

## REVIEW

# The application of neutron scattering to the relation between chain dimensions and miscibility for polyolefins

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A method is described that can predict the way the great majority of polyolefins mix with each other just based on knowledge of their chemical architecture. The miscibility of saturated hydrocarbon polymers (polyolefins) is shown to be essentially controlled by the values of their solubility parameters as determined by several kinds of measurements, but most importantly from neutron scattering. Moreover, the way that these solubility parameters depend on the chain dimensions of the chains, is outlined.

A method to estimate chain dimensions by a correlation of the fraction of carbons that are on side branches vs the backbone is also given. The combination of these relations thus provides a very powerful mechanism to predict the mixing thermodynamics of polyolefins blends based simply on their chemical structure.

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## INTRODUCTION

Polyolefins, such as polyethylene, polyisobutylene and polypropylene, are the largest class of synthetic polymers. More than 100 million metric tons are produced each year worldwide.<sup>1</sup> These materials have enjoyed such great success because of a fortuitous combination of useful properties, among which are relatively low density, low cost of production, high strength, high chemical resistance and low dielectric constant and losses. About one third of all polyolefin materials are produced and used as blends of several different polyolefins. In some cases, these are blended in the melt, after polymerization, whereas often the products made in polymerization reactors are blends because of the presence of multiple catalyst species or multiple reactor environments. For all of these blends, the state of miscibility is critically important to their use. The past 20 years have seen a veritable explosion of information about the thermodynamics of polyolefin blends, which has shown that many of those in use today—those with molecular weights and compositions of commercial interest—are near the boundary of miscibility.<sup>2</sup> We also know that blends of polyolefins can have complex phase diagrams, displaying the same gamut of phase behavior as mixtures of monomeric liquids.

Beyond this commercial interest, polyolefin blends can serve as models for the polymer blends in general. The wealth of data on their miscibility provides a test for various theories of blend miscibility. For instance, mutual solubility of polyolefins turns out to be highly dependent on the details of the chemical architecture of the polymer chains, especially the degree, length and location of side groups.

The strong influence of chain architecture on the mixing of saturated hydrocarbon polymers gives us not only a way to probe the predictive power of various theories but also to design new materials from an understanding of the intrinsic properties of these polymers.

The main thesis of this paper is that the key parameter that differentiates the cohesive and mixing properties of polyolefins is a measure of their chain dimensions in the melt. In the first section below, a summary of the experimental results on polyolefin mixing is provided, and also a description about how these fit into a regular mixing scheme. It will then be shown how polyolefin solubility parameters correlate with chain dimensions, through the so-called packing length.<sup>3</sup> The third section describes why one might expect the cohesive energy of a polymer would depend on the chain size, and how this compares with a prediction of Schweizer and Singh from a PRISM model.<sup>4</sup>

## SUMMARY OF POLYOLEFIN MISCIBILITY DATA

The wealth of data on polyolefin blends that has been generated over the last several years has been compiled in a number of reviews.<sup>2,5</sup> One of the most interesting features of polyolefin miscibility that has been discovered in this work is the great range of phase behavior shown by these systems. Most polyolefin blends display UCST (upper critical solution temperature) phase diagrams with phase separation occurring upon cooling, but many are characterized by LCST (lower critical solution temperature) behavior by phase separating when heated. Some show both an LCST and an UCST. This great diversity

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in phase behavior may be regarded as surprising from saturated hydrocarbon polymers that interact only through dispersive, van der Waals forces.

The second interesting feature is that the great majority of these data can be explained by regular solution theory.<sup>6</sup> That is, interaction energy densities for most of these blends can be determined from the square of the difference between the solubility parameters of the two components, and that these solubility parameters are simply the square roots of the cohesive energy densities of the pure polymer. This is not universally true for polyolefin blends, and in fact several blends, especially those involving polyisobutylene,<sup>7</sup> show negative values of the interaction energy density. Nevertheless, regular solution theory does describe the miscibility data of around 90% of the blends, and for most of the irregular ones, the difference of the data from the regular solution predictions can be used to characterize the anomalies.<sup>8</sup> So the understanding of the origins of polyolefin solubility parameters underlies the understanding of polyolefin miscibility.

The most critical set of information for polyolefin solubility parameters has been the direct measure of miscible blend interaction energies from small-angle neutron scattering (SANS).<sup>9–20</sup> Important contributions have also come from determinations of phase diagrams by nuclear reaction analysis,<sup>21,22</sup> light scattering,<sup>23–26</sup> thermal analysis<sup>27</sup> and nuclear magnetic resonance.<sup>28,29</sup> Measurements of the dependence of specific volume on temperature and pressure (*PVT*) properties of polyolefins,<sup>30,31</sup> have provided data on their internal pressure, which is directly related to cohesive energy.

A large number of polyolefin solubility parameters have now been derived from neutron scattering and compiled.<sup>2</sup> Some of these values are shown in Table 1. These are polyolefins for which we have direct measures of density, melt chain dimensions<sup>32</sup> and solubility parameters derived from interaction energies measured on polyolefin blends by SANS. A significant hurdle in developing the

solubility parameter model of polyolefin miscibility is that the cohesive energies of the polymers cannot be directly measured (see below).<sup>6</sup> However, the solubility parameter values in Table 1 have been corroborated by measurements of the internal pressure of pure polyolefin components, which have been determined by the response of the polymer density to temperature and pressure (*PVT* data). The reader is directed to the study by Lohse and Graessley<sup>2</sup> (section II.D) for a fuller discussion of the relation of internal pressure to cohesive energy density, but it is worthwhile to point out that this relation for polyolefins is very similar to that seen for low molecular weight alkanes<sup>33</sup> for which both cohesive energy density and internal pressure can be directly measured. There is thus a great deal of confidence in these numbers, and as will be shown below, they can be used to predict the miscibility of polyolefin blends quite well.

It is well known that a chief distinguishing feature of polymer blends is that the entropy of mixing is very small, due to the large size of macromolecules.<sup>34</sup> This can be seen in the Flory–Huggins–Staverman<sup>35–37</sup> expression for the free energy of mixing:

$$\Delta G_m = RT \left\{ \frac{\phi_1 \rho_1}{M_1} \ln \phi_1 + \frac{\phi_2 \rho_2}{M_2} \ln \phi_2 \right\} + X_{12} \phi_1 \phi_2 \quad (1)$$

In equation 1,  $R$  is the gas constant,  $\rho_i$  is the density of polymer  $i$ ,  $\phi_i$  is the volume fraction of component  $i$ , and  $X_{12}$  is the interaction energy density between the two polymers. The interaction energy density is directly related to the more commonly used Flory interaction parameter,  $\chi_{12}$ , by the relation:

$$X_{12} = \frac{\chi_{12}}{v_0} RT \quad (2)$$

where  $v_0$  is a reference volume to normalize the value of  $\chi_{12}$ . When comparing the interactions for many different blends, the choice of  $v_0$  becomes arbitrary. To avoid confusion when comparing so many polymers and blends, herein the interaction energy density formulation of equation 1 will be used.

The power of regular solution theory is that it provides a way to predict miscibility in blends from parameters that are determined for the individual components. This basic parameter is the so-called solubility parameter for polymer  $i$ ,  $\delta_i$ , which is just the square root of the cohesive energy density of the polymer.<sup>6</sup> The cohesive energy is that which holds the molecules of a substance together in the condensed (liquid) state, and so is given by the heat of vaporization.<sup>33</sup> Obviously, this cannot be directly determined for most polymers, as they degrade at temperatures well below those at which they would boil. However, one can get reasonable estimates of  $\delta_i$  from *PVT* measurements and values can also be derived by redundancy from a large set of values for  $X_{12}$  when the number of blends is significantly greater than the number of component polymers.<sup>2</sup> One caution for the reader is that values of  $\delta_i$  from group contribution schemes do not work for polyolefins, as explained in Lohse and Graessley.<sup>2</sup>

Given the values of solubility parameters, it is quite simple to estimate the interaction energy density, since:

$$X_{12} = (\delta_1 - \delta_2)^2 \quad (3)$$

On the other hand, by measuring  $X_{12}$  for many pairs of polymers, one can extract values of  $\delta_i$  for the components, given the value for just one of them. (Herein, the reference value is taken to be that for atactic polybutene, determined from *PVT* evaluation of internal pressure) Such an assignment becomes more well founded when the number of blends measured is greater, and greater the redundancy of assigning solubility parameters. The values for the 17 polymers in Table 1 come from measuring  $X_{12}$  for 42 blends over a range of

**Table 1** Solubility parameters for selected polyolefin  $\delta$ , in units of  $\text{MPa}^{1/2}$

Polymer	$T$ (°C)				
	27	51	83	121	167
HPI-75	18.00	17.59	16.91	16.53	15.70
EB97	18.17	17.76	17.08	16.69	15.86
EB88	18.40	17.98	17.29	16.89	16.04
a-PP	18.39	17.98	17.33	16.95	16.11
EB78	18.66	18.24	17.54	17.13	16.27
HPI-50	18.68	18.26	17.56	17.14	16.29
EB66	18.90	18.48	17.77	17.35	16.48
alt-PEB	18.89	18.48	17.79	17.38	16.52
HHPP	18.99	18.55	17.84	17.41	16.53
EB52	19.18	18.74	18.03	17.60	16.72
alt-PEP	19.09	18.67	17.98	17.58	16.74
EB38		18.96	18.24	17.80	16.91
EB35		18.98	18.25	17.82	16.93
EB32		19.10	18.36	17.91	17.01
EB25			18.45	18.00	17.09
EB17				18.06	17.16
EB08				18.23	17.29

Abbreviations: alt-PEB, essentially alternating poly(ethylene-co-1-butene); alt-PEP, essentially alternating poly(ethylene-co-propylene); a-PP, atactic polypropylene; EBx, ethylene-butene random copolymer with x mole percent butene incorporation; HHPP, head-to-head polypropylene; HPDMBd-100; HPI-x, hydrogenated polyisoprene, x = 3,4 content of parent polyisoprene.

The data in this table are from Lohse and Graessley.<sup>2</sup>

temperatures. These values have been shown to work well in explaining in a number of polyolefin blend systems.<sup>38–41</sup> Note that the derivation of  $\delta$ 's from  $X_{12}$  needs to be performed at each temperature separately. Cohesive energy density, and so  $\delta$ , generally decreases as  $T$  increases, but at different rates for each polymer. This is the reason that, even under regular solution theory, all kinds of phase behavior (LCST and UCST) can be seen.

### CHAIN DIMENSIONS AND THE PACKING LENGTH

The packing length can be derived from a comparison of the occupied and pervaded volumes of a chain, and arises naturally in theories of polymer blend interfaces<sup>42</sup> and block copolymers,<sup>3</sup> as well as entanglements and rheology.<sup>43</sup> Consider first the occupied volume,  $V_{\text{occ}}$ , which is simply the volume per polymer molecule. This can be directly determined from the polymer density,  $\rho$ , Avogadro's number,  $N_A$ , and the molecular weight of the polymer molecule,  $M$ :

$$V_{\text{occ}} = \frac{M}{\rho N_A}. \quad (4)$$

The volume that is pervaded by a polymer chain is related to a measure of the chain size, such as its radius of gyration,  $r_g$ , or the distance between the chain ends,  $R$ . The Flory hypothesis<sup>44</sup> that polymer chains in the melt have the dimensions of ideal chains is now well confirmed by experimental evidence from SANS.<sup>32</sup> This means that the average of  $r_g^2$  is proportional to  $M$  (in the limit of large  $M$ ):

$$r_g^2 = KM. \quad (5)$$

The value of  $K$  depends on temperature and the chemical structure of the polymer, which control factors such as the probability of *trans* and *gauche* rotations of the backbone bonds. Moreover,  $R^2 = 6 r_g^2$ . As both  $V_{\text{occ}}$  and  $r_g^2$  are proportional to  $M$ , their ratio is a parameter independent of molecular weight and thus is a constant characteristic of the chemical structure of the polymer. This is called the packing length,  $l_p$ :

$$l_p = \frac{V_{\text{occ}}}{r_g^2} = \frac{M}{r_g^2 \rho N_A}. \quad (6)$$

The packing length is directly related to the statistical segment length of a polymer,  $b$ <sup>44</sup>. This quantity is also related to the size of the chain and is given by

$$b^2 = 6r_g^2 \frac{m_0}{M} = \frac{6r_g^2 N_A \rho v_0}{M} = \frac{6v_0}{l_p} \quad (7)$$

where  $m_0$  is the molecular weight of a monomer repeat unit and  $v_0$  its volume. Note that the definition of  $b$  requires the specification of a repeat unit, which is often problematic, especially for copolymers. Moreover, when comparing a number of different polymers, one needs to define a constant value of  $v_0$  as a reference volume, meaning that it will be arbitrary (just as it is for the Flory interaction parameter in equation 2). and so have no relation to the structure of the polymers. Because of this arbitrariness, the packing length formulation is more straightforward and more closely related to the actually measured parameters than is one using the statistical segment length. Another parameter often used to show how much larger the chain dimensions are than those expected from an unrestricted random walk model ( $R^2 = [M/m_0]l_o^2$ ) is the characteristic ratio,  $C_\infty$ <sup>44</sup>. This is given by

$$C_\infty = \frac{6r_g^2 m_0}{M l_o^2} = \frac{6m_0}{l_p^2 \rho N_A}. \quad (8)$$

Here  $l_o$  is the length of the repeat unit bond (0.154 nm for C–C single bonds). This can be very useful in comparing various polymers, as will be seen in the next section.

### MODELS OF CHAIN DIMENSIONS

In the following section, it will be shown that the solubility parameters of polyolefins correlate strongly with chain dimensions, and a rationale for this will be given. Although the melt chain dimensions for many polyolefins have been measured by neutron scattering,<sup>32</sup> the ability to predict miscibility becomes all the more useful if ways to estimate the sizes of polyolefin molecules can be found, especially for those that have not yet been synthesized. This is especially true, as SANS generally requires access to deuterated polymers and a neutron source. Estimates of the bulk melt dimensions are sometimes possible from dilute solution, theta-state values, but this only gives a qualitative idea of chain size and not a numerical value.<sup>43</sup> One method that often works to calculate polymer dimensions from first principles is the rotational isomeric state model,<sup>44</sup> but for many polyolefins, this has given results at odds with the experiment.<sup>43</sup> A promising new correlation of polyolefin chain dimensions with chemical structure has recently been found, and this is described in the rest of this section.

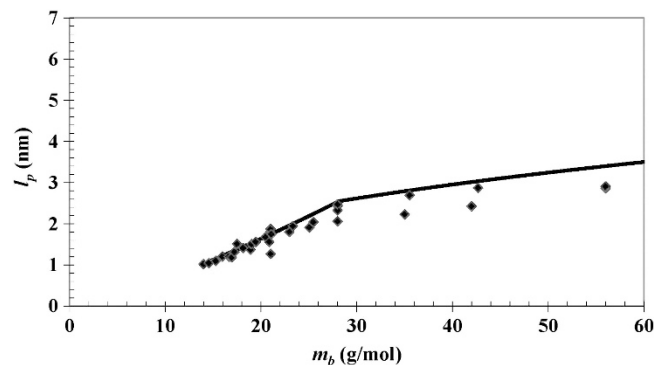
This correlation comes from an observation of how the dimensions of chains depend on a simple feature of the chemical architecture, which is  $m_b$ , the molecular weight per backbone bond.<sup>45</sup> In Figure 1  $l_p$  is plotted vs  $m_b$  at 190 °C for a wide range of polyolefins. Although there is not yet a clear physical model for these relations, it has been found that the dimensions of most polyolefin chains obey the following relations with  $m_b$  at 190 °C (for  $l_p$  in units of nm):

$$l_p = 0.0333m_b^{1.30} \quad 14 \text{ g mol}^{-1} < m_b < 28 \text{ g mol}^{-1} \quad (9a)$$

$$l_p = 0.627 m_b^{0.42} \quad m_b > 28 \text{ g mol}^{-1}. \quad (9b)$$

Of course, the values of  $l_p$  depend on temperature, but this dependence is fairly small and of secondary importance to that on  $m_b$ . Moreover, the temperature dependence of  $l_p$  is quite similar for most polyolefins, so the relative rankings are fairly consistent at all temperatures. Therefore, equation 9 satisfies the main objective of a reasonable estimate of chain dimension attributes. It is clear from Figure 1 that the relations in equation 9 work quite well for most cases. The clearest outlier is syndiotactic polypropylene, which is known to have large chain dimensions due to a preponderance of *trans* rotations.<sup>45</sup>

The variation of  $l_p$  with  $m_b$  is mostly due to changes in the 'thickness' of the chain (that is, how much of the chain is in the side



**Figure 1** Dependence of  $l_p$  on  $m_b$  at 190 °C. Solid line is from equation 9. A full color version of this figure is available at *Polymer Journal* online.

branches instead of in the backbone), but also is partly a result of differences in chain stiffness (that is, the tendency for *trans* vs *gauche* rotations). A good way to separate out the effects of stiffness is to look at how  $C_\infty$  depends on  $m_b$ . This is shown in Figure 2, and from equations 8 and 9 we have, at 190 °C:

$$C_\infty = 16.1m_b^{-0.30} \quad 14 \text{ g mol}^{-1} < m_b < 28 \text{ g mol}^{-1} \quad (10a)$$

$$C_\infty = 0.859m_b^{0.58} \quad m_b > 28 \text{ g mol}^{-1}. \quad (10b)$$

Another representation of this is to plot  $C_\infty$  vs  $f$ , the fraction of carbons that are in the backbone. For polyolefins,  $f$  is simply given by  $14/m_b$ . This gives the corresponding dependence of  $C_\infty$  depends on  $f$ , which is shown on Figure 3:

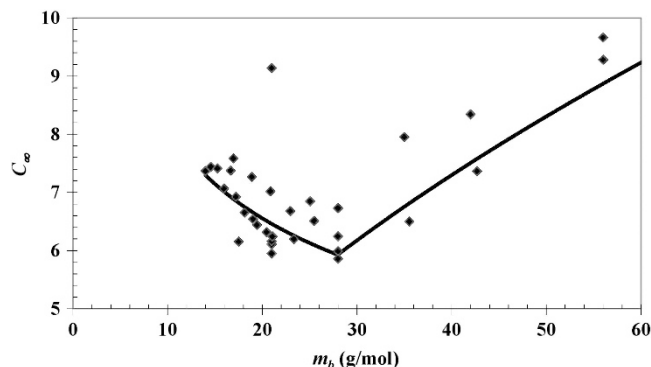
$$C_\infty = 7.29f^{0.30} \quad 0.5 < f < 1.0 \quad (11a)$$

$$C_\infty = 4.14f^{-0.58} \quad f < 0.5. \quad (11b)$$

In Figure 3, one can see that  $C_\infty$  reaches a minimum of about 5.9 at  $f = 1/2$ , that is, when half of the polymer is in the backbone and half is in the branches. This applies to both atactic polybutene, with an ethyl branch for every two backbone carbons, and an ethylene-octene copolymer with 33 mol% octene, with a hexyl branch for every six backbone carbons. One might speculate that this is the point at which the presence of the branches is most effective at changing the bond rotations of the backbone, that is, at increasing the proportion of *gauche* rotations. For  $f > 1/2$ , there are significant long stretches of methylene segments that will favor *trans* rotations. For  $f < 1/2$ , the branches are longer than the spacings between them, and so the chain cannot twist enough to avoid eclipsing of the branches with each other. However, it would be good to put this empirical observation on a firmer foundation of understanding. Moreover, it is important to point out the exceptions to this rule, such as syndiotactic polypropylene and polyisobutylene, as the utility of such materials depends on their special values of chain dimensions. However, the relations shown in equations 9, 10 and 11 can be used to give a rough estimate of the dimensions of most polyolefins, and so an estimate of their melt properties.

#### DEPENDENCE OF $\delta$ ON $l_p$

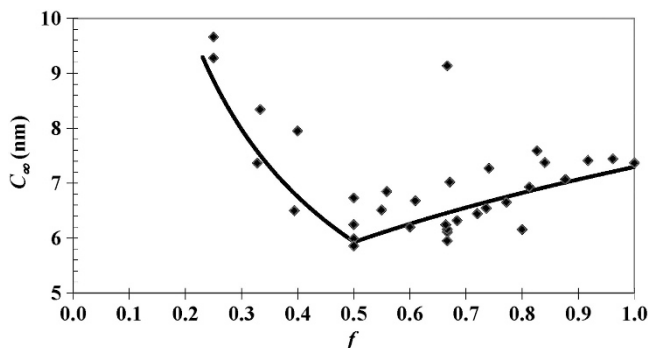
In Figure 4, the values of  $\delta$  are plotted vs  $l_p$  for a number of polyolefins at several temperatures, showing that there is a clear correlation of solubility parameter with chain dimensions. This correlation of polyolefin miscibility with their chain dimensions has been noted by several authors,<sup>2,46</sup> but the explanations for this have been quite different. Fredrickson *et al.*<sup>47</sup> have developed a theory of mixing based on the idea that a mismatch in component values of  $l_p$



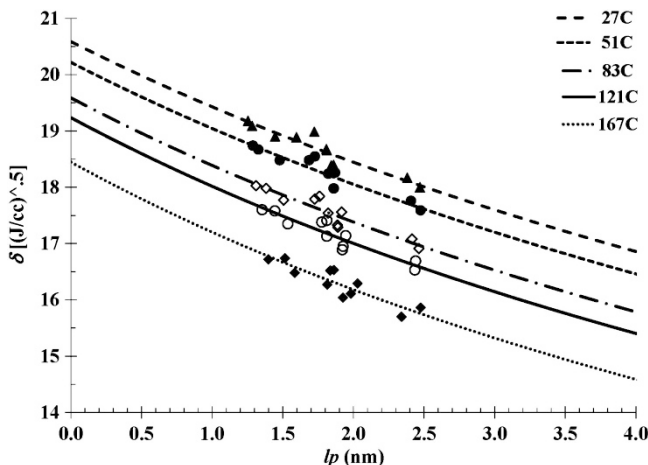
**Figure 2** Dependence of  $C_\infty$  on  $m_b$  at 190 °C. Solid line is from equation 10. A full color version of this figure is available at *Polymer Journal* online.

or  $b$  will lead to a loss of configurational entropy upon mixing. This is a different explanation for polyolefin miscibility than the one described herein<sup>2</sup> based on solubility parameters, which in concept at least emphasizes local enthalpic contributions to the free energy of mixing. How does one distinguish between entropic and enthalpic contributions to the interactions controlling miscibility? As the solubility parameters for different polyolefins decrease with temperature at different rates (see Table 1), the difference between any two of them and so  $X$  can have any sort of dependence on  $T$ , simply due to enthalpic interactions. It is thus not possible to separate ‘enthalpic’ and ‘entropic’ contributions to  $X$  simply from its temperature dependence.

There are now several pieces of evidence that indicate rather conclusively that the enthalpic contribution dominates in the case of polyolefin blends. First of all, the dependence of the values of  $\delta$  derived from SANS on branching structure for high molecular weight polyolefins closely parallels that for the solubility parameters for saturated hydrocarbons of low molecular weight derived from their heats of vaporization.<sup>30</sup> For example, whether considering the cohesive energy data for a series of  $C_8$  alkanes<sup>33</sup> or the SANS-based solubility parameters for the corresponding polymers, it is clear that the normal, linear molecules have the highest values of  $\delta$ , and that the longer and more frequent the branching, the lower these values become. Even effects associated with details of the branch architecture, such as higher values for molecules with methyls on adjacent carbons rather than on alternating ones, are reproduced with  $C_8$  analogs. The  $C_8$  alkanes do not have the configurational entropy



**Figure 3** Dependence of  $C_\infty$  on  $f$  at 190 °C. Solid line is from equation 11. A full color version of this figure is available at *Polymer Journal* online.



**Figure 4** Solubility parameters of polyolefins vs packing length.

characteristic of the polymers, so the distinctions within both groups are most likely due to enthalpic effects.

Secondly, Maranas *et al.*<sup>48</sup> have simulated the cohesive energy densities of a number of polyolefins with interactions based solely on enthalpic interactions. These results agree very well with the values determined from neutron scattering or PVT experiments. Finally, the impact of deuterium labeling on miscibility has also been well explained due to enthalpy. Bates *et al.*<sup>49</sup> noted that deuterium substitution changes the polarizability of a molecule or repeat unit, and so affects its cohesive energy. Their enthalpy-based model quantitatively explains the effect of deuteration on interaction strength, so there is no need in that case to invoke configurational entropy arguments. So the circumstantial case for an enthalpic origin of the cohesive energy of polyolefins is strong.

But why should the chain dimensions of polyolefins determine the enthalpy of their interactions? In a qualitative sense, this has to do with the degree to which the non-bonded neighbors of a monomer or repeat unit are from the same or different molecules. The overall number of van der Waals interactions per unit volume in a polyolefin melt does not depend very much on the chemical architecture of that chain, as the densities of nearly every polyolefin is about the same as that of all the others. However, the more tightly the polymer is coiled (at a given molecular weight), the more likely it is that a nearest neighbor is from another monomer on the same chain, and not from another molecule. The van der Waals, non-bonded interactions between such intramolecular monomers will not contribute to cohesive energy. Monomers on more open coils will have a larger fraction of close neighbors from other molecules, which increases its cohesive energy density.

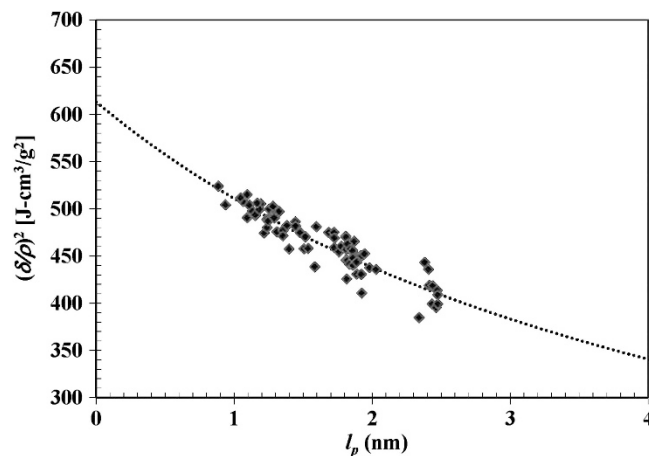
This argument has been made quantitative in the PRISM theory of Schweizer and Singh.<sup>4</sup> This is based on a theory of liquids that has been successfully applied to many polymer problems. The chains are modeled as 'threads' with variable thickness that can be related to  $l_p$ . A quite simple expression for the dependence of  $\delta$  on temperature and chain dimensions comes from this model:

$$\delta = \frac{\rho N_A}{m_0} \left[ \frac{2\pi\epsilon a^3}{\left(1 + \frac{l_p}{2\pi a}\right)} \right]^{1/2} \quad (12)$$

In equation 12,  $a$  and  $\epsilon$  are parameters that represent the length and energy scales of the interactions between the polymers. To examine how well equation 12 works, the experimental data in Figure 4 are plotted as  $(\delta/\rho)$  vs  $l_p$  in Figure 5. The fit to equation 12 is excellent and gives  $a = 0.80$  nm and  $\epsilon = 6.53 \times 10^{-4}$  eV, or  $\epsilon/k = 7.6$  K (taking  $m_0 = 14$  g mol<sup>-1</sup> for a methylene unit), which are reasonable values for the van der Waals potential typical of polyolefin blends. The power of equation 12 is that it allows the prediction of polyolefin miscibility by simply knowing chain dimensions. Even when these have not (or can not) been measured directly by a method such as neutron scattering, a way to estimate the chain dimensions (say, by a simulation or a relation such as equation 9) can thus lead to a well-founded prediction of the cohesive energy of that polymer and so its miscibility with other polyolefins.

## CONCLUSIONS

The miscibility of saturated hydrocarbon polymers (polyolefins) has been shown to be essentially controlled by the values of their solubility parameters as determined from SANS or PVT measurements. Moreover, these solubility parameters can be derived from a knowledge of the chain dimensions of the chains, which is most conveniently expressed through the packing length,  $l_p$ . Even when the



**Figure 5** Plot of  $\delta/\rho$  vs  $l_p$  for polyolefins. Dotted line is the fit from equation 12 with  $a = 0.80$  nm and  $\epsilon/k = 7.6$  K. A full color version of this figure is available at *Polymer Journal* online.

dimensions are not known directly, they can be estimated for many cases by a correlation of the fraction of carbons that are on side branches vs the backbone. This string of relations thus allows for a very powerful mechanism to predict who polyolefins can mix based simply on their chemical structure.

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