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Application of Integral Equation Theory to Polyolefin Liquids and Blends

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Introduction

The ability to model the packing of polymers in melts and blends is important in many polymer applications. One significant application is the development of new polymer blends. It would be exceedingly helpful to the materials chemist if molecular modeling could be employed to predict the thermodynamics and phase behavior of hypothetical polymer alloys before embarking on a time consuming and expensive synthesis program.

The well known Flory-Huggins theory[1] has been remarkably successful in describing many aspects of polymer mixing from a qualitative point of view. This theory is known, however, to suffer from several defficiencies which can be traceable to the fact that: (1) It is a lattice model requiring both monomer components to have the same volume; and (2) A mean field or random mixing approximation is made which effectively ignores chain connectivity. Because of these limitations the Flory-Huggins theory does not include packing effects and cannot be used to make quantitative molecular engineering calculations.

Recently Curro and Schweizer[2-6] developed a new approach for treating polymer liquids and mixtures based on methods developed for small molecule[7-9] and atomic liquids[10]. This new modeling approach, which we call PRISM theory, is an extension to polymers of the Reference Interaction Site Model (RISM Theory) developed by Chandler and Andersen[7-9] to describe the statistical mechanics of small molecule liquids. The PRISM theory is a continuous space description of a polymer liquid, which includes chain connectivity and nonrandom mixing effects in a computationally tractable manner.

The primary output from PRISM calculations is the average structure or packing of the amorphous liquid given by the radial distribution function denoted as g(r). This radial distribution function can then be employed to deduce thermodynamic or structural properties of interest. In this brief report we describe the theoretical approach and demonstrate its application to polyethylene (PE), isotactic polypropylene (iPP), syndiotactic polypropylene (sPP), and polyisobutylene (PIB) liquids and blends.

PRISM Theory

Let us consider a homopolymer melt of polymer chains each consisting of N identical repeat units or sites. If the chains are long we can neglect end effects and consider all the sites to be equivalent. We are interested in calculating g(r) defined as the *intermolecular* radial distribution function. g(r) can be considered as proportional to the density of intermolecular sites (from different chains) about a fixed site on a particular chain. For an ideal gas g(r) =1.0 since the molecules are packed randomly. For a perfect crystal, on the other hand, g(r) would consist of a series of lines corresponding to the various lattice spacings. For an amorphous polymer melt of interest here, we expect g(r) to show evidence of imperfect structure at short distances, but to decay to unity (random packing) on distances larger than the radius of gyration of the chains.

In order to calculate g(r) we make use of integral equation approaches developed for small molecule and atomic liquids. Let the total correlation function h(r) be defined as h(r)=g(r)-1. We then make use[2-6] of the "Generalized Ornstein-Zernike" equation of Chandler and Andersen[7-9] to define the direct correlation function C(r)

$$h(r) = \iint d\vec{r}_1 d\vec{r}_2\, \omega(|\vec{r}-\vec{r}_1|)\, C(|\vec{r}_1-\vec{r}_2|)\left[\omega(r_2)+\rho h(r_2)\right] \qquad (1)$$

where ρ_m is the density of sites.The *intramolecular* function ω(r) contains all the information about the molecular structure of the polymer chains and is defined according to[2-6]

$$\omega(r) = \frac{1}{N}\sum_{\alpha,\gamma=1}^{N}\omega_{\alpha\gamma}(r) \qquad (2)$$

with $\omega_{\alpha\gamma}(r)$ being the probability of sites α and γ on the same chain being a distance r apart. ω(r) is considered to be a known function and is inputted to the PRISM theory from a separate single chain calculation based on the hypothesized structure of the particular polymer of interest.

Up to this point the theory is formally exact.We have, however, insufficient information to solve the problem since we have two unknown functions h(r) and C(r), and only one equation, Eq. (1). In order to make the problem solvable we need another *closure* relation. An approximate closure condition can be developed by taking advantage of the experimental fact the the direct correlation function C(r) is short range. This reasoning leads to the well known Percus-Yevick closure[10] which is particularly simple for hard sphere interactions between sites.

$$\begin{aligned} g(r) &= 0 \quad \text{for } r < d \\ C(r) &\equiv 0 \quad \text{for } r > d \end{aligned} \qquad (3)$$

The first part of Eq. (3) is exact since hard spheres of diameter d cannot penetrate beyond r=d. The second condition is approximate and is a consequence of C(r) being a short range function of r. Eqs. (1)-(3) are written for polymers where each monomer is represented by a single type of site. These equations can be easily generalized to cases where the monomeric structure contains an arbitrary number of overlapping, spherical sites.

Eqs. (1) and (3) lead to an integral equation for g(r) of a homopolymer melt and can be solved for any particular polymer structure specified through ω(r) in Eq. (2). If one is interested in qualitative trends in melts on long length scales, ω(r) can be calculated from Gaussian, freely-jointed, or semiflexible models. If one is interested in making quantitative calculations on polymers of specific structure, the rotational isomeric state scheme[11,12] or a single chain simulation can be employed to obtain ω(r).

Applications of the Theory

Most blends of polyolefins are known to be highly incompatible in the melt state even though the chemical structures of the components are very similar. Because of the similarity in chemical structures the Flory-Huggins theory predicts that many of these blends would have miscibility at experimentally relevant temperatures. In order to obtain insights into the reasons for the incompatibility, we performed PRISM calculations on polyethylene (PE), isotactic and syndiotactic polypropylene (iPP and sPP), and polyisobutylene (PIB) melts and blends.

Good agreement[12] between PRISM theory and x-ray scattering experiments was found previously for PE melts at 430 K. Fig. (1) shows the structure factor of iPP at 453 K predicted from PRISM theory along with recent experimental x-ray scattering results[13] of Habenschuss and Londono. Similar results were found for the cases of sPP and PIB melts.

PRISM theory was then applied to mixtures of these polyolefins. For the PE/iPP mixture, PRISM theory predicts[14] UCST behavior with the critical temperature being over an order of magnitude higher than predicted from the Flory-Huggins theory. In the PE/iPP mixture, nonrandom mixing of the chain segments, neglected in Flory-Huggins theory, amplifies the destabilizing effect due to the attractive interactions between monomers. Thus nonrandom mixing greatly enhances incompatibility in the PE/iPP blend. It is interesting to note that according to PRISM theory, the blend could be made

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compatible by subtle adjustment of the dispersive interactions between sites.

Fig. (2) shows the heat of mixing as a function of composition calculated from PRISM theory for the iPP/sPP mixture. Note that the heat of mixing is positive which suggests that a mixture of the stereoregular forms of polypropylene would exhibit incompatibility. Recently Maier and coworkers[15] have found experimental evidence for incompatibility in the atactic/syndiotactic polypropylene mixture.

Conclusions

We have developed a computationally tractable formalism (PRISM theory) that can be used to calculate the structure and equilibrium properties of amorphous polymer liquids and alloys. PRISM theory has been validated against experimental scattering measurements, as well as large scale computer simulations, and has been shown to give accurate, though approximate, predictions for the structure of polymers in the condensed phase.

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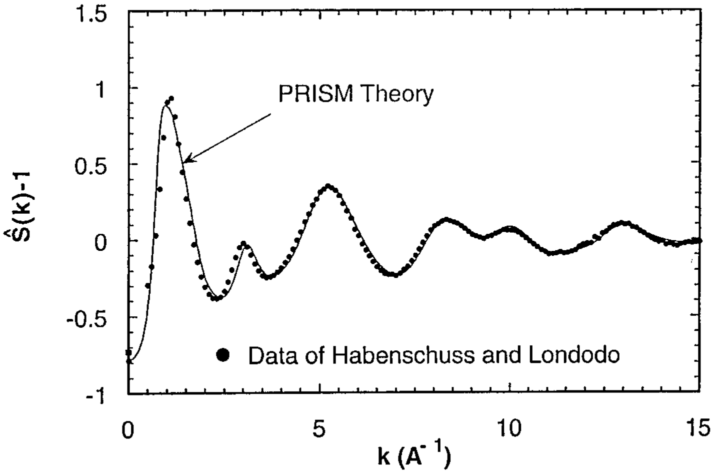

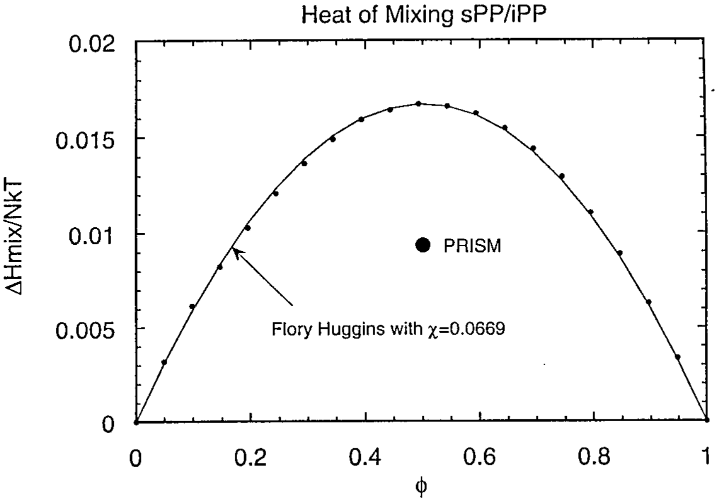

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