Determination of the Polymer–Polymer Interaction Parameter for the Polystyrene–Polybutadiene Pair

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ABSTRACT: The light scattering technique was utilized to measure the phase separation temperatures (cloud points) of mixtures containing a polystyrene and a polybutadiene of various molecular weights and also of mixtures containing a polystyrene and a random or block copolymer of styrene and butadiene. The data was analyzed to obtain the polymer–polymer interaction parameter for the styrene–butadiene pair as a function of temperature and concentration. The value of the parameter deduced from the homopolymer mixtures agrees well with that obtained from the mixtures containing a copolymer. The polymer–polymer interaction parameter thus evaluated was compared with a theoretical expression derived on the basis of the Flory equation-of-state theory. The effect of free volume disparity between the two components was found to play a relatively minor role in determining the interaction parameter when the two polymers lack any specific interactions which would make them mutually miscible.

The study of properties of multicomponent polymer systems, such as polymer–polymer blends and domain-structured block copolymers, is currently attracting wide research interest. A number of symposium proceedings[1–8] and monographs[9–10] on the subject have recently been published. The properties of such systems depend critically on the degree of mutual compatibility of the component polymers, and much effort has been devoted to finding compatible polymer pairs.[12] When they are not compatible, the properties are influenced greatly by the morphology of the segregated domains and the nature of the interface between them.

The basic thermodynamic principles governing the compatibility and the domain formation are fairly well understood, and their application to individual polymer systems requires only the knowledge of the value of the polymer–polymer interaction parameter and its dependence on temperature, composition, etc. Unfortunately, the values of the interaction parameter have been evaluated experimentally so far for a very limited number of polymer pairs, and even less is known about their dependence on temperature and other variables. In this work we evaluate the interaction parameter for the pair polystyrene–polybutadiene from the measurement of the phase separation temperature (cloud point).

In most of the polymer mixtures which are known to be truly compatible, the degree of their compatibility decreases with increasing temperature, and the phenomenon of lower critical solution temperature (LCST) is exhibited. Such mixtures usually owe their compatibility to the presence of some specific favorable interactions between the two components. At higher temperatures the effect of the favorable interaction is reduced[13,14] while the unfavorable effect of the free volume change on mixing increases, eventually leading to phase separation above LCST. Recent theoretical analyses,[14–16] based on corresponding states theory[17,18] and Flory equation-of-state thermodynamics,[11–21] give a fairly good understanding of the thermodynamics of these compatible polymer mixtures, at least in qualitative terms.

For incompatible polymer mixtures, the need to know the polymer–polymer interaction parameter arises because of its influence on the morphology of the domain structure and the thickness of the transition layer between the domains. A number of recent theoretical treatments deal with the stability of block copolymer domains and the domain interface thickness[30–32] in polymer blends and block copolymers. A "pseudomelting" transition in block copolymers, ascribed to the dissolution of microdomain structure, has been observed by viscoelastic[32,34] and small-angle X-ray scattering measurements,[35] and a determination of the interface thickness by small-angle X-ray scattering has been reported.[36,37] In order to compare the various theories against these experimental results, reliable values of the polymer–polymer interaction parameter are sorely needed. In a previous publication[38] we estimated the polymer–polymer interaction parameter for a few nonpolar polymer pairs on the basis of the Flory equation-of-state thermodynamic theory. In this work we determine the value for the polystyrene–polybutadiene pair experimentally. This pair is chosen because it is the constituent of the block copolymers most often studied. Moreover, they are nonpolar hydrocarbon polymers for which theories of polymer liquids and mixtures are likely to apply more quantitatively.

Not many methods are available for evaluation of the interaction parameter for polymer mixtures. The most practical among them is the one relying on the determination of binodal and spinodal temperatures as a function of the composition. The binodal curve can be determined most easily by observation of the cloud points. The spinodal curve can be determined by a light scattering method as described by Scholte[39] and by its refinement, "the pulse induced critical scattering" recently developed by Gordon et al.[40] In this work we employ a laser light scattering technique to measure the cloud point.

The difficulty of performing thermodynamic measurements on polymer mixtures stems partly from their high viscosity. The major difficulty, however, arises from the fact that the binodal and spinodal points for most polymer pairs occur outside a practical experimental temperature range. For this reason studies on mixtures of lower homologue members of the polymers are often substituted.[41–43] But the interaction parameters evaluated for oligomer mixtures have to be extrapolated with caution. Oligomers have a higher proportion of end segments and can therefore be substantially different chemically from the corresponding polymers. More importantly, oligomers have a higher free volume than polymers. This is manifested, for example, by the much higher thermal expansion coefficients exhibited by oligomers.[44] Since the change in free volume on mixing is now known to be an important factor in the polymer–polymer interaction parameter, the effect of the dependence of free volume on chain lengths has to be properly taken into account. For this reason, in this work, we have endeavored to employ component polymers of as high chain lengths as possible. One way of increasing the chain lengths, without at the same time

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Table I
Description of Polymer Samples Studied[a]

sample desig	polym type	composition, wt %: styrene	composition, wt %: butadiene	unsaturation: % trans	unsaturation: % vinyl	mol wt: M_n	mol wt: M_w	M_w/M_n	source
PS2	styrene homopolymer	100	0			2 220 (VPO)	2 400 (η)		Pressure Chemical
PS3	styrene homopolymer	100	0				3 500 (η)[b]	1.06 (GPC)	Pressure Chemical
PS5	styrene homopolymer	100	0			5 200 (VPO)	5 480 (LS)	1.10-1.14 (GPC)	Goodyear
PBD2	butadiene homopolymer	0	100	53	6	2 350 (VPO)		1.13 (GPC)	Goodyear
PBD26	butadiene homopolymer	0	100	40	34	25 000 (GPC)	26 000 (GPC)		Phillips[c]
R50/50	random copolymer	50	50	55	27	24 000 (GPC)	24 000 (GPC)		Phillips[c]
R25/75	random copolymer	25	75	46	31	27 000 (GPC)	29 000 (GPC)		Phillips[c]
B25/75	diblock copolymer	25	75	42	30	27 000 (GPC)	28 000 (EPC)		Phillips[c]

[a] All the data given are those provided by the supplier of the sample, except where noted. [b] Determined in this work. See the text. [c] Kindly synthesized specifically for this study by Dr. H. L. Hsieh of Phillips Petroleum Co.

raising the cloud points too high, is to employ a copolymer as a component of the mixture. Both random and block copolymers have been tested out for this purpose and have been found to serve the purpose well, as described in detail below.

Experimental Section

1. **Material.** All polymer samples used in the study are listed in Table I. All have fairly narrow molecular weight distributions. For sample PS3, the characterization data given by Pressure Chemical Co. are M_v = 3600, M_n = 3570, and M_{nk} (from stoichiometry) = 4000. From the $[\eta]$ values of samples PS2 and PS3 determined in cyclohexane at 34.5 °C, we determined that M_v of sample PS3 must be 1.45 times the M_v value of sample PS2. Accepting the value M_v = 2400 given for sample PS2, we therefore assigned M_v = 3500 for sample PS3.

All polymers were purified by reprecipitating from cyclohexane solution into methanol which contained small concentrations of antioxidants (Plastanox LTDP and Antioxidant 330) and a light stabilizer (Tinuvin P), amounts of which were calculated to give about 0.2% each in the final dried polymer. When the polymer mixture was heated under vacuum prior to sealing the sample tube, however, much of these additives were lost through sublimation, and only very small amounts appeared to have remained in the mixture during the cloud point measurements.

2. **Procedure.** Weighed amounts of two polymers for a mixture (about 0.3 g total) were placed in a glass tube of about 0.5-cm inner diameter. A long glass rod, with a piece of iron attached at the top, was inserted to serve as a magnetically activated stirrer. The tube was attached to a vacuum line and heated to about 200 °C with stirring to expel volatile impurities before its top was sealed off with the stirrer still inside.

The sample tube was inserted in the axial position of a cylindrical aluminum block, heated with resistance wires wound around its surface. Holes, drilled in radial directions in the block, served as light paths for incident and transmitted beams and for the lights scattered at 30 and 90° angles. A low-power 2-mW He–Ne laser was used as the light source, and a photodiode (EG&G HAV-1000 with a sensitivity of 7×10^6 V/W at R_f = 20 MΩ for 6328-Å wavelength light) was used as the detector. Although at a 30° angle the scattered intensity was higher, it was more susceptible to optical misalignment, and therefore all reported measurements were performed at a 90° scattering angle.

A thermocouple inserted into the heating block near the sample cavity served to monitor the temperature, and another thermocouple, similarly placed, was used for controlling the temperature by means of a temperature programmer. The temperature was cycled repeatedly from about 7 °C below the cloud point to about 10 °C above it at a constant heating and cooling rate. The temperature lag between the sample and the monitoring thermocouple was calibrated initially at various heating/cooling rates by means of a third thermocouple inserted in a simulated sample tube containing silicone oil.

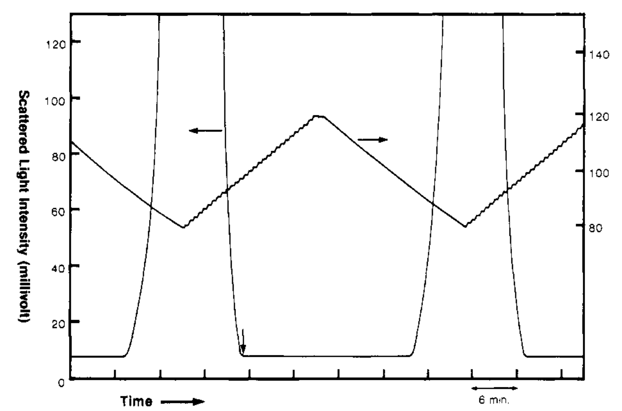

Figure 1. Example of chart recording obtained in the cloud point measurement. The mixture containing 92 wt % PS2 and 8 wt % PBD2 was cycled between 80 and 120 °C at a constant heating/cooling rate of 2°/min. The thermocouple output is recorded to indicate the temperature. The output voltage of the photodetector placed at a 90° scattering angle gives the intensity of scattered light. The point (indicated by an arrow) at which the scattered light intensity on heating reduces to the baseline level is taken as the cloud point.

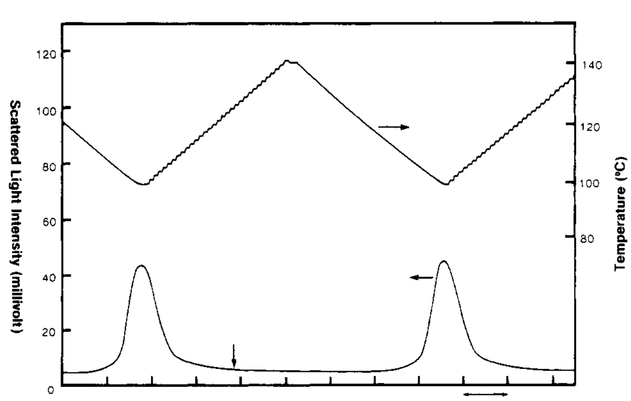

Figure 2. Example of chart recording, similar to the one shown in Figure 1, illustrating a particularly difficult case where the turbidity changes very slowly with temperature. The mixture contains 3.4 wt % PS2 and 96.6 wt % PBD26.

The output from the detector and the monitoring thermocouple was recorded on a two-channel chart recorder. Figures 1 and 2 show two examples of such records, one in which the turbidity changes very rapidly with temperature and another in which the turbidity changes relatively slowly, making the determination of the cloud point more difficult. The deviation of the scattered intensity from the flat base line was taken to indicate the presence of turbidity and is denoted by an arrow in Figures 1 and 2. The temperature at which the turbidity first appeared on cooling was usually lower by a few degrees (up to 8 °C in some cases) than the temperature at which the turbidity disappeared on heating. The temperature on heating was taken as the cloud point. Different heating/cooling rates were initially tried, and it was found that the difference in the determined cloud points between 0.5 and 2 °C/min was usually far less than 2 °C. All subsequent measurements were performed at 2 °C/min. Repeatability of the cloud point on successive temperature cycles was good, but there was a general tendency for it to creep up on successive cycles. For cloud points above 200 °C, the successive temperatures were often higher by more than 1 °C, suggesting thermal degradation of the sample, and in such cases they were extrapolated back to the zeroth cycle to obtain the cloud point corresponding to the initial mixture. Samples showing successive differentials of more than 3 °C were discarded, as this seemed to indicate that they had received insufficient vacuum treatment before sealing.

Polymer-Polymer Interaction Parameter

The Gibbs free energy change accompanying the mixing of component 1 of molar volume V_1 with component 2 of molar volume V_2, evaluated for unit volume of the mixture, can be written as

$$\Delta G_M = RT[(1/V_1)\phi_1 \ln \phi_1 + (1/V_2)\phi_2 \ln \phi_2] + \Lambda\phi_1\phi_2 \quad (1)$$

where ϕ_1 and ϕ_2 are the volume fractions of the components. The first term in eq 1 is the combinatorial part of the free energy of mixing as given by the classical Flory-Huggins treatment, and the second term, often called noncombinatorial or residual free energy of mixing, is the part of the free energy of mixing not accounted for by the combinatorial term. The quantity Λ is in general a function of T, p, and the composition of the mixture, but the utility of eq 1 rests on the fact that its dependence on these variables is only moderate in most cases. For polymer mixtures, in fact, it turns out that in the zeroth approximation Λ can be regarded as a material constant dependent on the chemical nature of the pair but independent of temperature, concentration, and the chain lengths of the components. Equation 1 is regarded here as defining the polymer-polymer interaction parameter Λ. So defined, it is given a numerical value in units of cal/cm^3, thus allowing a direct comparison with the cohesive energy densities of the components.

It has been more customary to express the strength of polymer-polymer interaction by means of the χ parameter. When they do not depend on the composition, Λ and χ are related to each other by $\chi = \Lambda V_r/RT$, where V_r is a volume of reference. The meaning of the reference volume V_r depends on the context of the discussion. For solvent-polymer interaction, V_r is almost always defined as the molar volume of the solvent molecule. For polymer-polymer interaction, V_r is equated either to the molar volume of one of the components or more often to the volume of a segment or a lattice. There is, however, no unique way of defining the segment or lattice size in polymer-polymer mixtures because all the thermodynamic properties (except surface properties) of the mixture depend only on the ratios of molecular to segment volumes. The numerical value of χ can, therefore, be specified only in reference to an arbitrary proportionality constant, thus making it ill-suited to serve as a material constant. A further reason for our preference of Λ over χ is that for incompatible polymer mixtures (having their upper critical solution temperature above room temperature) the polymer-polymer interaction is mostly enthalpic rather than entropic and Λ remains approximately constant while χ decreases rapidly with increasing temperature.

For solvent-polymer systems, χ is commonly evaluated from the residual chemical potential of the solvent rather than the residual free energy of mixing. When χ and Λ depend on the composition of the mixture, the simple relation between them, given above, does not hold, unless Λ is also defined in terms of the residual chemical potential. We retain the definition of Λ in eq 1, given as a measure of the residual free energy of mixing, even when Λ varies with concentration. This is preferred because most theories of polymer mixtures, block copolymers, and polymer interfaces are formulated in terms of the free energy of mixing, rather than the chemical potentials of the components.

The compositions of the coexisting two phases, to which a homogeneous polymer mixture separates on lowering (or raising) the temperature, can be calculated by solving eq 1 for a common tangent in the plot of ΔG_M vs. ϕ_1. At the cloud temperature the overall polymer composition is equal to one of the compositions thus calculated. When we know Λ as a function of T and ϕ_1 for a given polymer pair, we can calculate the expected cloud point curve readily. The converse is not true. From the experimental cloud points determined for a number of mixture compositions, Λ can be evaluated by means of eq 1 only if the functional form of the dependence of Λ on ϕ_1 is known.

Preliminary examination of the obtained experimental data showed that Λ depends on both the temperature and the composition moderately. The simplest functional form incorporating these dependencies is

$$\Lambda = \lambda_0 + \lambda_1\phi_1 + \lambda_T T \quad (2)$$

The values of the constants λ_0, λ_1, and λ_T giving the best fit to experimentally determined cloud points were evaluated by the method of nonlinear least squares on a computer. The coefficients thus obtained are listed in Table II. The binodal curves calculated with the use of these values are drawn in Figures 3-5 to show the degree of fit. For those runs for which the concentration range is rather limited, the evaluation of the λ_1 term was not justified, and λ_1 was set to zero. According to Koningsveld,[43] for polydisperse polymers the spinodal curve is determined by the weight-average molecular weight. It is not clear what type of molecular weight average is appropriate for a binodal curve, and therefore the least-squares calculation was performed with both the weight- and number-average molecular weights. It turned out that only the value of λ_0 was affected, and in Table II the one based on the weight average is given first and the one based on the number average is enclosed in parentheses.

The cloud point curve obtained by Koningsveld and co-workers[43] for the mixtures containing polyisoprene ($M_n \approx 2700$) and polystyrene ($M_n \approx 2100$ and 2700) showed two maxima. They state that such a curve can be fitted with a $\Lambda(\phi_1)$ function containing a first- and a second-order term in ϕ_1, with the absolute value of the second-order term larger than that of the first-order term. In order to see the effect of the second-order term, we replaced $\lambda_1\phi_1$ in eq 2 with $\lambda_2\phi_1^2$ and again sought a best fit on a computer but obtained no recognizable improvement in the degree of fit. Use of both the first- and second-order terms would have resulted in a slightly better fit, but probably not enough to justify the use of an additional adjustable parameter. As is seen in Table II, the concentration de-

Table II
Polymer-Polymer Interaction Parameter[a] Determined from Cloud Point Measurements

pair no.	component 1	component 2	f_{B2}[b]	λ_0	λ_1	λ_T	Λ	Λ/f_{B2}^2	d ln Λ/dT
1	PS2	PBD2	1	1.03[c] (1.10)[d]	−0.05	−0.0026	0.61[e]	*e*	-4.3×10^{-3} [e]
2	PS3	PBD2	1	0.99 (1.06)	0.11	−0.0023	0.70		−3.3
3	PS5	PBD2	1	0.87 (0.93)	0.21	−0.0016	0.74		−2.2
4	PS2	PBD26	1	1.13 (1.20)	*f*	−0.0023	0.79		−2.9
5	PS3	PBD26	1	0.98 (1.05)	*f*	−0.0016	0.74		−2.2
6	PS5	R50/50	0.549	0.31 (0.32)	0.060	−0.00084	0.214	0.71	−3.9
7	PS2	R25/75	0.785	0.62 (0.66)	−0.067	−0.00088	0.455	0.74	−1.9
8	PS3	R25/75	0.785	0.64 (0.68)	*f*	−0.0012	0.460	0.75	−2.6
9	PS2	B25/75	0.785	0.55 (0.58)	0.00	−0.00088	0.418	0.68	−2.1

[a] Given in units of cal/cm³. [b] Volume fraction at 150 °C of butadiene in component 2. [c] Value based on weight-average molecular weight. [d] Value based on the number-average molecular weight. [e] Evaluated for 150 °C and ϕ_1 = 0.5. [f] Not enough concentration range covered for evaluation of λ_1.

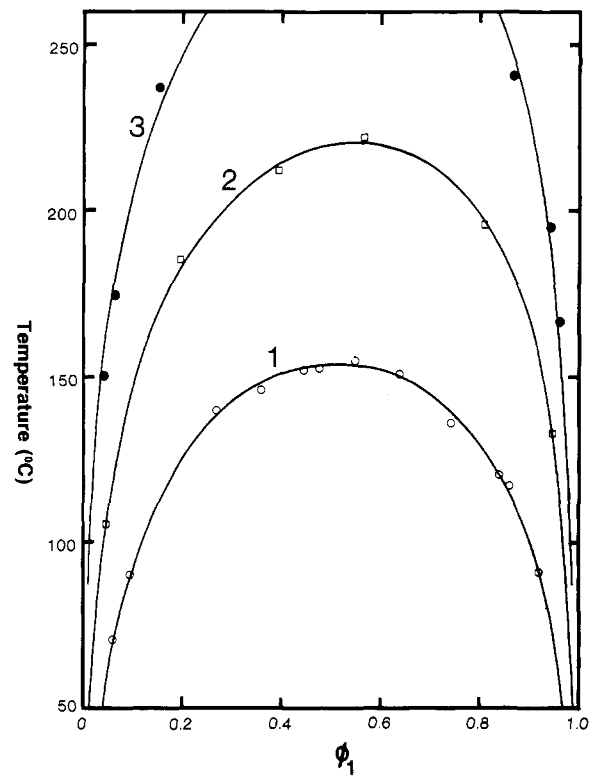

Figure 3. Cloud points plotted against ϕ_1 for the pairs 1 (PS2–PBD2), 2 (PS3–PBD2), and 3 (PS5–PBD26). The values of λ_0, λ_1, and λ_T, determined by nonlinear least-squares and tabulated in Table II, are used to calculate the curves shown (eq 1 and 2).

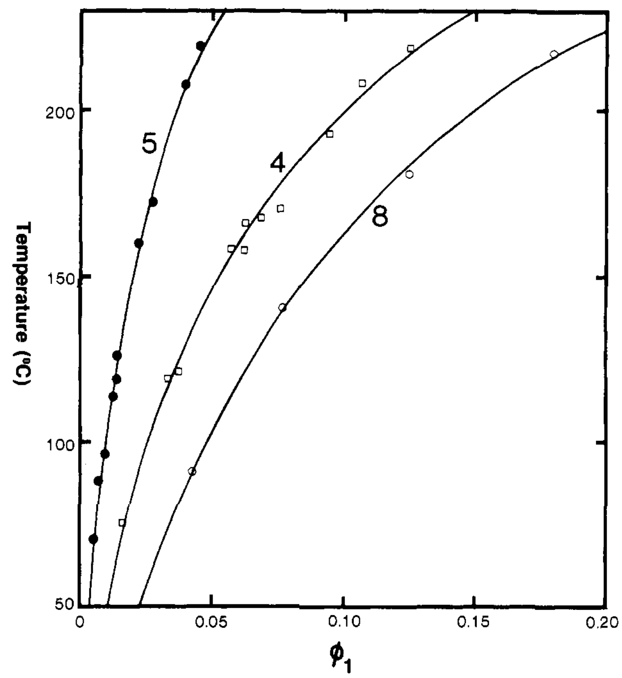

Figure 4. Cloud points plotted against ϕ_1 for the pairs 4 (PS2–PBD26), 5 (PS3–PBD26), and 8 (PS3–R25/75). The curves represent the least-squares fit.

pendence is fairly small and both positive and negative coefficients are obtained with different pairs. The temperature dependence shown by various mixtures, on the other hand, is very consistent, and the temperature coefficient is negative. Thermodynamic discussions of polymer compatibility by various workers[14,15] stressed the importance of the disparity in the free volume and thermal expansion coefficients of polymer components and led to an expected positive temperature dependence. This apparent contradiction is resolved when we examine the theoretical prediction more closely in a later section.

Mixing of Copolymers

The polymer–polymer interaction parameter Λ_{AB} between two homopolymers A and B can be determined, to a good approximation, by studying the miscibility between a homopolymer and a copolymer, or between two copolymers, the copolymers consisting of monomers A and B. The degree of compatibility between the two copolymers can be enhanced when the difference in the comonomer compositions in the copolymers is made smaller. Let us call the two copolymers components 1 and 2 and designate their compositions by f_{Ai} and f_{Bi}, where f_{Ai} is the volume fraction of comonomer A in component i and f_{Bi} is equal to $1 - f_{Ai}$. If we determine the polymer–polymer interaction parameter Λ_{12} between these copolymer components by means of eq 1 in the same way as has been used for homopolymer mixtures, the obtained value is likely to be smaller than Λ_{AB}, since the difference between copolymers 1 and 2 is much smaller than the difference between homopolymers A and B. These two are related to each other by

$$\Lambda_{12} = \Lambda_{AB}(f_{A1} - f_{A2})^2 = \Lambda_{AB}(f_{B1} - f_{B2})^2 \quad (3)$$

In the case of block or graft copolymers, experimental determination of Λ_{12} by eq 1 is meaningful only if the two phases which are formed at the cloud points from phase separation of a homogeneous mixture are also homogeneous in themselves and do not contain the usual microdomain structures. This is realized, as the various block copolymer theories predict, when the segment block lengths are relatively short in comparison to the magnitude of Λ_{AB}. The use of random copolymers is validated to the extent that the very short sequences of monomer type A

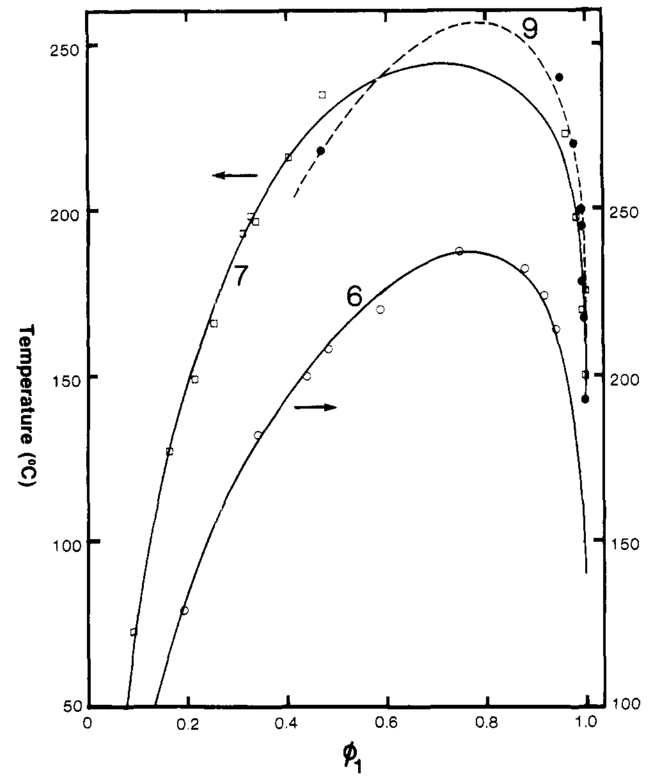

Figure 5. Cloud points plotted against ϕ_1 for the pairs 6 (PS5–R50/50), 7 (PS2–R25/75), and 9 (PS2–B25/75). The curves represent the least-squares fit.

(many of them only one or two repeat units long) can be considered to behave the same way as similar sequences in a homopolymer A do in their interaction with neighboring segments. Our data presented below suggest that this is a valid assumption.

The relation (3) can be derived readily if we assume that Λ arises purely from van Laar type heat of mixing. Then, relation 3 is obtained by counting the number of A–B contact pairs present in the mixture and by subtracting from it the number of A–B contact pairs which were already present in the copolymers 1 and 2 before mixing. An algebraic rearrangement of the expressions given by Scott[45] on copolymer mixing can also lead to relation 3. In order to show that its validity is more general than these lattice calculations suggest, we present the following derivation.

The noncombinatorial or residual free energy of mixing ϕ_1 cm^3 of copolymer 1 and ϕ_2 cm^3 of copolymer 2 to form 1 cm^3 of the mixture, according to eq 1, is $\Lambda_{12}\phi_1\phi_2$ (when the volume change on mixing is neglected). Next, we perform the following thought experiment. (1) All the chemical bonds between monomers A and B in copolymer 1 are severed and instead new bonds are formed to join A to A and B to B, so that ϕ_1 cm^3 of copolymer 1 is transformed into two separate phases, $\phi_1 f_{A1}$ cm^3 of homopolymer A and $\phi_1 f_{B1}$ cm^3 of homopolymer B. The free energy change accompanying this process is of three parts: (a) the chemical bonding energy term arising from the different types of chemical bonds formed, (b) the combinatorial entropy term for sorting out the different monomers, initially randomly mixed, to two separate phases, and (c) the residual free energy term arising from the change in the environment surrounding each monomer unit, equal to $-(\Lambda_{AB} f_{A1} f_{B1})\phi_1$. When Λ_{AB} depends on concentration, the value of Λ_{AB} appropriate to $\phi_A = f_{A1}$ is implied here, provided that the environment surrounding monomer A in the copolymer 1 is essentially the same as that surrounding monomer A in the mixture containing f_{A1} cm^3 of homopolymer A and f_{B1} cm^3 of homopolymer B. (2) In the similar process of decomposing copolymer 2 into homopolymers A and B, the residual free energy change is equal to $-(\Lambda_{AB} f_{A2} f_{B2})\phi_2$, Λ_{AB} this time taking the value appropriate to $\phi_A = f_{A2}$. (3) Starting from the combined batches of homopolymers A and B thus obtained, the above process of interchanging the chemical bonds is now reversed, to attain the mixture of copolymers 1 and 2. The change in the residual free energy in this step is $\Lambda_{AB}(\phi_1 f_{A1} + \phi_2 f_{A2})(\phi_1 f_{B1} + \phi_2 f_{B2})$, with the value of Λ_{AB} appropriate to $\phi_A = \phi_1 f_{A1} + \phi_2 f_{A2}$.

In the above three-step process of forming the mixture of copolymers 1 and 2 through the intermediate phases consisting of homopolymers only, the numbers of various chemical bonds broken and formed cancel out each other exactly. As far as the noncombinatorial free energy is concerned, we can write

$$\Lambda_{12}\phi_1\phi_2 = \Lambda_{AB}(\phi_1 f_{A1} + \phi_2 f_{A2})(\phi_1 f_{B1} + \phi_2 f_{B2}) - \Lambda_{AB} f_{A1} f_{B1}\phi_1 - \Lambda_{AB} f_{A2} f_{B2}\phi_2 \quad (4)$$

The three Λ_{AB}'s here differ from each other somewhat when Λ_{AB} depends on concentration. The equality holds rigorously only if the combinatorial free energy of mixing is accurately represented by the first term in eq 1. The use of eq 1 for evaluation of Λ means that any deviation of the combinatorial entropy from the Flory–Huggins expression will be included in the value of Λ obtained. If this is the case, then the equality in eq 4 will hold only after the contribution of the combinatorial effect is subtracted from Λ_{12} and Λ_{AB}.

If the equality in eq 4 is assumed valid and the concentration dependence of Λ_{AB} is neglected, then collecting the terms on its right-hand side leads to eq 3.

In this work the cloud point measurements were performed on four different pairs in which component 1 was always a styrene homopolymer but component 2 was a random or block copolymer. In Figures 4 and 5, the pairs numbered 6, 7, 8, and 9 are those involving a copolymer. The values of the coefficients λ_0, λ_1, and λ_T, evaluated by the same nonlinear least-squares method as for the homopolymer mixtures, are also listed in Table II. Λ_{12} values thus evaluated are much smaller than the corresponding values for the homopolymer mixtures. But when Λ_{AB} is calculated by dividing Λ_{12} with f_{B2}^2, the resulting value agrees very well with Λ obtained from homopolymer mixtures. Even the temperature coefficient λ_T, when divided by f_{B2}^2, leads to values agreeing very well with the homopolymer mixture values. The usefulness of eq 3 is thus demonstrated.

The diblock copolymer B25/75 has a segregated microdomain structure at room temperature, which does not "melt" out completely until above 200 °C, as examined by small-angle X-ray scattering.[35] However, when the copolymer is mixed with a large excess of a styrene homopolymer, it evidently dissolves into a homogeneous solution and thus permits the determination of the cloud points. As seen in Figure 5, cloud point curve 7 for the pair PS2 and R25/75 (a random copolymer) is somewhat different from curve 9 for the pair PS2 and B25/75 (a diblock copolymer of a similar composition). Whether this difference in the cloud points reflects any real difference in the thermodynamic behavior between a random and a block copolymer is difficult to say at this time because the observed difference might have come from small differences in the comonomer compositions or molecular weights.

The present results show that the Λ_{AB} values determined from studies on mixtures containing random copolymers agree well with those determined with homopolymer mixtures. This is gratifying because it opens a very practical avenue for determining the polymer–polymer interaction parameter for many polymer pairs for which the cloud point measurement would otherwise be impractical. The agreement obtained also illustrates that the nonbonded segmental interaction responsible for Λ is little affected by the types of neighboring segments joined by covalent bonds. More importantly perhaps, it shows that the Flory–Huggins expression represents the combinatorial term for polymer mixtures to a surprisingly good approximation.

Comparison with the Equation-of-State Theory

In recent years a number of workers[17-21,46,47] have contributed to the refinement of the theories of polymer liquids and mixtures over the original Flory–Huggins treatment. All these theories recognize the importance of the equation-of-state contribution to the free energy of mixing or the effect on mixing arising from the difference in the free volumes of the pure components. We will make use of the results of these theories, especially the one due to Flory and his co-workers,[19-21] to analyze the value of the polymer–polymer interaction parameter obtained in this work.

Prigogine and his school have shown that the principle of corresponding states can be applied to polymer liquids[48,49] when the reduction in the external degrees of freedom[50] for polymers due to the increase in chain length is properly taken into account. Thus, once the values of three characteristic constants, such as p^*, v^*, and T^*, are evaluated for a given polymer liquid, its thermodynamic properties can be represented completely by means of universal functions defined in terms of the reduced variables $\tilde{p} = p/p^*$, $\tilde{v} = v/v^*$, and $\tilde{T} = T/T^*$. The same universal functions can also be used to describe mixtures, provided there is a way of predicting the characteristic constants of the mixture from those of the pure component liquids. The mixing rules commonly adopted are of the form

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - Z_{12}\phi_1\phi_2 \tag{5}$$

$$p^*/T^* = \phi_1 p_1^*/T_1^* + \phi_2 p_2^*/T_2^* \tag{6}$$

The characteristic pressure p^* has the dimension of energy density (e.g., cal/cm^3) and Z_{12} is a parameter denoting the change in the energy density on mixing. Z_{12} varies with ϕ_1 to some extent, as will be discussed more fully below.

By dividing the free energy G per unit volume of a pure liquid by its p^*, one obtains $\tilde{G}$, a dimensionless universal function of the reduced variables $\tilde{T}$ and $\tilde{p}$, according to the principle of corresponding states. The same is true for the mixture, provided only the noncombinatorial part of the free energy is included in G. For experimental results performed under atmospheric pressure, $\tilde{p}$ is practically equal to zero for the pure components and for the mixture, and $\tilde{G}$ is then regarded as a function of $\tilde{T}$ only. One can therefore write

$$\Lambda\phi_1\phi_2 = p^*\tilde{G}(\tilde{T}) - \phi_1 p_1^*\tilde{G}(\tilde{T}_1) - \phi_2 p_2^*\tilde{G}(\tilde{T}_2) \tag{7}$$

Following Patterson,[18] $\tilde{G}(\tilde{T}_1)$ and $\tilde{G}(\tilde{T}_2)$ are expanded in a Taylor series around $\tilde{T}$, and terms up to second order are retained. Then, using eq 5 and 6, we obtain

$$\Lambda = Z_{12}\left[-\tilde{G}(\tilde{T}) + \tilde{T}\frac{\partial\tilde{G}}{\partial\tilde{T}}\right] - \frac{\tilde{T}^2}{2}\frac{\partial^2\tilde{G}}{\partial\tilde{T}^2}\frac{p_1^*p_2^*}{\phi_1 p_1^* + \phi_2 p_2^*}\left[\left(\frac{\tilde{T}_1 - \tilde{T}_2}{\tilde{T}}\right)^2 + \frac{Z_{12}^2}{p_1^*p_2^*}\phi_1\phi_2\right] \tag{8}$$

Since $Z_{12} \ll p^* \approx p_1^* \approx p_2^*$, eq 8 can be approximated to

$$\Lambda = Z_{12}\left[-\tilde{G}(\tilde{T}) + \tilde{T}\frac{\partial\tilde{G}}{\partial\tilde{T}}\right] - \frac{\tilde{T}^2}{2}\frac{\partial^2\tilde{G}}{\partial\tilde{T}^2}p^*\left(\frac{\tilde{T}_1 - \tilde{T}_2}{\tilde{T}}\right)^2 \tag{9}$$

Here the first term represents the change in the energy density due to the foreign segment contact and the second term arises from the change in free volume on mixing. This is a variant of a similar expression originally derived by Patterson[17,18] but is now given in a form symmetric with respect to components 1 and 2.

In the Flory equation-of-state theory,[19-21] the free energy G per unit volume is given, except for an additive term dependent on a geometrical factor, by

$$G/p^* = -3\tilde{v}\tilde{T}\ln(\tilde{v}^{1/3} - 1) - 1/\tilde{v}^2 \tag{10}$$

From this, the equation of state for $\tilde{p} = 0$ is obtained as

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{11}$$

Equations 10 and 11 together constitute the reduced free energy function $\tilde{G}(\tilde{T})$. When this is substituted in (9), we obtain Λ as

$$\Lambda = \frac{Z_{12}}{\tilde{v}^2} + \frac{3}{2}\frac{\tilde{T}}{\tilde{v}}\frac{p^*}{1 - 4\tilde{T}\tilde{v}}\left(\frac{\tilde{T}_1 - \tilde{T}_2}{\tilde{T}}\right)^2 \tag{12}$$

In Flory's equation-of-state theory, Z_{12} is given as

$$Z_{12} = \frac{1}{\phi_1(s_1/s_2) + \phi_2}(X_{12} - TQ_{12}\tilde{v}) \tag{13}$$

Thus, Z_{12} is interpreted as a free energy density rather than an energy density. The term $-TQ_{12}\tilde{v}$ in effect corrects for the deficiency of the Flory–Huggins expression for the combinatorial entropy of mixing. The contact entropy parameter Q_{12} is frequently neglected partly because of its small magnitude but also often simply for the lack of any clear basis for evaluating it. A composition dependence of Z_{12} arises when the ratio s_1/s_2 is not unity, where s_i stands for the surface-to-volume ratio of a molecule of component i. Equation 13 also illustrates that by definition the contact energy parameter X_{12} and the entropy parameter Q_{12} are not symmetric with respect to the two components; that is, $X_{12} \neq X_{21}$ and $Q_{12} \neq Q_{21}$. This is unfortunate because it detracts from their possible utility as fundamental molecular parameters dependent only on the chemical structures of the component molecules.

In order to be able to compare eq 12 with our experimental values of Λ, we need the values of the characteristic parameters for the two component polymers concerned. The parameters for polystyrene at 150 °C, evaluated by Flory and co-workers,[51] are $T^* = 8299$ K, $\tilde{v} = 1.2105$, $p^* = 114$ cal/cm^3 (extrapolated from lower temperatures), and $\alpha = 5.81 \times 10^{-4}$ deg^{-1}. For polybutadiene $\tilde{v}$ and T^* can be evaluated from the knowledge of its thermal expansion coefficient α by means of the relation

$$\tilde{v}^{1/3} - 1 = \alpha T/3(1 + \alpha T) \tag{14}$$

which is derived from the equation of state (11). Taking the value $\alpha = 7.5 \times 10^{-4}$ deg^{-1} given in ref 52 (or $\alpha = 6.85 \times 10^{-4}$ given by Patterson and Robard[14]), we obtain for 150 °C $T^* = 7177$ K (or 7542 K) and $\tilde{v} = 1.261$ (or 1.242). Evaluation of p^* requires knowledge of either the isothermal compressibility or the thermal pressure coefficient, neither of which is available for polybutadiene. For the purpose of the present discussion, however, not much error is introduced by taking the approximation $p_1^* \approx p_2^* \approx p^*$.

The relative magnitudes of the two terms on the right of eq 12 can now be estimated. At 150 °C and $\phi_1 = 0.50$, the characteristic parameters for the mixture are given by $T^* = 7697$ K (or 7902 K) and $\tilde{v} = 1.235$ (or 1.226) (the values in the parentheses being those based on $\alpha = 6.85 \times 10^{-4}$). The second term of eq 12 then becomes 0.220 cal/cm^3 (or 0.092 cal/cm^3), a fairly small fraction of the observed Λ value, which according to Table II lies between 0.70 and 0.80 cal/cm^3 (except the lowest molecular weight pair PS2-PBD2). Thus, most of the observed Λ value for the polystyrene-polybutadiene pair arises from the effect of foreign segment contacts and relatively little from the free volume disparity between the two component polymers, which the second term represents. The difference in α between polystyrene and polybutadiene is about as large as any that would be observed between a pair of commonly studied polymers. It appears therefore that, except when Λ is very small, the effect of the free volume change on mixing can be neglected, in the first approximation, in discussing the polymer-polymer interaction parameter. If so, the scheme of predicting the polymer-polymer interaction parameter from the solubility parameter difference

$$\Lambda = (\delta_1 - \delta_2)^2 \tag{15}$$

is justified, at least when Λ is positive and not extremely small.

When compatibility of polymer pairs exhibiting a LCST behavior has been discussed, the importance of the free volume disparity has been stressed.[14,15] If the compatibility indeed arises from negligibly small magnitudes of both the contact and free volume term in eq 12, then even a slight increase in the second term with increasing temperature would be sufficient to induce incompatibility. The several truly compatible polymer pairs so far found, however, owe their compatibility mostly to the presence of specific interactions which render Λ negative. The occurrence of a LCST behavior for such systems probably arises, as pointed out by Robard and Patterson,[13] more because of weakening of the specific interaction at higher temperature and less from an increased contribution of the free volume disparity.

We now discuss the temperature coefficient of Λ. The first term in eq 12 has a negative temperature dependence because of the $\tilde{v}^{-2}$ factor while the second term has a positive dependence. The experimental result, indicating a negative temperature coefficient, is in accord with the conclusion above that the second term is relatively insignificant. If Z_{12} itself is temperature independent, then

$$\partial \ln \Lambda / \partial T \leq 2(\partial \ln \tilde{v} / \partial T) \tag{16}$$

the equality holding when the second term is zero. Since $\tilde{v}$ is a function of the mixture composition ϕ_1 as well as of T, its temperature coefficient appropriate for comparison with the experimental values of Λ is somewhat ill-defined, but $\partial \ln \tilde{v}/\partial T$ can be taken as approximately equal to the average of the thermal expansion coefficients for polystyrene and polybutadiene, i.e., 6.7×10^{-4} deg^{-1}. The values of $-\partial \ln \Lambda/\partial T$ calculated from the entries in Table II lie mostly (with the exception of pairs 1, 2, and 6) between 2.0×10^{-3} and 3.0×10^{-3} deg^{-1}. Although these are somewhat larger than 1.3×10^{-3} estimated for $2(\partial \ln \tilde{v}/\partial T)$, it nevertheless suggests the essential correctness of the equation-of-state theory in indicating that the temperature coefficient of Λ is negative and is given largely by the dilation in volume with temperature. It also explains the results that for pairs 1 and 2 consisting of polymer components of lower molecular weights and hence of higher thermal expansion coefficients than the rest, the temperature coefficient of Λ also turns out larger in absolute magnitude.

The fact that the observed temperature dependence of Λ is consistently larger than expected from the thermal expansion alone may suggest that the entropic term in Z_{12}, as given in eq 13, cannot be totally neglected. The observed discrepancy can, in fact, be accounted for if we assign a small positive value to Q_{12} so as to have $TQ_{12}\tilde{v}/X_{12} \approx {}^1/_3$. Previously the Q_{12} term was evaluated explicitly for several systems. For binary mixtures of normal alkanes,[53] the observed chemical potential can be fitted best when the ratio $TQ_{12}\tilde{v}/X_{12}$ is given a value slightly less than half, while for polymer-solvent mixtures,[20,55-57] the ratio is given a negative value ranging from -0.5 to -2. The absolute magnitude of the ratio, ${}^1/_3$, required in the present mixtures is therefore comparable to those previously determined. Although it is puzzling why the sign of Q_{12} is not always the same, we may note that in the two cases where Q_{12} is positive the components of the mixtures are of comparable sizes. The present work at least shows that an accurate determination of the temperature coefficient of Λ for polymer-polymer mixtures can be helpful (because of the relatively small contribution of the free volume term) to elucidate the nature of the Q_{12} parameter.

Finally we discuss the concentration dependence of Λ. When the contribution of the second term in eq 12 is small and neglected, Λ is given by a product of Z_{12} and $\tilde{v}^{-2}$, both of which depend on ϕ_1. The expression for Z_{12} in eq 13 contains a factor s_1/s_2 denoting the disparity between the two components in their surface-to-volume ratios. When Bondi's scheme[54] for estimating the van der Waals volume and surface area is used, the ratio s_1/s_2 for polystyrene-polybutadiene turns out to be 1.15. Remembering that $\tilde{v}$ for PS is smaller than for PBD, we recognize that, as ϕ_1 increases, the increase in $(X_{12} - TQ_{12}\tilde{v})/\tilde{v}^2$ is counterbalanced by the increase in $\phi_1(s_1/s_2) + \phi_2$. Therefore, unless the value of s_1/s_2 is considerably larger than unity, $Z_{12}/\tilde{v}^2$ should not depend strongly on ϕ_1. Using numerical values $Z_{12} = 1.30$ cal/cm^3, $Q_{12} = 0.000\,83$ cal/(deg·cm^3), and $T = 150$ °C, we find $Z_{12}/\tilde{v}^2$ to change from 0.54 at $\phi_1 = 0$ to 0.52 at $\phi_1 = 1$. The experimental result summarized in Table II shows that the coefficient λ_1 is small in all cases where evaluated, in essential agreement with the above deduction. The occurrence of both positive and negative values of λ_1 probably arises partly from the difficulty of representing the temperature and concentration dependence of Λ by a single linear function as given in eq 2. The values of λ_1 and λ_T evaluated to give the best fit by a nonlinear least-squares method are mutually correlated to some extent.

In a previous publication[38] the value of Λ for polystyrene-natural rubber was calculated by means of the equation-of-state theory on the basis of literature data on polymer solution studies. The concentration dependence of the predicted Λ values given there was much larger than found in this work for polystyrene-polybutadiene. The s_1/s_2 value, used for the prediction, was 1/1.9, obtained by multiplying the s_1/s_2 values reported in the literature: 1/2.0 for polystyrene-cyclohexane, 1/0.62 for cyclohexane-polyisobutylene, 0.58 for polyisobutylene-benzene, and 1/0.90 for benzene-natural rubber. Small errors in the individual values quoted could have led to a sizable cumulative error, making the value 1/1.9 unreliable. The present work suggests that the Bondi scheme is apparently a valid way of estimating s_1/s_2 values.

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On the Nonexistence of Crankshaft-like Motions in Dilute Solutions of Flexible-Chain Molecules[1]

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ABSTRACT: A poly(ethylene oxide) was prepared which had incorporated into the middle of the polymer chain a dichromophoric residue capable of intramolecular excimer formation. The ratio of excimer and monomer emission intensities, I_d/I_m, for the polymer and a low molecular weight analogue was measured over a range of temperatures. The apparent activation energies derived from these data were virtually identical for the polymer and its analogue, proving that conformational transitions in the backbone of polymer chains cannot involve two near-simultaneous hindered rotations ("crankshaft-like motions"). At low polymer concentrations, I_d/I_m for the labeled polymer is only slightly lower than for analogous low molecular weight compounds, but the factor by which excimer formation is decreased by incorporation of the dichromophoric residue into the polymer chain increases with the addition of unlabeled polymer. The decrease of the excimer yield of either polymer or analogue at increasing concentration of polymer for polymers with different chain length is similar for solutions with the same macroscopic viscosity.

Hindered rotation around a bond in the backbone of a flexible polymer molecule has been perceived to present the conceptual problem represented schematically in Figure 1. If rotation takes place around one bond only with no change in the conformation of the rest of the molecule (Figure 1a), then a large part of the chain has to move through the viscous medium with a prohibitive expenditure of energy. This difficulty was circumvented by proposing[2-5] that two hindered rotations take place simultaneously in what has been described as a "crankshaft-like motion" (Figure 1b) so that only a short section of the chain would have to move through the medium. This concept was originally meant to apply to conformational transitions of polymers in bulk, but it was

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