Macromolecules **2000,** *33,* 8865−8869

Intramolecular Effects on the Thermodynamics of Polymers

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Received June 20, 2000; Revised Manuscript Received September 11, 2000

ABSTRACT: It has long been assumed that intramolecular screening effects strongly affect the thermodynamics of polymer systems. Thus, models such as the liquid state PRISM theory explicitly separate the intramolecular contributions from intermolecular interactions in enumerating the thermodynamics of polymer systems. Here we show that the normalized difference between the cohesive energy density, η, and the internal pressure, $\Pi \equiv \partial U/\partial V]_T$, $\Delta \equiv (\Pi - \eta)/\Pi$, which is essentially equal to zero for small molecules interacting purely through dispersive forces, allows for a direct measure of the intramolecular screening effect for polymer systems. These results are substantiated by analytical results derived from the lattice fluid model equation of state. We have also considered the behavior of several pure polyolefins from molecular dynamics simulations and find that Δ assumes a nearly universal value of 0.25 ± 0.02. While our results stress the importance of intramolecular screening effects in determining the thermodynamics of polymer systems, they also suggest that the assumption that $\eta \approx \pi$, which is commonly employed in the application of regular solution theory to polymers, may be grossly in error.

I. Introduction

The connectivity of chain molecules automatically dictates that the probabilty of intramolecular contacts is enhanced relative to intermolecular contacts. Such effects, which typically propagate a distance of R_G, the unperturbed radius of gyration of the chain, are termed as the "correlation hole" effect by deGennes.[1] The importance of these correlation hole effects has been previously recognized, for example in the PRISM liquid state theory, where the inter- and intramolecular pair distribution functions are explicitly separated.[2] While conceptually obvious, the experimental observation of the role of this correlation hole effect on system thermodynamics has not been documented.

Some indirect evidence exists from hydrogen-bonding systems. In this case one considers two species: one which is capable of self-association, while the other only participates in intermolecular association. By measuring the fraction of hydrogen-bonded groups through infrared spectroscopy, the equilibrium constants for the hydrogen-bonding interactions can be determined. The equilibrium constants determined from small molecule analogues are much larger than those determined from the polymeric counterparts.[3] Since the bare hydrogen-bonding interactions are expected to be equivalent in the two cases, it has been argued that the polymer groups show reduced intermolecular hydrogen bonding due to the correlation hole effect.[3] Through this indirect approach it was determined that roughly 30% of all nearest-neighbor contacts experienced by a chain moiety must be intramolecular.

To our knowledge no direct scheme has been devised to measure the role of intramolecular interactions in the thermodynamics of polymer blends. We now take a detour and focus our attention on the miscibility of polymeric mixtures which is generally understood through the use of the 50 year old Flory free energy of mixing, ΔG_{mix}.[4] This is nothing more than the regular solution analogue for polymers,[5]

$$\beta \Delta G_{\mathrm{mix}} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi \phi_1 \phi_2 \qquad (1)$$

Here ϕ_i and N_i are the volume fraction and chain length of component i, while χ is the Flory interchange energy parameter. β $[\equiv 1/k_B T]$ is the thermodynamic temperature. By exploiting the analogy to regular solution theory, and utilizing Berthelot scaling, it follows that $\chi \equiv \beta V_M (\delta_1 - \delta_2)^2$.[4] V_M is the molar volume of the mixture, and δ_i is the Hildebrand solubility parameter of component i, which is the square root of the cohesive energy density, η.[5−7]

$$\delta \equiv \sqrt{\eta} \approx \sqrt{\frac{\Delta U_{\mathrm{vap}}}{V_L}} \qquad (2)$$

V_L is the saturated liquid volume of the material, and ΔU_{vap} is the internal energy change on vaporization. While this approach precludes negative χ values, it is very useful since it utilizes pure component properties alone to predict the energetics of the mixture. Over 80% of chemically similar polyolefin blends examined appear to be describable by this polymer version of regular solution theory, attesting to its current relevance.[6−9] For most polymers it is impossible to measure the enthalpy change of vaporization. Consequently, the following approximation is utilized:[5,10]

$$\eta \approx \Pi \equiv \left[\frac{\partial U}{\partial V}\right]_{T,\mathrm{satd}} \qquad (3)$$

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10.1021/ma001062c CCC: $19.00

Π is the internal pressure of the system, which is evaluated at the saturated liquid density. Since Π can be determined directly from PVT measurements, it is readily accessible for a polymeric material.[6,11] This approximation, which is exact for any system that strictly follows the van der Waals equation of state (see below), has been proven to be remarkably accurate for small molecules that interact purely through dispersive forces.

Recent experimental work of Krishnamoorti et al.[6,11] utilized small-angle neutron scattering on polymer mixtures to determine differences in the δ values of the constituents and estimated Π values from PVT data. They found that the approximation embodied in eq 3 is not accurate, but rather that the η and Π values were proportional to each other. In fact, $\Delta \equiv 1 - \eta/\Pi = 0.28 \pm 0.11$ at 167 °C for most hydrocarbon-based polymers they studied. We shall show using analytical ideas and an equation of state that, to a very good approximation, the quantity Δ reflects the fraction of nearest-neighbor contacts that are intramolecular in origin. Computer simulations on hydrocarbon-based polymers, which show that the proportionality constant between η and Π is independent of chain architecture, are then presented to substantiate these ideas. In addition to providing a molecular basis for expecting that $\eta \neq \Pi$ for polymer systems, these results also provide a simple experimental route to stress the important role of chain connectivity effects in polymer thermodynamics.

II. Theory

A. Analytical Development. We begin by considering the identity

$$-\rho_{\mathrm{L}}^{3}\left[\frac{\partial(U/\rho)}{\partial\rho}\right]_{T,\mathrm{L}} = \rho_{\mathrm{L}}U_{\mathrm{L}} - \rho_{\mathrm{L}}^{2}\left[\frac{\partial U}{\partial\rho}\right]_{T,\mathrm{L}}$$

where U and V [$\equiv 1/\rho$] are intensive variables. While this identity is valid at all densities, we focus on the saturated liquid, which we denote by the subscript L. We now write this equation in a more familiar form by utilizing the energy of the gas phase, denoted by the subscript V, which is in equilibrium with this liquid:

$$\begin{aligned} -\rho_{\mathrm{L}}^{3}\left[\frac{\partial(U/\rho)}{\partial\rho}\right]_{T,\mathrm{L}} &= \frac{U_{\mathrm{L}} - U_{\mathrm{V}}}{V_{\mathrm{L}}} + \frac{U_{\mathrm{V}}}{V_{\mathrm{L}}} + \left[\frac{\partial U}{\partial V}\right]_{T} \\ &= -\eta + \Pi + \frac{U_{\mathrm{V}}}{V_{\mathrm{L}}} \end{aligned} \tag{4}$$

where we have utilized the standard definitions for the cohesive energy density,

$$\eta = \frac{U_{\mathrm{V}} - U_{\mathrm{L}}}{V_{\mathrm{L}}}$$

and the internal pressure (eq 3). For small molecule fluids far from their critical points $U_{\mathrm{V}} = 0$ since the vapor is an ideal gas. Further, experimentally it is well-known that $\eta \approx \Pi$ for small molecule systems which interact through dispersive forces alone. Since this implies that U/ρ is effectively independent of density, it appears that simple small molecule liquids can be relatively accurately modeled by a van der Waals description. We now consider the extension of these ideas to a polymeric fluid and stay within a van der Waals description of the liquid macromolecular phase. In particular, we employ the framework of a lattice model to simplify our calculations. It is assumed that chains are placed on a lattice of coordination number z and that each polymer–polymer nearest-neighbor interaction is associated with an energy of ϵ. The lattice is partially occupied by polymer, and the density is defined as $\rho = n_{\mathrm{p}}/[(n_{\mathrm{p}} + n_{\mathrm{h}})v_0]$, where n_{p} is the number of polymer segments on the lattice, n_{h} is the number of holes, and v_0 is the volume of a lattice site. α is the probability that a monomer experiences an intramolecular contact, a quantity we shall assume to be independent of density. On assuming a random mixture of holes and intermolecular polymer–polymer contacts, a simple expression for the total energy of the system can be derived,

$$U = \frac{z\epsilon}{2}\left[\alpha + \frac{(1-\alpha)\rho v_0}{1-\alpha\rho v_0}\right] \tag{5}$$

The first term on the right-hand side arises from intramolecular contacts, while the second term arises from our assumption that intermolecular contacts correspond to a random mixture of holes and intermolecular interactions. We now employ this expression in eq 4 to obtain

$$-\eta + \Pi + \frac{U_{\mathrm{V}}}{V_{\mathrm{L}}} = \frac{z\epsilon}{2}\left[\rho_{\mathrm{L}}\alpha - \frac{\alpha\rho_{\mathrm{L}}^{3}v_0^{2}(1-\alpha)}{(1-\alpha\rho v_0)^{2}}\right] \tag{6}$$

The first term on the right-hand side [in the brackets] is nothing but $U_{\mathrm{V}}\rho_{\mathrm{L}}$, and thus we are left with the result

$$\Pi - \eta = -\frac{z\epsilon}{2}\,\frac{\alpha\rho_{\mathrm{L}}^{3}v_0^{2}(1-\alpha)}{(1-\alpha\rho v_0)^{2}} \tag{7}$$

We now evaluate Π from the energy expression (eq 5) and obtain

$$\Pi = -\frac{z\epsilon}{2}\rho_{\mathrm{L}}^{2}\frac{(1-\alpha)v_0}{(1-\alpha\rho v_0)^{2}} \tag{8}$$

from which we finally obtain

$$\Delta \equiv 1 - \frac{\eta}{\Pi} = \alpha(\rho_L v_0) \tag{9}$$

Since most equations of state for typical high polymer liquids yield $\rho_{\mathrm{L}}v_0 \approx 0.85{-}0.95$, we suggest that, to within an error smaller than 15%,

$$\Delta \approx \alpha \tag{10}$$

This is the essential result of our analysis, one which provides a simple means of approximately quantifying the role of intramolecular contacts on the thermodynamics of homopolymers.

B. Application to Specific Equations of State. Here we examine the numerical predictions made by several popular equations of state for polymer liquids. The Sanchez–Lacombe model has $\alpha = 0$; i.e., no distinction is made between intra- and intermolecular interactions in the energy calculation.[12] This automatically leads to $\Delta = 0$. Note that the same can be shown for the Flory–Orwell–Vrij model.[13] The Panayiotou–Vera [PV] implementation of the lattice fluid model[14] incorporates the fraction of intermolecular contacts as fol-

Table 1. Δ Predicted by the Panayiotou−Vera Model[14] and from the Infinite Molecular Weight Extrapolation from MD Simulations for Saturated Hydrocarbon Polymers

polymer	density (lattice fluid model) [$\rho_L v_0$]	Δ LF model	Δ MD simulations
polybutene	0.85	0.17	0.24
poly(ethylene−propylene)	0.839	0.168	0.25
poly(ethylene−butene)	0.842	0.168	0.23
head-to-head polypropylene	0.837	0.167	0.26
head-to-tail polypropylene	0.838	0.168	0.25
polyethylene		0.176	0.23
polyisobutylene	0.878	0.176	
polystyrene	0.920	0.184	
poly(vinyl methyl ether)	0.865	0.173	

lows. The central variable is the fraction of external contacts per segment, q/N, which is $1 - \alpha$, in the nomenclature used above.

$$zq = zN - 2N + 2 \qquad (11)$$

N is the chain length, and z is the lattice coordination number. This equation takes into account the fact that, although a chain of length N can have zN nearest-neighbor contacts, $2N - 2$ are accounted for directly by chain connectivity. In the limit $N \rightarrow \infty$, $q/N \equiv (z - 2)/z$, which is independent of chain length. Note that this approach, which only accounts for bonded neighbors in the evaluation of intramolecular interactions, thus yields an α value that is effectively independent of density. The value of Δ obtained from this model can be calculated from the equation of state and eqs 3 and 4 or from the equivalence of q/N and $1 - \alpha$ given above. In either case we obtain

$$\Delta \equiv [1 - q/N](\rho_L v_0) \qquad (12)$$

We have fit the PV equation of state to PVT data for a number of hydrocarbon-based polymers, to obtain an estimate of $\rho_L v_0$ for each material. By utilizing these estimates and $z = 10$ in eq 12, we find that, as shown in Table 1, the ratio $\Delta \approx 0.17$ for seven hydrocarbon polymers and for two other common polymers.

These results are necessarily model dependent. However, by recognizing that $\rho_L v_0 \approx 0.80-0.95$ (Table 1) depending on system temperature and pressure, to an error of less than 15%, we can neglect the model dependent $\rho_L v_0$ and write

$$\Delta \approx 1 - q/N \qquad (13)$$

where $1 - q/N = 0.20$ if $z = 10$. It should be noted that, although the error in this approximation is a function of temperature and pressure, nevertheless eq 13 is still a robust description of the properties of the polymer liquid.

C. Molecular Dynamics Simulations. To lend credence to the analytical ideas presented above, we have conducted molecular dynamics simulations of united atom models for several hydrocarbon-based polymers. The details of the simulations have been presented in earlier work,[7] and we therefore only sketch the essential details of these calculations.

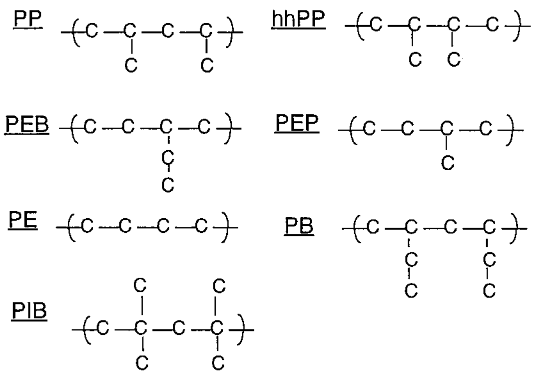

Figure 1. Repeat unit architectures for simulated hydrocarbons. The hydrogens are omitted for clarity.

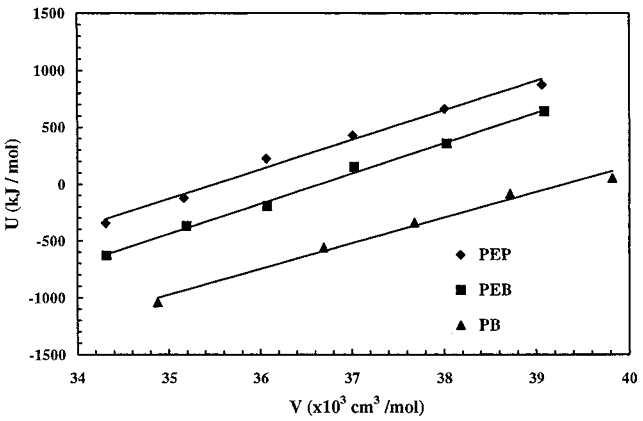

Figure 2. Internal energy as a function of volume for simulated hydrocarbons. The results for PB have been shifted vertically by 300 kJ/mol for clarity. The simulation uncertainties in the energy are smaller than the points.

The repeat units for the materials whose simulation results are presented in this paper are shown in Figure 1. The simulation model used in this work is a direct extension of the optimized force field for liquid hydrocarbons (OPLS) introduced by Jorgensen et al.[15] The united atom description is used; i.e., interactions between C, CH, CH_2, and CH_3 groups are considered, as opposed to interactions between individual carbon and hydrogen atoms. A distinction is made between methyl groups attached to secondary, tertiary, and quaternary carbons. Bonded nearest-neighbor interactions are represented by constraint forces, keeping the separation at 1.54 Å, and bond bending and torsion angle potentials were introduced. The nonbonded forces are characterized by Lennard-Jones (LJ) interaction sites located at the center of mass position of each united atom. Simulations were conducted in the (N,V,T) ensemble with a time step of 5 fs at a temperature of 150 °C.

The number of chains was 50. The volume is assigned on the basis of experimental densities at 150 °C and 0.1 MPa. The only material for which oligomeric densities are available is polyethylene. For the others, densities are assigned on the basis of polymer densities and the PE oligomer/polymer ratio at 150 °C. A constant temperature is maintained using the velocity rescaling algorithm of Berendsen et al.[16] The equations of motion are integrated using the standard velocity−Verlet algorithm,[17] and the bond length was kept constant using the RATTLE algorithm.[18] After equilibration of 500 ps, cohesive energy density data are collected over 1 ps intervals for 375 ps. In calculating the cohesive energy density, the energy of vaporization is taken to be the intermolecular portion of the total energy. Internal pressure determinations require calculation of the total potential energy values (i.e., inter- and intramolecular energies) at various densities. The internal pressure is

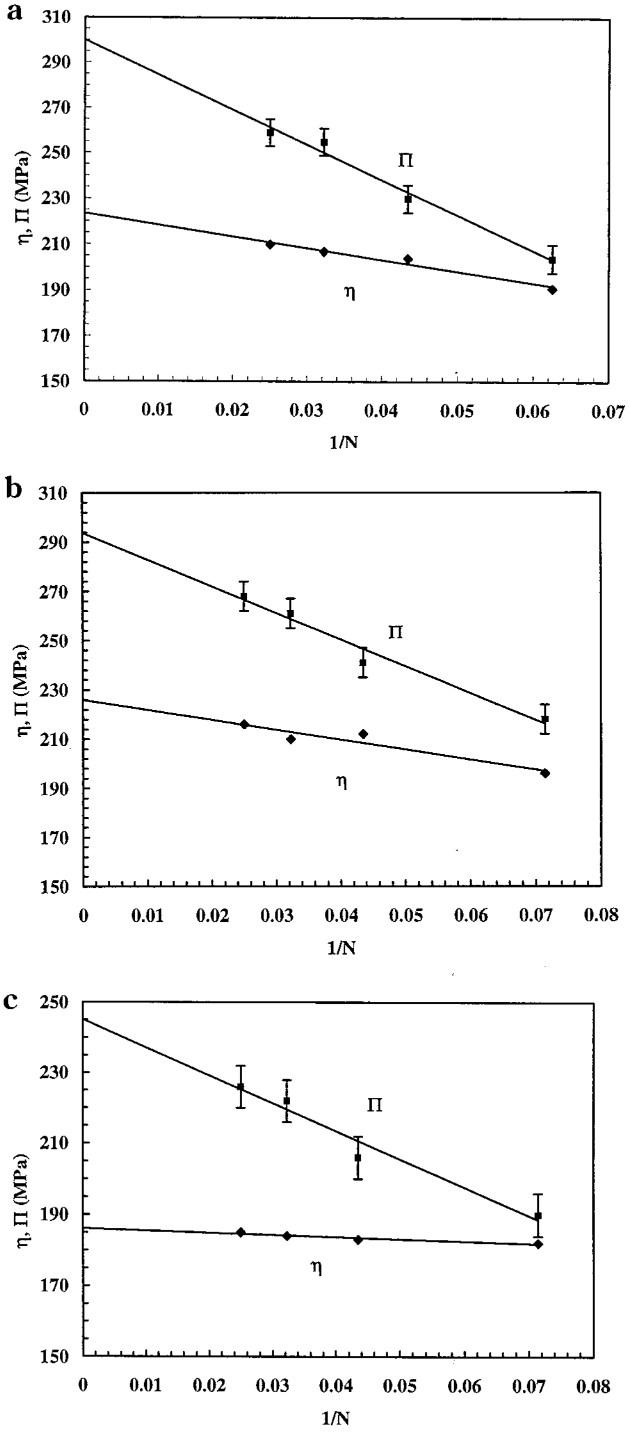

Figure 3. Chain length dependence of cohesive energy density and internal pressure for PEP (a), PEB (b), and iPB (c). Note that the simulation uncertainties for the cohesive energy density are smaller than the points.

then assigned as the slope of the energy versus volume plot over its linear region. Such a plot is shown in Figure 2. Alternatively, the energy versus volume curve was fit to a polynomial, the derivative of the curve taken, and the value of the internal pressure assigned as the slope at the ambient density. Both procedures result in similar values of the internal pressure.

For each polymer, we take four oligomeric analogues of 14, 23, 31, and 40 united atoms, respectively, in a series of simulations. Polymeric values of the cohesive energy density and the internal pressure are obtained by extrapolating to infinite chain length. Both quantities are plotted versus inverse of chain length, and the *y*-intercept is taken as the polymeric value. Plots of this nature are shown in Figure 3. It is obvious from the figure that both quantities are linear in 1/*N*. The polymeric internal pressure values obtained from simulation should strictly correspond to the experimentally derived values. Any differences can be attributed only to the ability of the model to describe these materials and the errors involved in extrapolations of the simulated internal pressure values. Figure 4 shows the simulated values of internal pressure plotted against the corresponding experimental values derived from PVT data. Reasonable agreement is obtained in all cases.

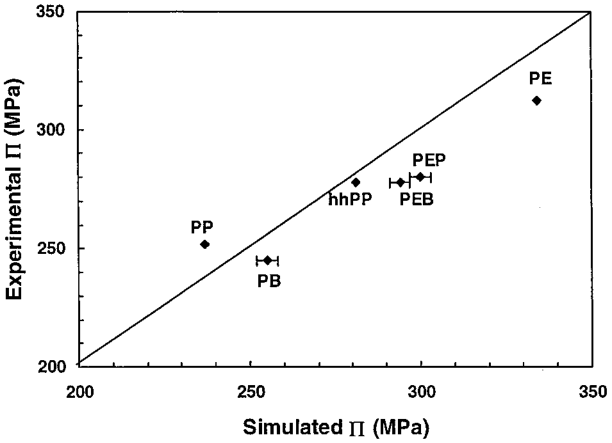

Figure 4. Comparison of simulated and experimental internal pressures. The solid line represents $\Pi_{\text{exp}} = \Pi_{\text{sim}}$. Only uncertainties inherent in the new simulation data are plotted.

For all six hydrocarbon polymers we simulated, we find $\Delta \approx 0.25 \pm 0.02$ (Table 1). It is interesting to note that this value remains approximately constant throughout a large variation in local chain architecture. While the numerical value of Δ obtained from the simulations is somewhat different from that of the lattice calculation, it is reassuring that both approaches predict ratios independent of chain architecture. The lattice calculations can be made to agree with MD results by varying the value of *z*, but we see this as a curve fitting exercise.

Taking an average value for $\rho_L v_0$ of 0.85 at 150 °C, the fraction of intramolecular contacts is $\alpha \approx 0.30$. In the only other such assessment of which we are aware, Monte Carlo simulations on a cubic lattice were employed at a packing fraction of 0.85. Oligomeric size chains were considered, as in this work, and the extrapolated long chain result was $\alpha \approx 0.38$.[3]

III. Conclusions

We have shown that the cohesive energy density, η, is not equal to the internal pressure, Π, the quantity which is obtainable experimentally for polymeric molecules. Note that, since $\alpha \approx 1 - \eta/\Pi$, the extent of this inequivalence is a measure of the fraction of contacts of a chain monomer that are effectively intramolecular. This is a significant finding since the role of chain connectivity on system thermodynamics has been the focus of many models such as the liquid-state theory PRISM,[2] as well as more recent models for hydrogen-bonded systems.[3] Our results provide the first direct means of targeting this issue and thus determining the role of connectivity on polymer thermodynamics. Since our findings for Δ do not vary significantly between materials, they suggest that the fraction of intramolecular contacts is independent of the particulars of the chain molecule in question, at least for these relatively flexible chains. This is consistent with findings from hydrogen-bonded systems where a similar result was obtained.[3] This conclusion is verified through computer simulations on an admittedly limited number of polymers, and thus we conclude tentatively that for truly long polymers η and Π can be used interchangeably with a universal constant of proportionality. This will obviously break down if polymers are blended with monomers or oligomers where α does not assume its infinite molecular weight asymptotic limit. In these cases the η and Π values of the two components will be proportional to each other, but with different proportionality constants. It is important to stress that the validity of these ideas to other classes of polymers remains to be explored before the generality of these conclusions is verified.

Acknowledgment. Financial support from the National Science Foundation, Division of Materials Research [DMR-9804327], is gratefully acknowledged. We thank Boris Veytsman for his comments.

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MA001062C