strong segregation” regime.[24] The very strong hydrogen-bonding interactions of the α hydrogen and the nitrogen group at the para position in the pyridine ring in P4VP cause the large χ value and will be shown to contribute to the large $\tilde{\kappa}$ in Table 1. It is known that the optimal hydrogen bond strength occurs when the “bond” angle is 180°, and because of steric factors, the intermolecular interactions between an α hydrogen on the backbone of one P2VP chain segment cannot easily satisfy this angle with another segment containing a nitrogen at the ortho position. In the case of the para nitrogen in P4VP, this optimal bond angle can more easily be satisfied.

To demonstrate the usefulness of the unique properties available from these studies, we now apply the bulk and surface quantities in two separate calculations. First, we can use the solubility parameter difference (δ) from our computed CED values of both polymers to estimate the χ parameter[26]

$$\begin{aligned} X &= (\delta_{\mathrm{PS}} - \delta_{\mathrm{P4VP}})^2 \\ \delta &= \mathrm{CED}^{1/2} \\ \chi &= Xv_o/kT \end{aligned} \qquad (11)$$

where $v_o = 1.7 \times 10^{-22}$ cm^3/mol of repeat units is the mean reference volume calculated from the actual melt specific volumes measured by *PVT* techniques for the two polymers and T is in Kelvin. Note that X is the interaction density and has units of pressure, but χ is dimensionless. The calculated value is $\chi = 1.1$. Although the CED values are accurate, specific interactions would be operative across the interface and would *not* be represented in such a calculation based on pure-component values of δ. Thus, one would expect this value of χ to be an underestimate because the specific interactions in P4VP are not well accounted for in such a calculation.

We can also calculate a polymer/polymer interfacial tension for PS/P2VP or P4VP, and this would also be a lower limit, i.e., the strong specific interaction in P4VP or even P2VP would tend to drive the value of interfacial tension even higher than the following estimate. Using the new values of γ for P4VP (i.e., 50 mN/m at 183 °C from Figure 4), the contact angle of PS on P4VP of $\theta = 10.9°$ at 183 °C,[24] and Young's equation

$$\gamma_{\mathrm{P4VP}} = \gamma_{\mathrm{PS}} \cos\theta + \gamma_{\mathrm{PS/P4VP}} \qquad (12)$$

we estimate a value of interfacial tension of $\gamma_{\mathrm{PS/P4VP}} = 21.4$ mN/m at 183 °C. $\gamma_{\mathrm{PS/P4VP}}$ can be used in the equation of Helfand et al. given previously[24] to predict yet another value of $\chi = 4.3$, somewhat higher than that estimated from solubility parameter differences and closer to the upper limit of the values given previously.[24] The validity of the Helfand analysis for χ values in this range is suspect because the predicted interface width is much smaller than the persistance length of the polymer.

Finally, we have attempted to measure surface tensions of nylon 66, nylon 11, and nylon MPMD-12 with little success on over 30 samples that we have tried over the years because degradation and “oxidized” skin formation on the surface of the higher temperature melt. One related sample that gave good results was an aliphatic semicrystalline “polyamide ester” copolymer that contains 36 mol % nylon 66. The composition is given in the Experimental Section. Accurate Wilhelmy surface tensions were measured for this sample, and the value of $\tilde{\kappa}$ was large (0.72), consistent with interactions from hydrogen bonding as would be expected for a polyamide. Assuming that the value of $\tilde{\kappa} = 0.72$ can be used for the nylon 66 homopolymer, we obtain the surface tension values shown in Figure 5, which we believe are quite accurate. Because of the lower density of amide groups, based on the trend from PET to PBT materials, we expect that a similar but slightly lower value of $\tilde{\kappa}$ will lead to reasonably accurate values of γ for the longer aliphatic chain polyamides. The *PVT* data are readily available for these and other polymers, and the predictions should be accurate even if one cannot measure their surface tensions experimentally. One example is the data for nylon MPMD-12 shown in Figure 5.

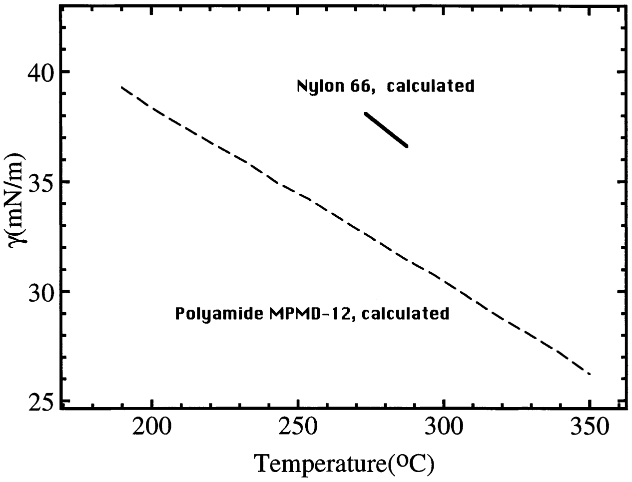

Figure 5. Surface tensions for nylon 66 and polyamide MPMD-12 calculated using the most dependable parameters available (see text).

Table 2. Polynomial Fits of Surface Tension Data

	A_o (mN/m)[a]	slope (mN/m °C^{-1})	temp range (°C)[b]
hexadecane (C16)	29.0	−0.094	25−100
PE (C2000)	35.6	−0.065	130−220
PS	41.5	−0.068	150−230
PPO	33.94	−0.073	10−180
PEO	46.7	−0.08	70−190
PCAP	44.4	−0.068	100−125
PEKK	63.8	−0.08	298−345
PBT, poly(butylene terephthalate)	59.3	−0.08	220−250
poly(trimethylene terephthalate)	53.8	−0.067	265−289
PET	54.2	−0.0646	240−320
P-2VP, poly(2-vinyl pyridine)	46.7	−0.063	184−230
P-4VP, poly(4-vinyl pyridine)	74.1	−0.128	250−260
poly(amide ester) copolymer	60.4	−0.08	160−190
nylon 66[c]	64	−0.115[c]	270−290
polyamide MPMD-12[c]	54.55	−0.081	190−350

[a] $\gamma = A_o +$ slope x T, where temperature is in °C. [b] The temperature range of the experimental data is given; for some of the systems, the range is narrow and one should be careful in extrapolating too far from this range. [c] The values for these polyamides are from theory but should be as reliable as experimentally measured values of surface tension. The range of data for nylon 66 is rather narrow, so the slope is probably not accurate.

Surface tensions over the indicated temperature ranges are summarized in Table 2. Except for some of the polyamides, these values are experimentally measured. Some values are considerably higher in general compared to previous literature, and we believe that they are much more accurate.[27] For example, the values for PET and nylon 66 at 270 °C from this study are 37 and 39 mN/m, respectively. From the *Polymer Handbook*, the values at the same temperature are 28.3 and 30.3 mN/m, respectively.[27] Our value for PET was measured experimentally on four different samples,[21] so we are confident in its accuracy. We have found similar discrepancies for nylon 11.

The values of CED in the melt are also given in Table 1. Recall that these results were determined from surface tension values combined with *PVT* (P_i) data for most of the polymers. The values of CED for some of the high melting materials are quite sensitive to the onset of degradation, which causes the *PVT* data to become less accurate. This onset is easily determined by examination of the *PVT* data. For example, one can look for the occurrence of an anomolously high compressibility, and after this point, the data should not be used. For polymers such as PET or nylon 66, we can reliably determine the values only in the low-temperature range of the melt. The values should show a slight decrease with increasing temperature, but they are relatively constant over narrow temperature ranges.

Conclusions

Melt surface tensions and independently measured internal pressures (P_i) derived from *PVT* data were used to determine the fundamental thermodynamic bulk property CED. To correctly correlate γ with bulk properties, the surface must have the same composition as the bulk, i.e., there can be no surface excesses such as those one might encounter with copolymers. The results show that P_i deviates from CED to different levels depending on the chemical structure of the system of interest. Such a deviation was explained for some materials by the presence of strong specific polar or hydrogen-bonding interactions in the bulk. They would have a different influence on P_i than they would on CED because CED is a direct measure of the interaction energy between molecules and P_i is simply the response of the internal energy to a change in volume (eq 1). The magnitude of the discrepancies can be characterized in terms of the ratio $n = P_i/\mathrm{CED}$, and for fluoropolymers, polyethylene, and poly(4-vinylpyridine), $n = 1.7$, 1.2, and 0.9, respectively. The large discrepancy between values of $n = 0.9$ for poly(4-vinylpyridine) and $n = 1.2$ for polyethylene can cause inaccuracies of approximately 30% in the magnitude of predicted surface tensions if one mistakenly uses P_i instead of CED. The value of $n = \sim 1.2-1.3$ is typical of hydrophobic to moderately polar oligomers and polymers (e.g., polyethylene or PEO, Table 1), and the detailed results allow one to quantify the very important quantity CED. Experimental melt surface tensions could not be directly measured for a few polar polymers, but values of n could be measured for similar chemical structures, and thus assuming this value of n allows the conversion of P_i into accurate values of γ.

Acknowledgment. We thank G. Zahr of DuPont CRD for his important contributions of materials and ideas and W. Kampert and B. Haley for their experimental work.

References and Notes

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MA0202437