Search for a Model Polymer Blend

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The thermodynamics of binary and multicomponent mixtures comprising polymethylbutylene, polyethylbutylene, and polymethylbutylene-block-polyethylbutylene was studied by small-angle neutron scattering. The Flory-Higgins interactions parameter, deduced from these measurements, was independent of blend composition, as well as molecular weight and molecular architecture of the components, over the accessible temperature (27–201°C) and pressure (0.01–0.86 kbar) range. At temperatures above 130°C, the interaction parameter becomes independent of pressure. These findings are compared with previous experimental studies on the thermodynamics of polymer blends. To our knowledge, this level of agreement with the Flory-Huggins theory has not been seen in any other polymer blend.

Introduction

The Flory-Huggins theory (Staverman and Van Saten, 1941; Flory, 1942; Huggins, 1942) continues to play a central role in the modeling of the liquid state. The theory, originally developed for solutions of flexible polymer chains in a low molecular weight solvent, has found wide acceptance, well beyond its originally intended scope. It was generalized by Scott (1952) to multicomponent mixtures containing several polymeric species, including polymer blends without any solvent. Semi-empirical extensions have been used to describe mixtures of small molecules (Prausnitz, 1986). It lies at the heart of the Gibbs-DiMarzio theory of glassy polymers (Gibbs and DiMarzio, 1958), where the nonpolymeric components are voids, that is, free volume. More recently, it has been used to describe complex fluids where the polymeric components are emulsified, wormlike mesophases, stabilized by surfactants (Menes et al., 1995).

One of the strengths of the Flory-Huggins theory is its simplicity. The entropy of mixing is calculated assuming noninteracting, flexible chains. The enthalpy of mixing is calculated assuming random, pairwise contacts between the constituent monomers. The theory is built on many simplifying assumptions such as incompressibility and no volume changes in mixing. In some respects this theory is analogous to the virial equation of state, where the first virial coefficient accounts for pairwise, intermolecular interactions. Quantitative agreement between the virial equation and experimental data from simple gases such as N_2 was crucial for establishing the role of intermolecular interactions in gases (Van Ness and Abbott, 1982).

The importance of simple theories that capture the essential features of more complex physical systems is well recognized. The identification of model experimental systems that are in quantitative agreement with theory is equally important. The underlying assumptions of theories are often difficult to verify directly, and such experiments provide support for their validity. They also provide a rational direction for the development of more comprehensive frameworks. Given the wide acceptance of the Flory-Huggins theory, it may seem surprising that model systems, exhibiting quantitative agreement with the theory, have not been clearly identified.

Two-parameter models are generally required to describe the thermodynamics of small molecule, liquid mixtures (Van Ness and Abbott, 1982; Prausnitz, 1986). Polymeric liquids contain additional complexity due to effects such as chain connectivity. It is therefore unreasonable to expect the Flory-Huggins theory, which (like the virial equation) contains only one parameter, to be applicable to a large number of systems. One expects the theory to be valid in a limited range of temperatures and densities. However, the range of conditions over which polymer systems can be studied is limited due to phenomena such as chain degradation and vitrifi-

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cation. Without model systems, it is unclear if the temperatures and densities at which the theory is applicable can be reached in laboratory experiments. Pioneering studies by Flory and coworkers showed that experimental data from polymer solutions were inconsistent with the Flory-Huggins theory (Eichenger and Flory, 1968). It was argued that this was due to large differences in the pure component properties (such as compressibility). Blends of high polymers are better suited for testing theories, because the pure component properties are more closely matched.

According to the Flory-Huggins theory, the free energy of mixing in a binary mixture of two polymers labeled A and B is given by

$$\frac{\Delta G_m}{kT} = \left[\frac{\phi_A \ln \phi_A}{\upsilon_A N_A} + \frac{(1-\phi_A)\ln(1-\phi_A)}{\upsilon_B N_B} \right] + \frac{\chi}{\upsilon}\phi_A(1-\phi_A) \tag{1}$$

where ΔG_m is the free energy change on mixing per unit volume, k is the Boltzmann constant, T is the absolute temperature, ϕ_A is the volume fraction of component A in the mixture, N_i is the number of monomers per chain of component i, υ_i is the volume of each monomer of component i, χ is the Flory-Huggins interaction parameter, and υ is an arbitrary reference volume. In this work the reference volume υ is set equal to 100 $\mathring{A}^3$. All the parameters in Eq. 1 except χ can be determined from the characteristics of the pure components.

A useful feature of the Flory-Huggins theory is that it can be extended to multicomponent systems without introducing additional parameters. In this article we are interested in multicomponent mixtures of two homopolymers A and B, and an A-B diblock copolymer. Following Scott (1952), ΔG_m for this mixture is given by

$$\begin{aligned}\frac{\Delta G_m}{kT} = \Bigg[& \frac{\phi_A \ln \phi_A}{\upsilon_A N_A} + \frac{\phi_{AB} \ln \phi_{AB}}{\upsilon_A N_{Ab} + \upsilon_B N_{Bb}} \\ & + \frac{(1-\phi_A-\phi_{AB})\ln(1-\phi_A-\phi_{AB})}{\upsilon_B N_B} \Bigg] \\ & + \frac{\chi}{\upsilon}\{(\phi_A + f\phi_{AB})(1-\phi_A-\phi_{AB}+(1-f)\phi_{AB}) \\ & - f(1-f)\phi_{AB}\}\end{aligned} \tag{2}$$

where N_{Ab} and N_{Bb} are the numbers of A and B monomers in the block copolymer chain, and f is the volume fraction of A monomers in the block copolymer $f = N_{Ab}\upsilon_A/(N_{Ab}\upsilon_A + N_{Bb}\upsilon_B)$. As was the case with the binary result, all parameters in Eq. 2 except χ can be determined from characteristics of the pure components.

The first term, enclosed within square brackets in the righthand side (RHS) of Eqs. 1 and 2, represents the entropic contribution to ΔG_m which is assumed to be combinatorial in origin. The last term in the righthand side of Eqs. 1 and 2 represents noncombinatorial contributions to ΔG_m. If this contribution arises from random, pairwise contacts between A and B monomers, then χ for a given pair of monomers would depend only on T and would be independent of N_i and ϕ_i. However, if additional noncombinatorial contributions exist, then χ could be a complicated function of N_i and ϕ_i.

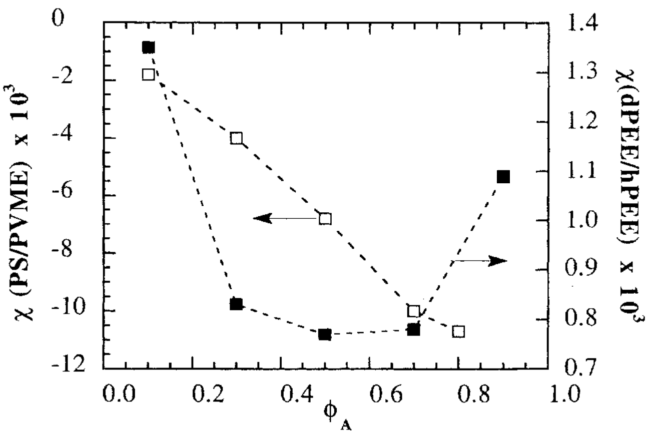


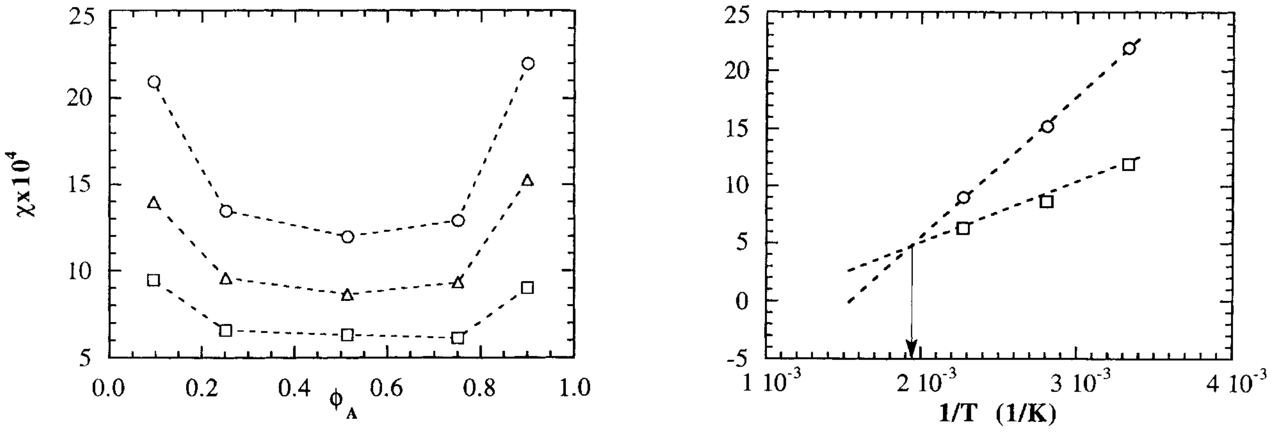
Figure 1. Composition dependence of χ in perdeuteropolystyrene/polyvinylmethylether blends (□) at 130°C (Han et al., 1988) and perdeuteropolyethylethylene/polyethylethylene (■) blends at 26°C (Bates et al., 1998).

In both cases, the deuterated component is defined as component A.

Results and Discussion

Early studies of the dependence of χ on N_i and ϕ_i in polymer blends were conducted by Han et al. (1988) and Bates et al. (1988). Han and coworkers studied polystyrene/polyvinylmethylether blends. They found that χ was independent of component molecular weights, but a strong function of composition. This is shown in Figure 1. It was recognized that the miscibility in this system was due to specific interactions between the styrene and vinylmethylether moieties, which are likely to cause a violation of the random mixing assumption. Bates and coworkers studied isotopic polymer mixtures such as polyethylethylene/perdeuteropolyethylethylene. The similarity of the pure component properties and the lack of specific interactions make these systems ideal for testing simple theories. Surprisingly, the χ parameter in these systems also showed a substantial composition dependence. Typical data obtained by Bates et al. are shown in Figure 1.

Graessley, Lohse, and coworkers identified a number of miscible polyolefins (Graessley et al., 1995; Balsara, 1996a). The dependence of χ on the composition for a particular pair of polyolefins (Krishnamoorti, 1994) is shown in Figure 2a. The composition dependence of χ for this system at room temperature (27°C) is qualitatively similar to that found in polyethylethylene/perdeuteropolyethylethylene mixtures (Figure 1). However, the variation of χ with composition becomes less pronounced with increasing temperature. In Figure 2b we show the temperature dependence of χ measured at $\phi_A = 0.52$ and 0.90. Linear extrapolation of measured data suggests that a composition independent χ will be obtained in the vicinity of 520 K, but the composition dependence is predicted to reemerge at higher temperatures (see Figure 2b).

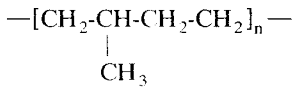


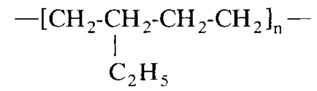
(a) (b)

Figure 2. (a) Composition dependence of χ in model polyolefin mixtures (H97/D88) at 23°C (○), 83°C (△), and 167°C (□); (b) the temperature dependence of χ in H97/D88 mixtures with $\phi_A = 0.52$ (□) and $\phi_A = 0.90$ (○).

Both polyolefins are ethylenebutene copolymers synthesized by saturating the C = C bonds in anionically synthesized polybutadiene. The letter indicates whether the saturation was carried out in the presence of H_2 or D_2 and the number represents the mol % of 1-2 units in the parent polybutadiene. The deuterated component is defined as component A. χ is expected to be independent of composition in the vicinity of 520 K.

In this article we present a summary of recent experimental measurements of χ in binary and multicomponent mixtures of polymethylbutylene (PM), polyethylbutylene (PE), and polymethylbutylene-block-polyethylbutylene (PM-PE)


$$—[CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}CH_2\text{-}CH_2]_n—$$


$$—[CH_2\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{C}}H_2\text{-}CH_2\text{-}CH_2]_n—$$

polymethylbutylene (PM) polyethylbutylene (PE)

Our findings are qualitatively different from those discussed in the preceding paragraphs.

The characteristics of the pure components used in this study are given in Table 1. The polymers were synthesized via anionic polymerization under high vacuum, and were nearly monodisperse (polydispersity index was less than 1.10). The polymer molecular weights were determined by light scattering. The composition of the block copolymer f was determined by 13_c NMR. The monomer volumes v_i were determined from density measurements on a density gradient column. Binary and ternary blends, comprising PM, PE and PM-PE, were prepared by solution blending, followed by evaporating the solvent. The χ parameter was determined from small angle neutron scattering measurements from single-phase mixtures containing one or two deuterium labeled components. These experiments were conducted at the National Institute of Standards and Technology at Gaithersburg, MD. Measurements were carried out at temperatures between 27 and 201°C. Most of the measurements were carried out at atmospheric pressure. A few binary blends were examined at elevated pressures up to 0.86 kbar in the NIST pressure cell (Hammouda and Bauer, 1995). The single-phase temperature range for each blend was determined from a combination of light and neutron scattering experiments (Lin et al., 1996; Balsara et al., 1996b). Corrections for the effect of deuterium substitution on χ for the atmospheric pressure data were made following the prescription of Rhee and Crist (1993) and Graessley et al. (1993), and we present estimates of χ for fully hydrogenous PM and PE chains.

Table 1. Characteristics of Polymers

Sample Desig.	Molec. Wt. (wt. avg.)*	Polydispersity Index**	N_i[†]	Vol. Fr. of PM in Block Copolymer (f)[††]
PM1	7.7×10^4	1.06	1,105	—
PM2	1.7×10^5	1.07	2,465	—
PE1	4.8×10^4	1.07	525	—
PE2	2.2×10^5	1.08	2,630	—
PM-PE	4.6×10^4	1.09	300–300[‡]	0.452

*From light scattering.

**From GPC. based on polyisoprene calibration, uncorrected for column dispersion.

[†] Based on C_5 and C_6 monomers given in text; the corresponding volumes are $v_{PM} = 136.4$ Å^3 and $v_{PE} = 162.0$ Å^3.

[‡] N_{PM}-N_{PE}.

[††] Based on ^{13}C NMR.

The results obtained at atmospheric pressure are given in Figure 3 where χ is plotted as a function of ϕ_{PE} at selected temperatures. Details regarding these measurements are given in an earlier article (Lin, 1996). Included in this figure are binary homopolymer blends (PM1/PE1, PM2/PE1, and PM2/PE2), blends of one homopolymer and a block copolymer (PE1/PM-PE, and PM1/PM-PE), as well as blends of two homopolymers and a block copolymer (PM1/PE1/PM-PE, and PM2/PE1/PM-PE). It is evident that χ at atmospheric pressure in the accessible temperature window (27–167°C) is independent of blend composition, component architecture (diblock copolymer vs. homopolymer), and component molecular weight.

SANS results from three binary PM/PE blends at elevated pressures are shown in Figure 4. All three blends contained partially deuterated PM2 chains. The fraction of H atoms replaced by D in this polyolefin was estimated to be 0.611 (Lin et al., 1996). We examined two PM2/PE1 blends with ϕ_{PE} =

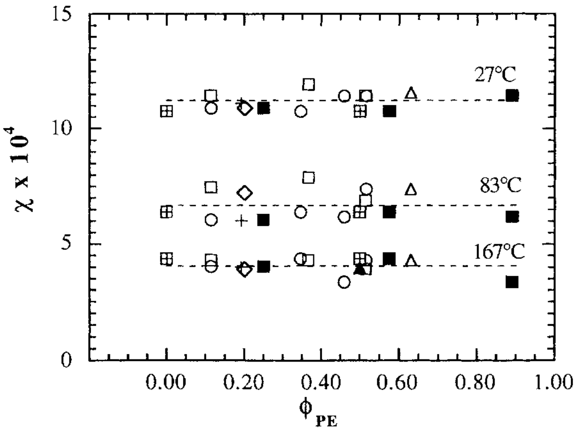


Figure 3. Dependence of the Flory-Huggins interaction parameter χ on the volume fraction of homopolymer PE in a variety of blends at 27, 83 and 167°C.

Filled squares: PM1/PE1 binary blends ($\phi_{PE\text{-}PM} = 0$). Open triangles: PM2/PE1 binary blends ($\phi_{PE\text{-}PM} = 0$). Filled triangles: PM2/PE2 binary blend ($\phi_{PE\text{-}PM} = 0$) at 167°C. Hatched squares: two component, 50/50 blends of PE1/PM-PE and PM1/PM-PE. Open squares: PM2/PE1/PM-PE blends with $\phi_{PE}/\phi_{PM} = 1.7$. Open circles: PM1/PE1/PM-PE blends with $\phi_{PE}/\phi_{PM} = 1.3$. Open diamonds: PM1/PE1/PM-PE blends with $\phi_{PE}/\phi_{PM} = 0.33$. Plus signs: PM2/PE1/PM-PE blends with $\phi_{PE}/\phi_{PM} = 0.33$. Typical absolute error in χ is about 10%. The dashed lines represent the mean value of χ at the 3 temperatures. The same symbol is used to represent χ from a given system at different temperatures.

0.586 and 0.797, and one PM2/PE2 blend with $\phi_{PE} = 0.839$. The temperature dependence of χ between deuterated PM and hydrogenous PE chains at 0.86 kbar (open symbols) and 0.01 kbar (filled symbols) is shown in Figure 4. The procedure for estimating χ from SANS data was identical to that used at atmospheric pressure; details regarding these measurements will be presented separately (Lefebvre et al., 1998). The data from the PM2/PE1 blends clearly show that the pressure dependence of χ becomes less pronounced with increasing temperature. This trend is confirmed by the high-temperature data obtained from the PM2/PE2 blend. The curves through the data are least-squares quadratic fits through the 0.86 kbar (dashed curve) and 0.01 kbar (solid curve). The deviations between the data and the least-squares fits are less than 1×10^{-4}, which is within estimated experimental error (Balsara et al., 1993). It is important to note that the blends that we have were examined under elevated pressure span over a wide range of thermodynamic regimes; the molecular weights of PE1 and PE2 differ by a factor of 5. The PM2/PE1 ($\phi_{PE} = 0.586$) blend was close to phase separation at room temperature and atmospheric pressure. Increasing the pressure to 0.86 kbar at room temperature resulted in phase separation and, hence, we could not estimate χ from the PM2/PE1 ($\phi_{PE} = 0.586$) blend under these conditions (see Figure 4). The PM2/PE2 blend was phase separated below 90°C at all pressures, while the PM2/PE1 ($\phi_{PE} = 0.797$) blend was single-phase over most of the accessible temperature and pressure range. In spite of these differences, the χ parameter measured from these three blends are in reasonable agreement with each other.

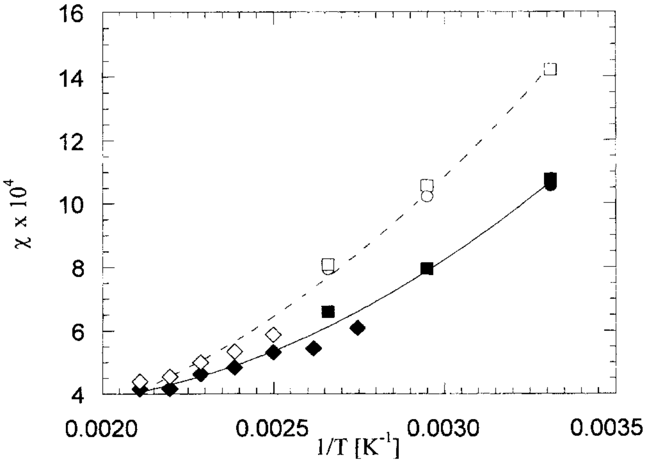


Figure 4. Dependence of the Flory-Huggins interaction parameter χ on 1/T for binary PM/PE blends at 0.86 kbar (◇, □, ○) and 0.01 kbar (◆, ■, ●).

(○,●), PM2/PE1 blend with $\phi_{PE} = 0.586$; (□,■), PM2/PE1 blend with $\phi_{PE} = 0.797$; (◇,◆), PM2/PE2 blend with $\phi_{PE} = 0.839$; ——, – – –, least-squares quadratic fits through the 0.86 kbar (– – –) and 0.01 kbar (——) data.

It is evident that the composition and molecular weight independence of χ in PM/PE blends observed at atmospheric pressure also holds at elevated pressures up to 0.86 kbar. In addition, χ in this system is nearly independent of pressure at temperatures greater than 130°C. One may argue that this independence is a more stringent signature of agreement with the Flory-Huggins theory, because the theory assumes that the blend is incompressible.

Most of the recent attempts at refining the Flory-Huggins theory (Bates et al., 1988; Bidkar and Sanchez, 1995; Foreman and Freed, 1997; Schweizer, 1993) lead to a composition-dependent χ parameter that does not vanish in any reasonable limit. It is clear that none of these theories are applicable to the PM/PE system. It now appears that the PM/PE system is not entirely exceptional. In a recent article Bates and coworkers report that binary blends of polyethylene and polymethylbutylene are characterized by a composition independent χ parameter at atmospheric pressure (Bates et al., 1998). In addition, Crist (1998a,b) suggests that the measured composition dependence of χ in many isotopic polymer blends may be due to systematic experimental errors. Many of the experimenters who made the measurements on isotopic polymer blends were present when this article was presented and none of them disagreed with Crist's conclusion regarding the role of systematic experimental error (Crist, 1988a,b). It thus appears that the search for model systems that obey the Flory-Huggins theory is nearing completion.

There is an intriguing similarity in the chemical structure of the polymer pairs that obey the Flory-Huggins theory. The local structural symmetry of isotopic blends was noted by Bates et al. (1988). In addition, the polyolefin chains used by Bates et al. in their more recent study (Bates et al., 1998) and those used in our study are similar in many respects. These polymers were obtained by saturating polydiene precursors. Polyethylene was derived from butadiene, polymethylbutylene from isoprene, and polyethylbutylene from ethylbutadiene. The diene polymerizations were conducted in hydrocarbon solvents which yield statistical copolymers with 93% 1-4 addition and 7% 3-4 addition in all three cases. It appears that some symmetry of local chain structure is needed for quantitative agreement with the Flory-Huggins theory.

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