

Compatibility of Polystyrene and Poly(methyl Methacrylate) in Benzene. Effects of Molecular Weight and Temperature

S.-D. HONG* and C. M. BURNS, *Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada*

Synopsis

The incompatibility of polystyrene and poly(methyl methacrylate) in benzene was examined at 20.1°, 40.0°, and 60.2°C. The incipient cloud points of solutions of equal weights of the two polymers were determined by a novel photometric method. Polystyrene samples with weight-average molecular weights in the range of 3.27×10^5 to 6.43×10^4 and poly(methyl methacrylate) samples with weight-average molecular weights in the range of 8.97×10^5 to 8.76×10^4 were used. Models describing the dependence on molecular weight of the critical concentration of a ternary polymer-polymer-solvent system, presented by Fuchs and by Kuhn et al., were examined in light of the experimental data. A modified model is proposed which gives an improved correlation of these results.

INTRODUCTION

In most cases, two different polymers possessing only slight differences in chemical composition exhibit a severely limited miscibility in common solvents and in the solvent-free state.¹ The present experiments were performed in order to determine the effects of molecular weight and temperature on these limits of miscibility or compatibility. Polystyrene and poly(methyl methacrylate) have been shown to demonstrate this limited compatibility.¹⁻⁴ For the present experiments, the limits of compatibility of equal weights of these two polymers in benzene were determined over a range of molecular weights and temperature, by observing the lowest concentration of total polymer at which phase separation occurs. This onset of phase separation is termed the incipient cloud point, because mixtures at higher concentrations are turbid due to the two phases present.

EXPERIMENTAL

Determination of the Incipient Cloud Point

The per cent transmittance of the mixture was measured with a Spectronic 20 Colorimeter (Bausch and Lomb) in the visible region. The wave-

* Present address: Department of Chemistry, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn, New York 11201.

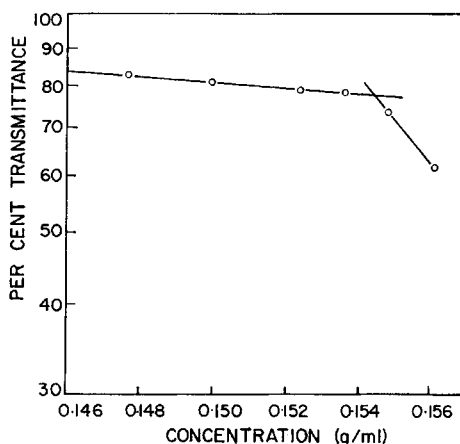


Fig. 1. Typical photometric determination of incipient cloud point. Equal weights of polystyrene and poly(methyl methacrylate) in benzene, 20.1°C, 510 $m\mu$.

length used was 510 $m\mu$, corresponding to the maximum transmittance of pure benzene. Pure benzene was used as the reference for 100% transmittance.

When the transmittance of the mixture was higher than 60%, the plot of the logarithm of the per cent transmittance against total polymer concentration was found to give a straight line with all samples. At concentrations around the incipient cloud point, a distinct discontinuous change in slope was observed. A typical plot of log per cent transmittance versus total polymer concentration can be seen in Figure 1. The concentration at the intersection of the two slopes was interpreted as the incipient cloud point. This point agreed with the visually observed cloud point and could be determined with improved precision by this photometric method.

Procedure

The photometric method was used to determine the cloud points of the polymer mixtures at 20.1° and 40.0°C. Cloud points were determined visually in the thermostat at 60.2°C in order to ensure constant temperature.

Polystyrene and poly(methyl methacrylate) were dissolved separately in benzene at concentrations slightly greater than those at which the cloud points would be expected. The solutions of polystyrene and poly(methyl methacrylate) were introduced into a 10-ml colorimeter tube in such proportion that the two polymers would be present in equal weights. The initial total combined volumes ranged from 2.5 to 6 ml. Thorough mixing was performed by bubbling a small amount of air through the mixture using a syringe needle. Evaporation of benzene by this bubbling procedure had been found to be negligible in preliminary experiments. The tube containing the mixture was then placed in the thermostated water bath. Temperatures of 20.1°, 40.0°, and 60.2°C were used, with the temperature reg-

ulated to $\pm 0.05^\circ\text{C}$. Sufficient time with intermittent shaking was allowed for the mixtures to reach thermal equilibrium and constant turbidity. Ten minutes was allowed at 20.1°C and 15 min at the higher temperatures. This amount of standing time has been shown to be sufficient for the development of turbidity.⁵

For the photometric measurements at the lower temperatures, the tube was removed from the water bath, dried, and insulated in tissue. Measurements were made within 1 min of removal from the water bath. At 60.2°C , the visual observations were made directly in the water bath.

For the next measurement, the mixture was diluted with benzene and again allowed to equilibrate. The increment of benzene added was normally 0.1 ml, with 0.05 ml being added in the vicinity of the incipient cloud point. Although the cloud points of all the samples were determined by diluting turbid mixtures of the two polymers, preliminary experiments showed that the same value of the cloud point could be obtained by evaporating solvent from a homogeneous solution of the two polymers.

In order to compare the results of this investigation more easily with those of earlier workers, the incipient cloud point was expressed as the volume fraction of total polymer in the mixture, C_v . The volume fraction can be calculated from the weight concentration of polymer by the following equation:

$$C_v = C_w \cdot V_{sp}$$

where C_w is the concentration of total polymer, in g/ml, and V_{sp} is the average of the partial specific volumes of the two polymers present.

The values of the partial specific volumes used were 0.91 for polystyrene and 0.80 for poly(methyl methacrylate).⁶ Changes in the values of the partial specific volumes due to dilution^{6,7} and to thermal expansion^{3,6} were considered sufficiently small to be neglected.

In all cases of mixing the polymer solutions with each other, and the combined mixtures with pure solvent, the volumes were assumed to be additive.

Materials

Polystyrene and poly(methyl methacrylate) covering a range of average molecular weights were prepared by fractionating samples of the polymers purchased from Borden Chemical Company. One sample of poly(methyl methacrylate) was used, and two samples of polystyrene with low and high average molecular weights were used. For the polystyrene samples, toluene was used as solvent and methanol was used as precipitant; for the poly(methyl methacrylate) sample, benzene was used as solvent and methanol was used as precipitant. Each fractionation was performed several times, and like fractions were combined.

In order to characterize the combined fractions obtained, the weight-average and number-average molecular weights were determined. Gel

permeation chromatography (Waters Associates) was used in the usual manner at 25°C using tetrahydrofuran as solvent. The polystyrene calibration curve was used for poly(methyl methacrylate) also, since it has been estimated that the error in molecular weight involved in such a procedure would be less than 2%.⁸

For the cloud point determinations, the five polystyrene fractions with the highest average molecular weights were used. Four fractions of poly(methyl methacrylate) covered this same molecular weight range. A fifth fraction of poly(methyl methacrylate) with a much higher molecular weight was included in the investigation. The actual molecular weight data for the polymer samples used are given in Table I.

TABLE I
Characterization of the Polymer Samples

Sample	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
Polystyrene	327,000	158,000	2.07
	220,000	114,000	1.93
	160,000	98,000	1.66
	73,000	36,400	2.02
	64,000	36,600	1.76
Poly(methyl methacrylate)	897,000	429,000	2.09
	326,000	223,000	1.46
	208,000	157,000	1.32
	138,000	102,000	1.35
	88,000	58,000	1.51

RESULTS AND DISCUSSION

Effect of Molecular Weight on Compatibility

Comparison with the Work of Fuchs³

Fuchs investigated the effects of a variety of solvents on the visual cloud point of the polymer pair poly(vinyl acetate)–polystyrene at room temperature. The weight-average molecular weights of the poly(vinyl acetate) samples were in the range of 10^4 to 10^6 . The values of the polydispersity ratio, \bar{M}_w/\bar{M}_n , were in the range of 1.55 to 4.7. Only one sample of polystyrene, with a weight-average molecular weight 3×10^5 and a polydispersity ratio about 4, was used. The polymers were mixed in equal weights.

This author³ reasoned that the solubility of each polymer should reflect the expansion of the molecule in solution. Hence, for the same molecular weight, the incipient cloud point concentration of polymer would be expected to increase with increasing values of the reduced viscosity (η_{sp}/c) in various solvents. The concentration at the cloud point would be expected to decrease with increasing molecular weight. He was able to obtain a

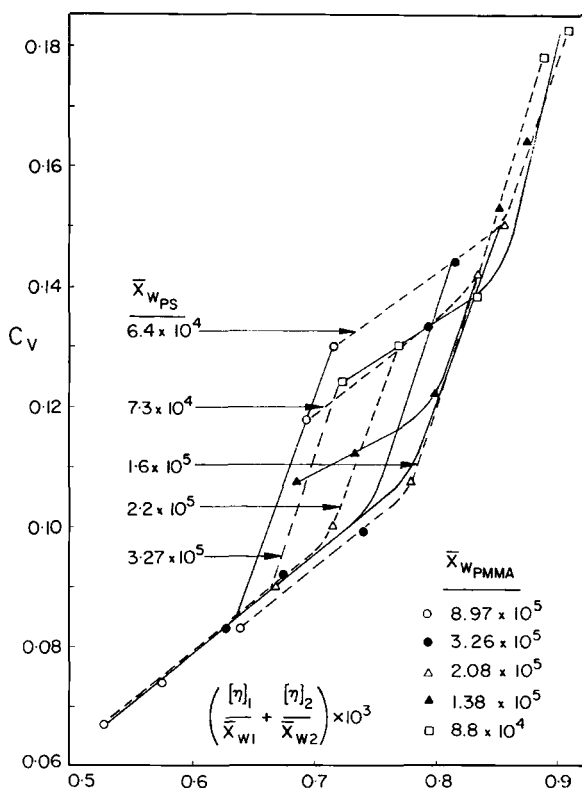


Fig. 2. Results at 20.1°C plotted according to Fuchs,³ eq. (1): C_v = volume fraction of combined polymers at the incipient cloud point; subscripts 1, 2 refer to polystyrene (PS) and poly(methyl methacrylate) (PMMA). Lines are drawn at constant weight-average molecular weight of one polymer in the binary polymer mixture.

linear fit of his results in various solvents and with various molecular weights of poly(vinyl acetate) with the following equation:

$$\left\{ \frac{(\eta_{sp}/c)_1}{x_{w1}} + \frac{(\eta_{sp}/c)_2}{x_{w2}} \right\} b = kC_v$$

where $(\eta_{sp}/c)_1$ is the reduced viscosity of polymer 1 at 1% concentration, x_{w1} is the weight-average degree of polymerization of polymer 1, b is a parameter which decreases with increasing values of \bar{M}_w/\bar{M}_n for the polyvinyl acetate, and k is a constant.

The results of the present investigation at 20.1°C are plotted according to Fuchs's equation in Figure 2, using the intrinsic viscosity instead of the reduced viscosity. The general trend of the equation is seen to hold. The points do not all lie on a single straight line, however, with the exception of the points at high molecular weights. An extrapolation of these points appears to pass near but not through the origin.

Comparison with the Work of Kuhn, Cantow, and Burchard⁴

Kuhn et al. made visual cloud point determinations on the mixture of polystyrene and poly(methyl methacrylate) in benzene at 20°C. Commercial monodisperse polystyrene samples having molecular weights ranging from 9.7×10^4 to 8.6×10^5 were used. The molecular weights of the poly(methyl methacrylate) ranged from 9.7×10^4 to 6.2×10^6 , with a \bar{M}_w/\bar{M}_n ratio of approximately 2.0. The weight ratio of polystyrene to poly(methyl methacrylate) was 0.04 in all cases.

When the reciprocal of the intrinsic viscosity of polystyrene was plotted against $\ln C_v$, parallel straight lines were obtained for the poly(methyl methacrylate) samples of different molecular weights. When the reciprocal of the intrinsic viscosity of poly(methyl methacrylate) was plotted against $\ln C_v$, similar parallel straight lines were obtained for the four polystyrene samples. This behavior was described by the following empirical equations:

$$\frac{1}{[\eta]_{\text{PS}}} = a_1 \ln C_v + f(M_{\text{PMMA}}) \quad (2)$$

$$\frac{1}{[\eta]_{\text{PMMA}}} = a_2 \ln C_v + f(M_{\text{PS}}) \quad (3)$$

where $[\eta]_{\text{PS}}$ and $[\eta]_{\text{PMMA}}$ are the intrinsic viscosities of polystyrene and poly(methyl methacrylate), respectively; a_1 and a_2 are constants, the slopes

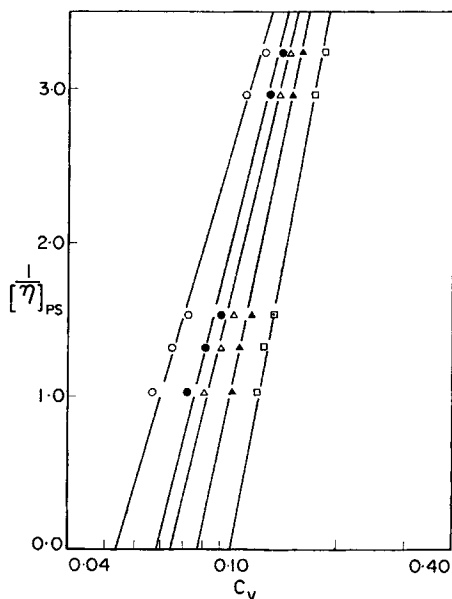


Fig. 3. Results at 20.1°C plotted according to the first equation of Kuhn et al.,⁴ eq. (2). Lines are drawn at constant weight-average molecular weight of poly(methyl methacrylate); (O) corresponds to the highest molecular weight fraction of PMMA.

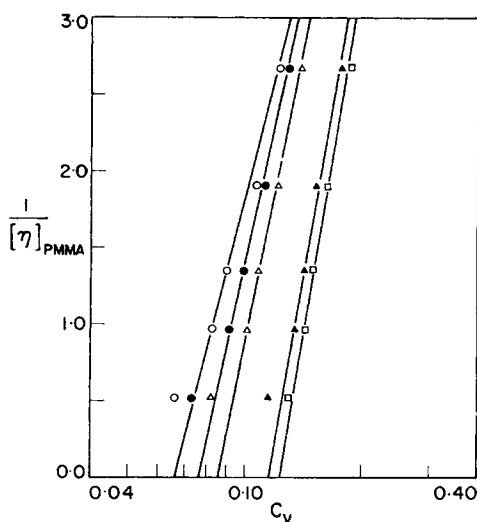


Fig. 4. Results at 20.1°C plotted according to the second equation of Kohn et al.,⁴ eq. (3). Lines are drawn at constant weight-average molecular weight of polystyrene. (○) corresponds to the highest molecular weight fraction of PS.

of the parallel straight lines; C_v is the volume fraction of total polymer in solution at the cloud point; and $f(M_{\text{PMMA}})$ and $f(M_{\text{PS}})$ are constants, depending on the molecular weights of poly(methyl methacrylate) and polystyrene, respectively.

The plots of eqs. (2) and (3) using the present experimental results at 20.1°C are shown in Figures 3 and 4. The samples of highest molecular weight of either polymer deviate from the straight lines. In addition, the straight-line portions are not parallel to one another. Similar deviations were observed at 40.0°C and 60.2°C. The deviation in behavior of these results from those of Kuhn et al. may be due to either the different molecular weight range or the different molecular weight distribution in the present study.

Development of a Modified Model

Since the models given so far do not fit our experimental data well, we now postulate a modified approach. If one plots $1/\bar{x}_{w\text{PS}}$ against C_v , where $\bar{x}_{w\text{PS}}$ is the weight-average degree of polymerization of the polystyrene sample and C_v is the volume fraction of polymers at the incipient cloud point, parallel straight lines can be obtained, as seen in Figure 5. Similarly, the plots of $1/\bar{x}_{w\text{PMMA}}$, where $\bar{x}_{w\text{PMMA}}$ is the degree of polymerization of poly(methyl methacrylate), against C_v are also parallel straight lines except for the deviation at the high molecular weight, as seen in Figure 6. Neglecting this deviation for the moment, the relation can be described by the following equations:

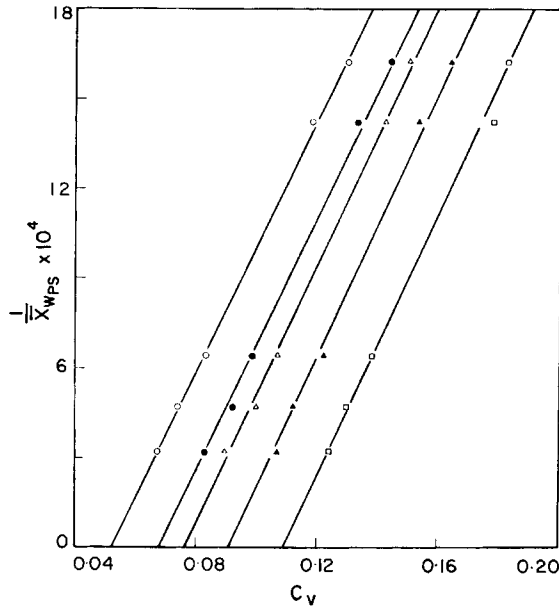


Fig. 5. Results at 20.1°C plotted according to the modified model, eq. (4). Lines are drawn at constant weight-average molecular weight of poly (methyl methacrylate). Symbols same as in Fig. 3.

$$\frac{1}{\bar{x}_{wPS}} = a_1 C_v + g(M_{PMMA}) \quad (4)$$

$$\frac{1}{\bar{x}_{wPMMMA}} = a_2 C_v + g(M_{PS}) \quad (5)$$

where a_1 , a_2 are constants, the slopes of the parallel straight-lines; and $g(M_{PMMA})$ and $g(M_{Pw})$ are constants depending on the molecular weights of the poly methyl(methacrylate) and polystyrene, respectively. The values of $1/a_1$ and $1/a_2$ obtained are summarized in Table II.

TABLE II
Values of Reciprocal of Coefficients of Equations (4) and (5)

	20.1°C	40.0°C	60.2°C
$1/a_1$	46.2	41.0	39.1
$1/a_2$	45.5	45.0	46.3

To make a plot similar to the one of Fuchs, it is necessary to rearrange eq. (4) or eq. (5):

$$\frac{\beta_{PS}}{\bar{x}_{wPS}} + \frac{\beta_{PMMMA}}{\bar{x}_{wPMMMA}} + \lambda = C_v \quad (6)$$

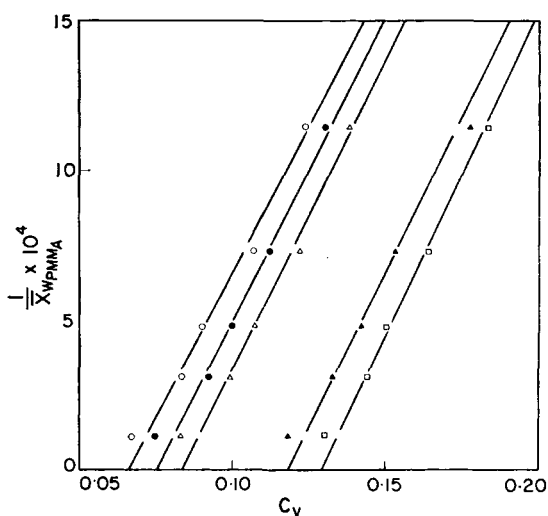


Fig. 6. Results at 20.1°C plotted according to the modified model, eq. (5). Lines are drawn at constant weight-average molecular weight of polystyrene. Symbols same as in Fig. 4.

where

$$\lambda = -\frac{1}{a_1 \bar{x}_{wPS}} - \frac{g(M_{PS})}{a_2} = -\frac{1}{a_2 \bar{x}_{wPMMA}} - \frac{g(M_{PMMA})}{a_1}$$

and

$$\beta_{PS} = \frac{1}{a_1}, \beta_{PMMA} = \frac{1}{a_2}.$$

A least-squares curve-fitting method can be used to estimate the values of β_{PS} , β_{PMMA} , and λ from our experimental data. Table III summarizes the values obtained.

TABLE III
Values of β_{PS} , β_{PMMA} , and λ for the Modified Model, Equation (6)

	20.1°C	40.0°C	60.2°C
β_{PS}	45.9	41.4	39.7
β_{PMMA}	53.1	53.3	50.7
λ	0.050	0.045	0.042

The plots using the modified model are shown in Figures 7 to 9. A reasonably good fit of the data has been achieved using this model. The values of β_{PS} approximate closely those of $1/a_1$ in Table II. The differences in the values of β_{PMMA} and $1/a_2$ are due mainly to deviations found with the highest molecular weight poly(methyl methacrylate).

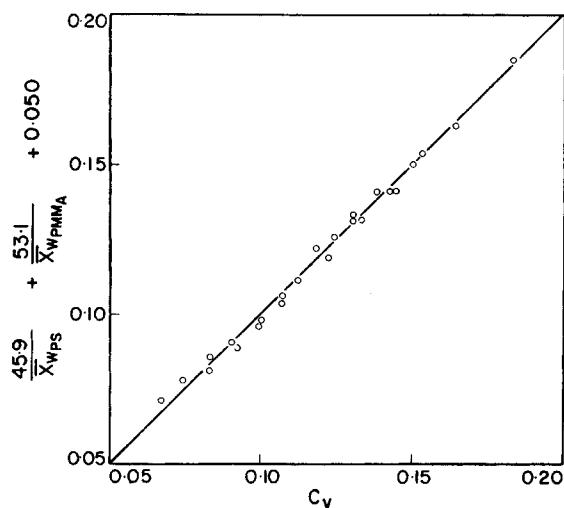


Fig. 7. Results at 20.1°C plotted according to the modified model, eq. (6).

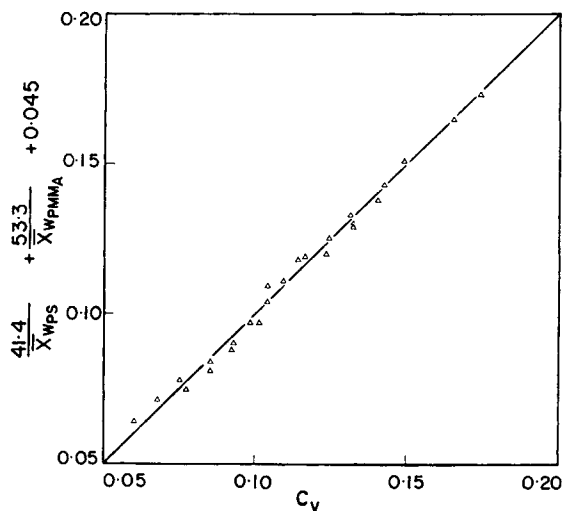


Fig. 8. Results at 40.0°C plotted according to the modified model, eq. (6).

This model, then incorporates the dependence of compatibility on molecular weight. Positive values of β_{PS} and β_{PMMA} indicate that compatibility of the two polymers decreases with increasing molecular weights of polystyrene and poly(methyl methacrylate), respectively. A large value of β would indicate that the point of phase separation will vary appreciably with changes in the average molecular weight of the corresponding polymer. Phase separation for equal weights of two polymers of infinite molecular weight would be expected to occur at a concentration of total polymers given by the value of λ . Hence, λ would be independent of molecular

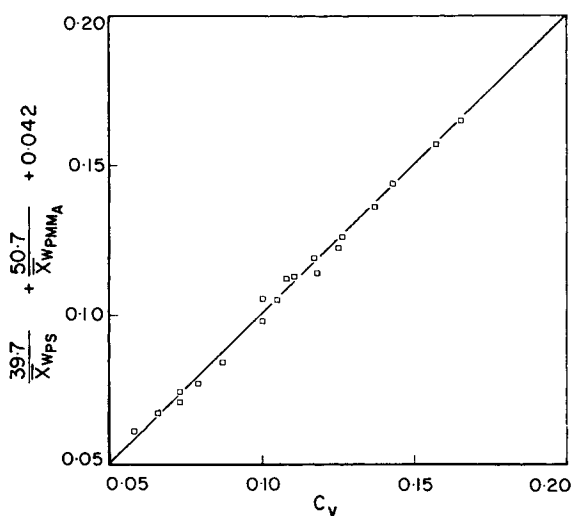


Fig. 9. Results at 60.2°C plotted according to the modified model, eq. (6).

weight and characteristic of the temperature and the chemical natures of the polymers and the solvent.

Effect of Temperature on Compatibility

Dobry and Boyer-Kawenoki¹ concluded from their observations that temperature affects phase separation only slightly, but higher temperature increases the rate of separation of two phases. In contrast, Kern² did find evidence of temperature influences. The polymer pair polystyrene-poly(methyl methacrylate) in *o*-xylene at a concentration slightly greater than the threshold concentration (the critical concentration at which the volume fractions of two polymer solutes are equal) at 25°C was found to merge to form a single phase at 85°C. The same two polymers in methoxybenzene slightly under the threshold concentration at 25°C separate into two phases at 85°C.

In our experiments, the compatibility of equal weights of polystyrene and poly(methyl methacrylate) in benzene was found to decrease with increasing temperature. The data in Table III show that both the coefficient β_{PS} and the parameter λ decrease monotonically through the range of 20.1° to 60.2°C. The coefficient for poly(methyl methacrylate), β_{PMMA} in Table III or $1/a_2$ in Table II, does not show a strong dependence on temperature. Thus, the cloud point at elevated temperatures occurs at lower total polymer concentration because of both the basic chemical nature of the polymers and the fact that lowering the molecular weight does less to enhance the compatibility at elevated temperatures for these two polymers. This decrease in compatibility with increasing temperature is consistent with the slightly exothermic heat of mixing of benzene solutions of polystyrene and poly(methyl methacrylate).⁴

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