

The Miscibility of Polymers: Interaction Parameter for Polybutadiene with Polystyrene*

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INTRODUCTION

It is generally considered that polybutadiene and polystyrene are not truly soluble in each other and that mixtures of the two are found to be heterogeneous if examined closely.^{1,2} However, solution theory predicts that the mutual compatibility of different polymers increases with decreasing molecular weight. We wished to see whether a homogeneous mixture could be obtained with polybutadiene and polystyrene of very low molecular weights. Accordingly, we measured the point of phase separation for pairs of polymers in toluene and other solvents, varying the molecular weights of the polymers. A pair of polymers which were miscible without solvent was not found, but the data have been used to calculate the polymer-polymer interaction parameter.

The calculation of interaction parameters was done with the aid of equations developed by Maron.³ It was necessary to modify these equations somewhat in order to apply them to systems of three components and of very low molecular weights at high concentrations.

The solubilities are strongly dependent upon polymer molecular weight, and likewise the calculations depend upon the measured values of molecular weight. Therefore, the accuracy of the present results suffers from the fact that whole polymers were used, rather than narrow molecular weight fractions. However, the equations and method of treating the data should prove equally applicable to more completely characterized systems.

EXPERIMENTAL DETAILS

Polymers were prepared in quart bottles using a 5°C. redox emulsion polymerization system; a typical recipe is given in Table I. The molecular weight was varied by changing the amount of mercaptan. Polymerizations were stopped with 0.2 part of sodium dimethyldithiocarbamate, and unreacted monomer was promptly removed with vacuum at 40°C. Conversions were kept below 70% in order to avoid the higher molecular weights and crosslinking which may occur at higher conversions. The

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latices were coagulated with methanol, and the polymers were washed several times with methanol and then water, and vacuum-dried at 50°C.

TABLE I
Polymerization Recipe

	Parts
Dodecyl benzene sodium sulfonate	3.5
Versene iron chelate (Dow Chemical Co.)	0.03
Sodium formaldehyde sulfoxylate	0.04
Water	200.0
Styrene	100.0
<i>tert</i> -Dodecyl mercaptan	10.0
Sodium hydrosulfite	0.02
<i>p</i> -Methane hydroperoxide	0.06

Molecular weights were determined either by osmometry or by ebullioscopic measurements in chlorobenzene; they are listed in Table II. Intrinsic viscosities were determined in toluene at 25°C. and these also are given in Table II. Polymer densities used in the calculations (0.892 for polybutadiene and 1.054 for polystyrene) are those given by Whitby.⁴

TABLE II
Maximum Miscible Polymer Concentration versus Molecular Weight for One-to-One Mixtures in Toluene

Polybutadiene			Total polymer, %	
No.	MW	$[\eta]_v$	Polystyrene: No. 1162B ^a	No. 1162C ^b
1161B	26,600 (osmom.)	99.0	19.0	23.3
1161C	14,000 (osmom.)	75.8	20.3	24.0
770A	1,670 (ebull.)	19.8	28.3	29.5
770B	1,110 (ebull.)	12.05	37.5	39.5

^a MW = 4080 (ebull.); $[\eta]_v = 12.33$.

^b MW = 2720 (ebull.); $[\eta]_v = 8.53$.

Stock solutions of about 40 g./l. polymer were prepared in the appropriate solvent which contained 0.2 g./l. Santovar A (Monsanto Chemical Co.) as antioxidant. Weighed portions of stock solutions, to give the desired ratio of polybutadiene to polystyrene, were placed in 4-oz. screw-cap bottles. Normally a total of 100 g. of solution was used. After thorough mixing, solvent was removed by evaporation till turbidity appeared, indicating the presence of two phases. Solvent was then added dropwise with shaking till the turbidity just disappeared. In most cases the end-point could be located within 2 or 3 drops of solvent, or 1-2% of the total solution weight. The solutions were then weighed and the polymer concentration was calculated. The temperature was room temperature, 23 ± 1°C.

RESULTS

Table II and Figure 1 show the per cent total polymer at the onset of turbidity for one-to-one mixtures, by weight, of polybutadiene and polystyrene of various molecular weights in toluene. Clearly, the limiting concentration is higher for lower molecular weights. However, the plots

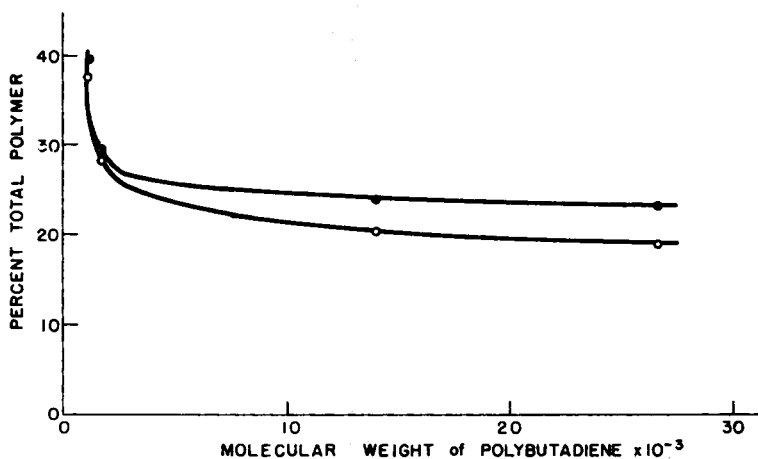


Fig. 1. Maximum miscible polymer-polymer concentrations versus molecular weight of 1:1 mixtures in toluene: (●) polystyrene, MW 2720; (○) polystyrene, MW 4080.

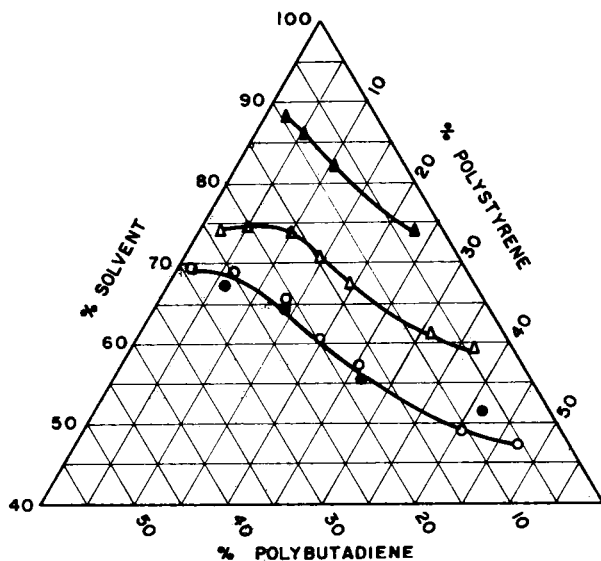


Fig. 2. Maximum miscible polymer concentration versus polymer ratios in various solvents. Polymers: (○) 770B, 1162C, in toluene; (●) 770B, 1162C in benzene; (Δ) 770A, 1162C in toluene; (▲) 770A, 1162C, in CCl_4 .

TABLE III
Maximum Miscible Polymer Concentrations for Various Polymer Ratios in Various Solvents

Solvent, %	Polystyrene, %	Polybutadiene, %
Toluene	No. 1162C	No. 770B
68.8	3.1	28.1
68.0	6.3	25.7
65.4	13.7	20.9
60.5	19.6	19.9
57.2	25.5	17.3
49.0	40.8	10.2
47.3	47.3	5.4
Benzene	No. 1162C	No. 770B
67.0	6.5	26.5
64.2	14.2	21.6
55.4	26.6	18.0
51.6	41.3	7.1
Toluene	No. 1162C	No. 770A
73.9	2.6	23.5
74.5	5.0	20.5
74.4	10.1	15.5
70.5	14.7	14.8
67.0	19.6	13.4
61.0	31.2	7.8
58.9	36.9	4.2
Carbon tetrachloride	No. 1162C	No. 770A
88.2	2.3	9.5
86.2	5.5	8.3
81.9	10.8	7.3
74.1	23.1	2.8

curve upward to such an extent that no estimate can be made of the molecular weights needed for 100% polymer, i.e., pure mixed polymer.

Table III and Figure 2 show the limiting miscible concentrations for polymers mixed in varying ratios and in various solvents. The phase diagrams obtained are generally similar to those for polymer mixtures reported by Dobry and Boyer-Kawenoki,¹ except that the total polymer concentrations are much higher in the present cases because of the lower molecular weights. For the same pair of polymers there is very little difference whether toluene or benzene is used as solvent. In carbon tetrachloride, a poorer solvent, phase separation occurs at distinctly lower concentrations. The diagrams are highly asymmetrical, indicating a greater tolerance of polystyrene for a little polybutadiene than vice versa.

At the point of saturation the free energy of mixing for the system must equal zero. Maron's theory of nonelectrolyte solutions³ modifies the usual equations expressing this equilibrium by including a term for the variation of the effective volume of a polymer molecule in solution and by allowing the usual interaction parameter to vary with concentration. These modifi-

cations have been used in treating the present data to see what effect they might have on the calculated results.

For two components with negligible volume change on mixing we have:

$$\Delta F_m = RT(X^\circ + \chi n_1 v_2) = 0 \quad (1)$$

in which

$$X^\circ = n_1 \ln v_1 + n_2 \ln v_2 + n_2 \ln(\epsilon/\epsilon^\circ) \quad (2)$$

In this expression the subscript 1 refers to the solvent, the subscript 2 to the solute, n is mole fraction, v is volume fraction, χ is the interaction parameter, ϵ is the effective volume factor for polymer in solution, and ϵ° is the effective volume factor for bulk polymer. For viscosity measurements of polystyrene solutions Maron et al.⁵ found that ϵ could be expressed as a function of concentration by:

$$1/\epsilon = 1/\epsilon_0 + S v_2$$

or

$$\epsilon = \epsilon_0 - S \epsilon_0 \epsilon v_2 \quad (3)$$

where S and ϵ_0 are constants. At a particular concentration $v_{2\infty}$ the viscosity approached infinity; at this point $\epsilon = \epsilon_\infty$ and $\epsilon v_{2\infty} = 1$. From this,

$$S = (\epsilon_0 - \epsilon_\infty)/\epsilon_0 \quad (4)$$

and

$$\epsilon = \epsilon_0/[1 + (\epsilon_0 - \epsilon_\infty)v_2] \quad (5)$$

The constant ϵ_0 is the value of the effective volume factor at infinite dilution and was shown to be related to the intrinsic viscosity, on the volume fraction scale, by:

$$\epsilon_0 = [\eta]_v/2 \quad (6)$$

The effective volume factor at maximum concentration, ϵ_∞ , was found to be approximately 4.0 for the polystyrene solutions, and the same value was satisfactory in the treatment of Maron and Nakajima⁶ of the rubber-benzene system. For the effective volume factor of bulk polymer, ϵ° , Maron has used the value for close-packed spheres, 1.35.

In applying this treatment to the present system, we immediately encounter two difficulties: the extension to a three-component system with two polymeric solutes, and the fact that the expression for ϵ gives unreasonable results in the high concentration range used in the present work. If $\epsilon_\infty = 4$ and $\epsilon_\infty v_{2\infty} = 1$, then $v_{2\infty} = 0.25$; one would expect that at 25% solids ϵv_2 would have reached its maximum and the viscosity become very high. In fact, a number of the saturation concentrations we have measured were over 40%, and the solutions were quite fluid. Furthermore, it is reasonable to expect ϵv_2 to approach a constant limiting value at high concentrations. A plot of ϵv_2 vs. v_2 according to eq. (5) is shown in Figure 3

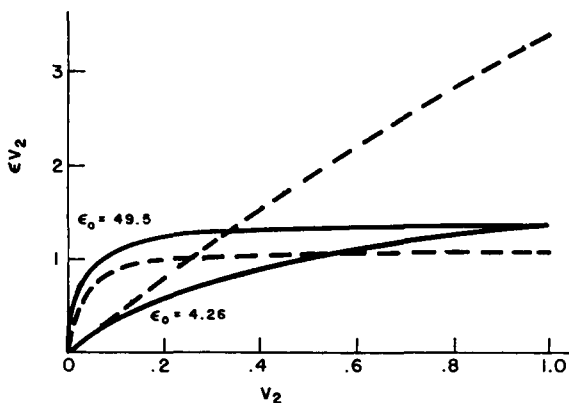


Fig. 3. Effective volume fraction versus volume fraction: (---) eq. (5); (—) eq. 7

for two polymers used in this series, No. 1161B for which $\epsilon_0 = 49.5$ and No. 1162C for which $\epsilon_0 = 4.26$. For the higher molecular weight polymer the behavior is reasonable, but for the lower molecular weight ϵv_2 reaches unreal values and shows no approach to a limit. If, instead, we let $\epsilon = \epsilon^\circ = 1.35$ at $v_2 = 1$, the expression for ϵ becomes:

$$\epsilon = \epsilon_0 / [1 + (\epsilon_0 - \epsilon^\circ)v_2/\epsilon^\circ] \quad (7)$$

Plots of ϵv_2 vs. v_2 according to eq. (7) are also shown in Figure 3. The curves are quite similar to those from eq. (5) if ϵ_0 is large, but very different for small values of ϵ_0 .

For a system consisting of two polymeric solutes in the same solvent, eqs. 1 and 2 become:

$$\Delta F_m = RT (X^\circ + \chi_{12}n_1v_2 + \chi_{13}n_1v_3 + \chi_{23}n_2v_3) \quad (8)$$

and

$$X^\circ = n_1 \ln v_1 + n_2 \ln v_2 + n_3 \ln v_3 + n_2 \ln (\epsilon_2/\epsilon_2^\circ) + n_3 \ln (\epsilon_3/\epsilon_3^\circ) \quad (9)$$

Equation (3) shows that the effective volume factor decreases linearly as the effective volume increases. If there are two polymeric solutes present, each of them can be expected to contribute to the crowding of the other (in the absence of attractive interaction), and so we assume:

$$\epsilon_2 = \epsilon_{20} - S_2\epsilon_{20}(\epsilon_2v_2 + \epsilon_3v_3) \quad (10)$$

and

$$\epsilon_3 = \epsilon_{30} - S_3\epsilon_{30}(\epsilon_2v_2 + \epsilon_3v_3) \quad (11)$$

At $v_2 + v_3 = 1$ we let $\epsilon_2 = \epsilon_3 = \epsilon^\circ$ which leads to:

$$S_2 = (\epsilon_{20} - \epsilon^\circ)/\epsilon_{20}\epsilon^\circ \text{ and } S_3 = (\epsilon_{30} - \epsilon^\circ)/\epsilon_{30}\epsilon^\circ \quad (12)$$

To facilitate manipulation we let

$$A_2 = S_2\epsilon_{20} = (\epsilon_{20} - \epsilon^\circ)/\epsilon^\circ \text{ and } A_3 = (\epsilon_{30} - \epsilon^\circ)/\epsilon^\circ \quad (13)$$

TABLE IV
Polymer-Polymer Interaction Parameters

Series	MW ₂	χ ₂₃	V ₂	α ₂₃ , l. ⁻¹	χ ₁₂ + χ ₁₃ (v ₃ /v ₂)
1162C	2720	72	2580	28	2.11
1162B	4080	112	3870	29	2.11

Eliminating S_2 and S_3 from eqs. (10) and (11) by means of eqs. (12) and (13) and solving for ϵ_2 by eliminating ϵ_3 gives:

$$\epsilon_2 = [\epsilon_{20} + (\epsilon_{20}A_3 - \epsilon_{30}A_2)v_3]/(1 + A_2v_2 + A_3v_3) \quad (14)$$

By means of eq. (14) ϵ_2 may be calculated from the data, and ϵ_3 is obtained from eq. (11) and values of ϵ_2 .

Except for the interaction parameters χ we can now calculate all the factors in eq. (8), which may be written:

$$-X^\circ/n_2v_3 = (n_1v_2/n_2v_3)[\chi_{12} + (v_3/v_2)\chi_{13}] + \chi_{23} \quad (15)$$

For the data in Table II the ratio v_3/v_2 is very nearly constant; a plot of $-X^\circ/n_2v_3$ vs. n_1v_2/n_2v_3 should be a straight line. Figure 4 shows that the plots are indeed linear; the resulting parameters are listed in Table IV. For comparison the table also lists $\alpha_{23} = \chi_{23}/V_2$, v_2 being the molar volume of component 2. The parameters derived from the two series of data are in excellent agreement.

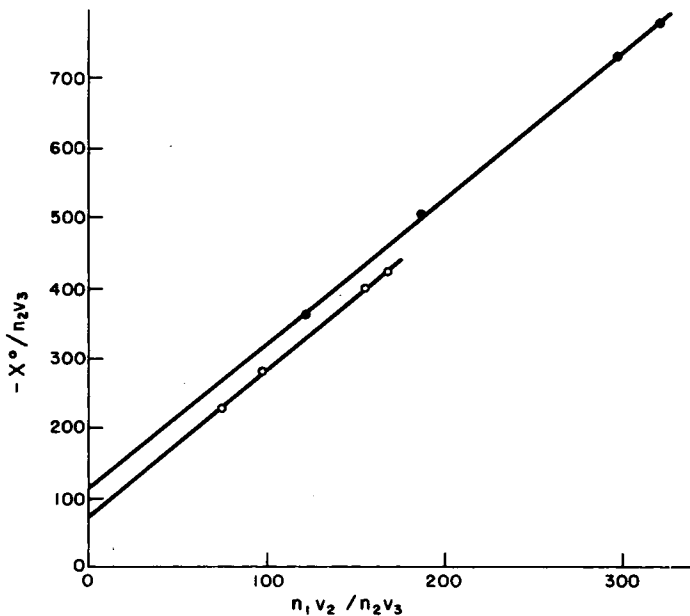


Fig. 4. Plots of X°/n_2v_3 vs. n_1v_2/n_2v_3 for obtaining interaction parameters: (O) 1162C series; (●) 1162B series.

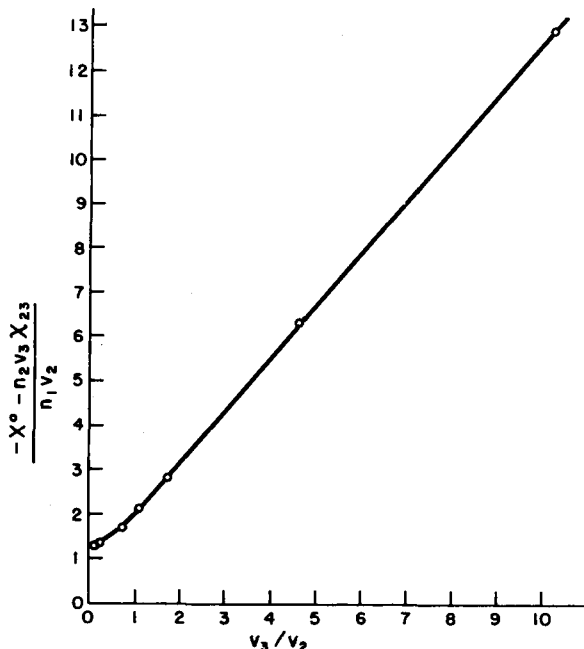


Fig. 5. Plot of $(-X^\circ - \chi_{23} n_2 v_3)/n_1 v_2$ vs. v_3/v_2 for determining polymer-solvent interaction parameters.

The values of χ_{23} may now be used in eq. (15) in the form:

$$(-X^\circ - n_2 v_3 \chi_{23})/n_1 v_2 = \chi_{12} + \chi_{13}(v_3/v_2) \quad (16)$$

to determine χ_{12} and χ_{13} . The data for polymers 1162C and 770B in toluene as shown in Table III have been plotted in Figure 5. From the fact that the line is curved one must conclude that χ_{13} varies with concentration, and therefore the method of plotting to determine these parameters is not valid. It is interesting that the sum $\chi_{12} + \chi_{13}v_3/v_2$ is apparently so nearly constant (Table IV). Maron and others^{7,8} have indicated that the parameters can be described by a linear relation:

$$\chi_{12} = \chi_{12}^\circ + \sigma_{12}v_2 \quad (17)$$

Substitution of such relations as eq. 17 into eq. 16 gives an equation with four unknowns. Since we have seven sets of data the problem is theoretically soluble, but trials have indicated that it is not worth the effort without data of greater precision.

The value for α_{23} found here is larger by an order of magnitude than that obtained by Allen et al.;⁹ they obtained $\alpha_{23} = 0.1 \text{ l.}^{-1}$ for polybutadiene and polystyrene by studying the equilibrium between two-phase systems with carbon tetrachloride as solvent. In estimating the reliability of the present results, the following points are pertinent. By far the biggest term in X° is the $n_1 \ln v_1$ term for the solvent. This determines the magni-

tude of χ_{23} and it depends only on the molecular weight and density of toluene and on the total polymer concentration at saturation. Since our polymers were not fractionated they undoubtedly contain a variety of molecular weights; a small amount of material with molecular weight significantly higher than average can be expected to lower appreciably the saturation concentration and thus raise the apparent value of α_{23} . An error in molecular weight determination does not have as large an effect. If all molecular weights are doubled, the calculated value of χ_{23} is just about doubled, and hence α_{23} is nearly unchanged.

If the calculations are performed without the effective volume factor term the results are qualitatively the same. A value for α_{23} of 36 l.⁻¹ is obtained instead of 28 l.⁻¹.

It is felt that the procedure outlined by these experiments, if applied to fractionated polymers, can easily yield reliable information about polymer-polymer interaction, except in cases in which the interaction is attractive and no phase separation occurs.

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Synopsis

We have measured the solubility of mixtures of polybutadiene and polystyrene in toluene, benzene, and carbon tetrachloride, using polymers of various molecular weights and mixed in various proportions. The equations developed by Maron for solutions of nonelectrolytes have been modified for three components and for solutions of low molecular weight polymers at high concentrations. The application of these equations has provided estimates of the polymer-polymer interaction parameter χ_{23} . The polymer-solvent interaction parameters χ_{12} and χ_{13} apparently are functions of the concentration and are not readily obtained from the present limited data.

Résumé

Nous avons mesuré la solubilité de mélanges de polybutadiène et de polystyrène dans le toluène, le benzène et le tétrachlorure de carbone et cela en employant des polymères de différents poids moléculaires mélangés dans différentes proportions. Les équations développées par Maron pour les solutions de non-électrolytes ont été modifiées pour trois composants et pour des solutions de polymères de faible poids moléculaire à concentrations élevées. L'application de ces équations a permis d'estimer le paramètre d'interaction polymère-polymère χ_{23} . Les paramètres d'interaction polymère-solvant χ_{12} et χ_{13} sont apparemment des fonctions de la concentration et ne peuvent pas être facilement obtenus à partir des résultats actuels.

Zusammenfassung

Die Löslichkeit von Gemischen von Polybutadien und Polystyrol in Toluol, Benzol und Tetrachlorkohlenstoff wurde an Polymeren von verschiedenem Molekulargewicht und Mischungen von verschiedener Zusammensetzung gemessen. Die von Maron für Lösungen von Nichtelektrolyten entwickelten Gleichungen wurden für drei Komponenten und für Lösungen von niedermolekularen Polymeren bei hohen Konzentrationen modifiziert. Die Anwendung dieser Gleichungen lieferte Werte für den Polymer-Polymer-Wechselwirkungsparameter, χ_{23} . Die Polymer-Lösungsmittel-Wechselwirkungsparameter, χ_{12} und χ_{13} sind offenbar konzentrationsabhängig und sind aus den vorhandenen, wenigen Daten nicht leicht zugänglich.

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