

# Compatibility of Polystyrene and Poly(methyl Methacrylate) of Various Molecular Weights in Toluene

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## Synopsis

Gel permeation chromatography has been successfully used to determine the compositions of the conjugate phases in the system of polystyrene and poly(methyl methacrylate) with toluene as solvent. Application of this method to equilibrated samples yields tie lines, binodal curves, and plait points. Polymer-polymer compatibility and the polymer-polymer interaction parameters at the plait points in this system were found to be strongly dependent on the molecular weights of the polymers.

## INTRODUCTION

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are two polymers that have been extensively studied individually, and much information and knowledge of these polymers has been collected and compiled. In the area of solution thermodynamics, however, relatively little is known about the manner in which PS and PMMA interact in solution. A literature survey revealed that only a few PS/PMMA/solvent systems have been investigated. For example, Dobry and Boyer-Kawenoki<sup>1</sup> in 1947 studied PS and PMMA in benzene, and Kern and Slocombe<sup>2</sup> in 1955 studied PS and PMMA in methylethyl ketone, by observing phase separation in these systems. In 1971 Hong and Burns<sup>3</sup> studied the system PS/PMMA/benzene and Vshivkov and Komolova<sup>4</sup> in 1980 studied PS-PMMA in ethylacetate, both by using the cloud point method. Quite recently, Lloyd et al.<sup>5,6</sup> have developed a convenient and reliable technique for investigating incompatibility in polymer-polymer-solvent systems, in which gel permeation chromatography (GPC) was used for analyzing the compositions in the conjugate phases of the ternary system. We have successfully used this technique in our study on the compatibility of PS and PMMA of various molecular weights in toluene. In this paper we report a strong dependency of polymer-polymer interaction parameters on the molecular weights of PS and PMMA.

## EXPERIMENTAL

### Polymer-Polymer-Solvent Systems

PS and PMMA standards of narrow molecular weight distribution were pur-

chased from Pressure Chemical Co. and Polymer Laboratory, Inc. respectively. Their characteristics as given by the suppliers are shown in Table I.

To study the effect of polymer molecular weight on the compatibility of PS and PMMA in toluene, the following combinations were made: PS100K + PMMA180K + toluene; PS100K + PMMA29K + toluene; PS37K + PMMA180K + toluene; PS37K + PMMA29K + toluene. Two other combinations were made: PS100K + PMMA69K + toluene and PS37K + PMMA69K + toluene, in which PMMA69K was an industrial grade PMMA of  $\bar{M}_w \approx 69,000$  and  $\bar{M}_w/\bar{M}_n \approx 2$  as measured by our GPC unit.

Approximately equal quantities (0.2–0.4 g) of each polymer were weighed into a small glass bottle of about 4-mL capacity. A measured quantity of reagent grade toluene was added to dissolve the polymers. The bottle was then tightly capped and shaken to form a uniform mixture. The mixture was allowed to equilibrate in a constant temperature room controlled at  $23 \pm 1^\circ\text{C}$  and ambient atmospheric pressure. In about 3–10 days the mixture separated into two distinct liquid phases. More than 3 weeks were given for each sample so that ample time was allowed for the mixture to approach equilibrium.

To determine the composition of each phase by GPC, portions were withdrawn from the phases with hypodermic syringes and weighed by difference. They were then diluted with tetrahydrofuran, the carrier solvent in our GPC, in standard volumetric flasks so that the dilution factor was known. The diluted polymer solutions were then analyzed by GPC.

A Waters Model 200 GPC unit was used which was fitted with columns packed with Styragel of specific pore size in the range of  $200\text{--}5 \times 10^5$  nm ( $2000\text{--}5 \times 10^6$  Å). Concentration of polymer in the eluent was detected by a differential refractive index (RI) detector in series with an ultraviolet (UV) detector set at 254 nm. Polymer concentration data in mV signals were recorded by a strip chart recorder and were collected and stored on diskettes by an Apple II microcomputer interfaced with the GPC unit.<sup>7</sup>

Areas under the GPC chromatograms were found to be proportional to the polymer concentrations in the injected sample. For a mixture of PS and PMMA in the injected sample, the RI chromatogram areas due to PS and due to PMMA were additive. Also we took advantage of the fact that PS absorbs UV light at 254 nm while PMMA does not. Thus, through a series of GPC chromatogram area vs. polymer concentration calibrations, the PS and PMMA contents in the two conjugate phases were determined. Details of this GPC technique have been reported elsewhere.<sup>5</sup>

## RESULTS AND DISCUSSION

In Figure 1 is shown a typical phase diagram for one of the six combinations. The phase envelope or binodal curve was obtained by joining loci of the conjugate

TABLE I  
Characteristics of Polymer Samples as Given by Suppliers

Polymer	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Code
Polystyrene	37,000	<1.05	PS37K
Polystyrene	100,000	<1.05	PS100K
PMMA	29,000	1.10	PMMA29K
PMMA	180,000	1.10	PMMA180K

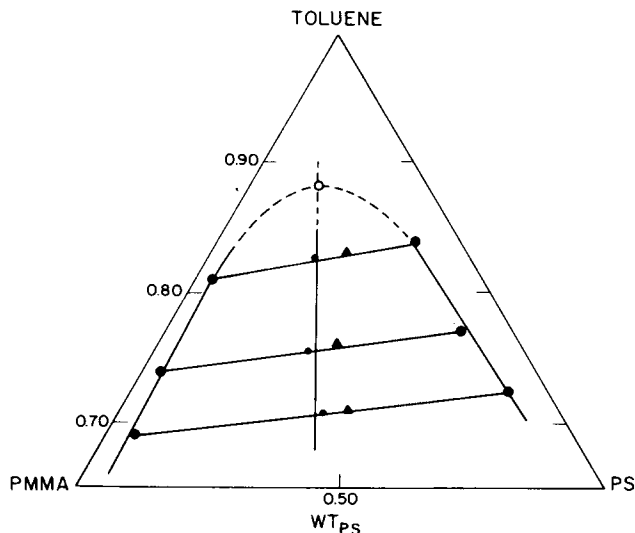


Fig. 1. Phase diagram of the system PS100K-PMMA69K-toluene at 23°C.

phase compositions. The solid triangles represent mix points of the starting PS-PMMA-toluene mixtures. The fact that the mix points lie on the tie lines indicates that the mass balance was satisfied in these systems. To locate the plait point, a combination of interpolation and extrapolation was made. The phase envelope was interpolated toward the solvent apex and a line joining the midpoints of the tie lines was then extrapolated to intersect the phase envelope. This intersection located the plait point.

In Figure 2 are shown all six phase diagrams, omitting the tie lines for the sake of clarity. The one nearest the solvent apex is that of the combination of the highest molecular weights among the six while the one farthest away from the solvent apex is that of the lowest molecular weight combination. In between these two envelopes lie the others, the order of which appears to correspond to the molecular weight of the polymers in the combinations. The higher PS-PMMA miscibility at lower polymer molecular weights is clearly indicated in Figure 2. If it were possible to make a visual extrapolation in this figure, it may be suggested that PS and PMMA become compatible when their molecular weights are very low.

According to the Flory-Huggins theory of polymer solution the change in Gibbs' free energy of mixing in a multicomponent system,  $\Delta G_m$ , can be given<sup>8</sup> as

$$\Delta G_m = RT \left( \sum n_i \ln \phi_i + V \sum \frac{\chi_{ij}}{V_i} \phi_i \phi_j \right) \quad (1)$$

where  $n_i$  is the number of moles of  $i$ th component,  $\phi_i$  its volume fraction,  $V_i$  its molar volume,  $V = \sum n_i V_i$  the total volume of the system, and  $\chi_{ij}$  the interaction parameter which characterizes intermolecular interaction.  $\chi_{ij}$  values for our PS-PMMA-toluene systems have been calculated and will be reported in detail in a separate communication. In this paper we examine the values of the PS(2)-PMMA(3) interaction parameter at the plait points,  $\chi_{23c}$ , of the phase envelopes in Figure 2.

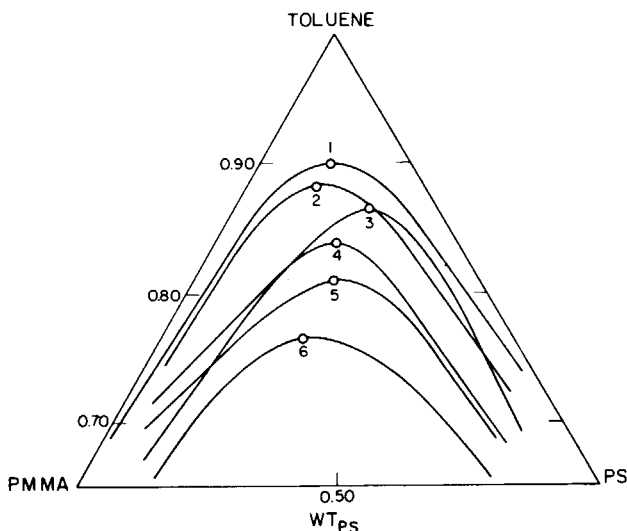


Fig. 2. Phase diagrams showing plait points of the systems: (1) PS100K-PMMA180K-toluene; (2) PS100K-PMMA69K-toluene; (3) PS37K-PMMA180K-toluene; (4) PS37K-PMMA69K-toluene; (5) PS100K-PMMA29K-toluene; (6) PS37K-PMMA29K-toluene; all at 23°C.

To calculate  $\chi_{23c}$  we use the equation by Scott<sup>9</sup>

$$\chi_{23c} = \frac{1}{2}(m_2^{-0.5} + m_3^{-0.5})^2(1 - \phi_1)^{-1} \quad (2)$$

where  $m_2$  and  $m_3$  are the ratios of the molar volumes of PS and PMMA to the molar volume of solvent, respectively, and  $\phi_1$  is the volume fraction of toluene, all taken at the plait point. Table II summarizes the concentrations and polymer-polymer interaction parameters of the systems at their plait points.

In order to interpret these values of the polymer-polymer interaction parameter, we can consider the basic and simplest expression of  $\chi_{ij}$ , which is given as<sup>10</sup>

$$\chi_{ij} = (Z\Delta W_{ij})/kT \quad (3)$$

where  $Z$  is a coordination number.  $\Delta W_{ij}$  is the energy change in the formation of an  $ij$  contact at the expense of  $ii$  and  $jj$  contacts according to the following stoichiometric equation:

$$\Delta W_{ij} = W_{ij} - \frac{1}{2}(W_{ii} + W_{jj}) \quad (4)$$

TABLE II  
PS-PMMA Interaction Parameters at the Plait Points,  $\chi_{23c}$

Polymer 2	Polymer 3	Wt % Toluene	Wt % PS	Wt % PMMA	$\chi_{23c}$
PS100K	PMMA180K	90.0	4.6	5.4	0.0235
PS100K	PMMA69K	88.3	4.7	7.0	0.0319
PS100K	PMMA29K	81.0	9.5	9.5	0.0330
PS37K	PMMA180K	86.5	9.0	4.5	0.0297
PS37K	PMMA69K	84.0	8.0	8.0	0.0341
PS37K	PMMA29K	76.5	9.5	14.0	0.0393

and the enthalpy change  $\Delta H_m$  is given as

$$\Delta H_m = Z \Delta W_{ij} n_i \phi_j \quad (5)$$

It has been generally recognized that the enthalpy change  $\Delta H_m$  in mixing polymers in a solvent is very small and the process is generally endothermic. Therefore, interaction parameters in such systems are usually very small and positive. The intermolecular interaction is a very short range effect. The distance through which two particles interact is so small, of the order of 0.4–0.5 nm (4–5 Å), that it can be assumed that there is either an interaction or no interaction at all. Therefore, for two components  $i$  and  $j$  to interact in a given environment at constant temperature  $T$ ,  $\Delta W_{ij}$  is expected to be of a constant small discrete value, so that

$$\chi_{ij} \propto Z \quad (6)$$

In Table II the  $\chi_{23c}$  values appear to increase as the molecular weights of PS and PMMA decrease, indicating higher PS–PMMA interaction when the polymer molecules are smaller. More frequent interactions can be expected of smaller molecules because of their higher mobility in solution and greater geometric accessibility.

The visual observation of Figure 2, which clearly shows the effect of molecular weight on PS–PMMA miscibility and the apparent trend in the increasing values of  $\chi_{23c}$  with decrease in the molecular weight of PS and PMMA, is in accord with the Flory–Huggins theory for binary systems, for which the change in Gibbs' free energy of mixing can be written as<sup>11</sup>

$$\frac{\Delta G_m}{RT} = V \{ \chi_{AB} \phi_A (1 - \phi_A) + (\phi_A \rho_A / M_A) \ln \phi_A + (\phi_B \rho_B / M_B) \ln (1 - \phi_B) \} \quad (7)$$

Equation (7) predicts that the tendency for components A and B to become miscible is inversely proportional to the molecular weights of the components,  $M_A$  and  $M_B$ .

A rough comparison can be made of the polymer–polymer interaction parameter at the plait point for the polystyrene and poly(methyl methacrylate) reported in this study with those obtained for these polymers with other solvents. In the case of our earlier work<sup>3</sup> of polystyrene of narrow molecular weight distribution with fractionated commercial poly(methyl methacrylate), the interaction parameter in the present study is of the same order of magnitude, but lower by a factor of 2. In the case of the work of Vshivkov and Komolova<sup>4</sup> with a polystyrene of  $\bar{M}_w$   $3.3 \times 10^6$  and a poly(methyl methacrylate) of  $\bar{M}_w$   $5 \times 10^4$  in ethyl acetate, the interaction parameter in the present study is of the same order of magnitude, but higher by about 40%.

## CONCLUSIONS

We have experimentally obtained binodal curves, tie lines and plait points for six different combinations of polystyrene and poly(methyl methacrylate) in toluene. Plait points were obtained by a combination of interpolation and extrapolation of the experimental data. The plait point depended on the molecular weights of the polymers, with the polymers of highest molecular weight having a plait point of lowest total polymer composition. The polymer–polymer

interaction parameter at the plait point ranged from 0.0235 for the highest molecular weight polymers to 0.0393 for the lowest molecular weight combination. This increase in polymer-polymer interaction parameter with decreasing molecular weight is attributed to an increased number of polymer-polymer contacts occurring in solution due to the higher mobility and greater accessibility of the lower molecular weight polymers.

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