Molecular Weights and Molecular Weight Distribution in Phase Equilibria of the Polystyrene-Poly(methyl methacrylate)-Toluene System

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Synopsis

The composite gel permeation chromatography (GPC) chromatogram of a mixture of polystyrene and poly(methyl methacrylate) has been successfully resolved into its component chromatograms by using a newly developed technique. This technique has made possible the calculation of $\overline{M}_w$ and $\overline{M}_n$ values of these polymers in the conjugate phases of the ternary systems with toluene as the solvent. Calculated $\overline{M}_w$ and $\overline{M}_n$ values of the two polymers indicated that the larger polystyrene molecules tend to stay in the top polystyrene-rich phase while its smaller molecules tend to stay in the bottom phase to interact with the other polymer. The reverse is true with the poly(methyl methacrylate) molecules. This tendency strongly suggests that interactions among the two polymers were accomplished mainly by their smaller molecules.

INTRODUCTION

In the study of phase equilibria of polymer-polymer-solvent systems much attention has been paid to the evaluation of the Flory-Huggins solvent-polymer and polymer-polymer interaction parameters and their interpretation. It is known that values of these interaction parameters are dependent on the size and concentration of the macromolecules involved.[1,2] A knowledge of the molecular weights of the polymers in the phases at equilibrium and the distribution of these macromolecules in the respective phases would be valuable and lead to a better understanding of how macromolecules interact in solution. Recently we reported[2,3] our study on the compatibility of polystyrene (PS) and poly(methyl methacrylate) (PMMA) of various molecular weights in toluene, concerning mainly the evaluation and interpretation of their interaction parameters. In this article we report the molecular weights and molecular weight distributions of PS and PMMA in the phase equilibria of this ternary system.

METHOD OF ANALYSIS

Compositions of the ternary system in the two liquid phases at equilibrium with each other were determined by the use of gel permeation chromatography (GPC). Details of this GPC method have been described elsewhere.[2,4] In essence, portions of known weight from each liquid phase were with-
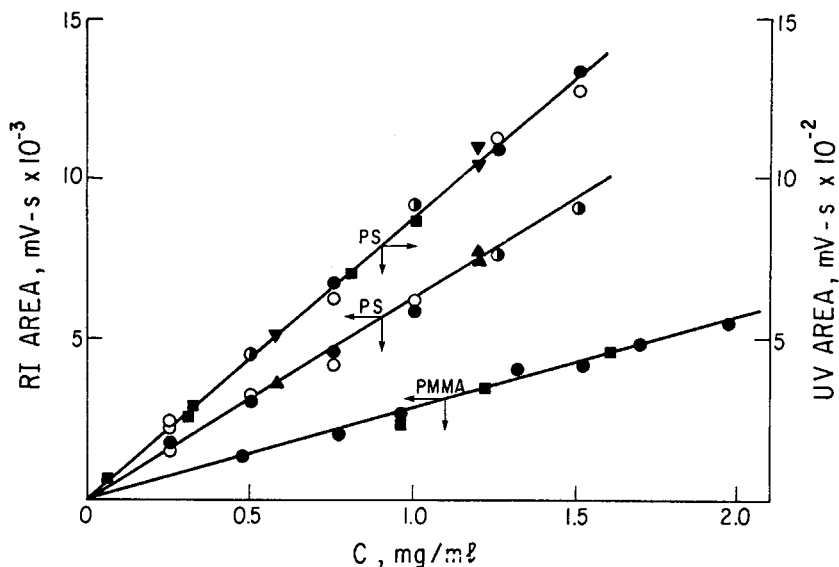
Fig. 1. GPC calibration curves using PS and PMMA standards. (■) Results from known PS and PMMA mixtures.

drawn with hyperdermic syringes and diluted in standard flasks with te-trahydrofuran, the carrier solvent in our Waters 200 GPC unit. This GPC unit was equipped with a refractive index (RI) detector and an ultraviolet (UV) detector in series and was interfaced to an Apple II microcomputer system.[5] Contents of the two polymers in the diluted solution were determined by GPC and the toluene content was determined by difference.

The area under a RI or an UV chromatogram was found to be proportional to the concentration of the polymer. As long as the two polymers $P2$ and $P3$ possess different refractive indices and different extinction coefficients for UV light at a given wavelength, the following chromatogram area vs. polymer concentration C relations hold

$$(Area)_{RI} = (Area)_{P2,RI} + (Area)_{P3,RI} \qquad (1)$$

$$= \epsilon_{P2,RI} \, C_{P2} + \epsilon_{P3,RI} \, C_{P3}$$

$$(Area)_{UV} = \epsilon_{P2,UV} \, C_{P2} + \epsilon_{P2,UV} \, C_{P3} \qquad (2)$$

where the ϵs are extinction coefficients obtainable from the slopes of the straight lines of chromatogram area vs. polymer concentration calibration curves (see Fig. 1). In our system the UV detector was set at 254 nm. Since PMMA does not absorb UV light at this wavelength, in a mixture of PS and PMMA the concentration of PS was directly determinable from its UV calibration curve, and the concentration of PMMA could be determined by subtracting the PS area equivalent from the total RI area. In our GPC-Apple II system each elution count takes 5 min and within this period 30 data points in millivolts were collected at equal intervals and stored in the
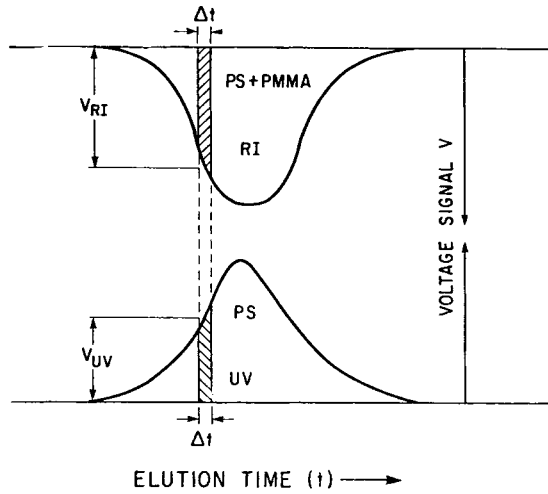
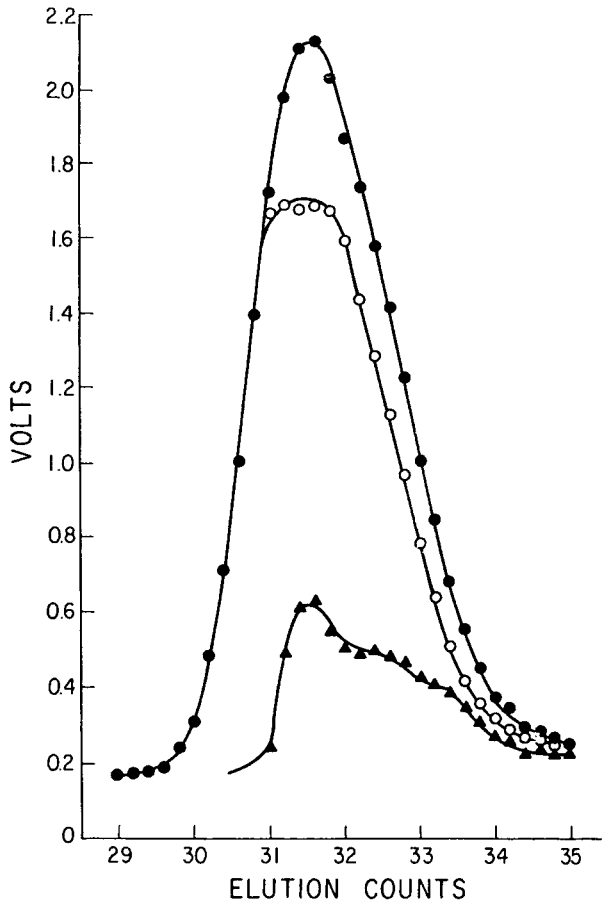Fig. 2. Schematic GPC chromatograms from RI and UV detectors.

Fig. 3.   Composite GPC chromatogram of PS and PMMA mixture and its resolved component chromatograms of PS and PMMA in the top phase in equilibrium with the bottom phase shown in Figure 4. (●) PMMA + PS in top phase, tie line (A), Table II; (○) PS; (▲) PMMA.

microcomputer. The area under the chromatogram was integrated by the computer. Figure 2 shows schematically the RI and UV chromatograms of a mixture of PS and PMMA.

Consider one very narrow slice in the RI and UV chromatograms at the same fraction of elution time Δt in Figure 2. When Δt is made small enough, it can be written that

$$(\text{Area})_{\text{UV}} = V_{\text{PS,UV}} \Delta t = \epsilon_{\text{PS,UV}} C_{\text{PS}}$$

$$\therefore C_{\text{PS}} = \frac{V_{\text{PS,UV}} \Delta t}{\epsilon_{\text{PS,UV}}} \tag{3}$$

$$(\text{Area})_{\text{RI}} = V_{\text{RI}} \Delta t = \epsilon_{\text{PS,RI}} C_{\text{PS}} + V_{\text{PMMA,RI}} \Delta t$$

$$= \frac{\epsilon_{\text{PS,RI}}}{\epsilon_{\text{PS,UV}}} V_{\text{PS,UV}} \Delta t + V_{\text{PMMA,RI}} \Delta t$$

$$\therefore V_{\text{PMMA,RI}} = V_{\text{RI}} - \frac{\epsilon_{\text{PS,RI}}}{\epsilon_{\text{PS,UV}}} V_{\text{PS,UV}} \tag{4}$$

All quantities on the right-hand side of eq. (4) are known so that the voltage signal due to the presence of PMMA in the mixture can be calculated when the attenuations for the RI and UV detectors are properly incorporated into the equation. Each V_{RI} value can now be resolved into its PS and PMMA component parts so that the total RI chromatogram of a PS and PMMA mixture can now be resolved back into its component PS and PMMA chromatograms.

RESULTS AND DISCUSSION

Figures 3 and 4 show two typical chromatograms and their PS and PMMA parts in the liquid conjugate phases. The top phase, Figure 3, contained mostly PS while the bottom phase, Figure 4, contained mostly PMMA. In all samples studied PS tends to accumulate in the top phase and PMMA in the bottom phase. With the help of molecular weight vs. elution volume calibration curves of PS and PMMA standards in our GPC system, $\overline{M}_w$, $\overline{M}_n$, and thus $\overline{M}_w/\overline{M}_n$ values of the respective polymers in the two phases can be calculated; that is to say the distribution of polymer species in the conjugate phases can now be determined.

We used two polystyrene standards from Pressure Chemical Company, two PMMA standards from Polymer Laboratory, Incorporated, and an industrial grade PMMA. Characteristics of these polymers are shown in Table I. The following six combinations were made: PS100K+PMMA180K+toluene, PS100K+PMMA69K+toluene, PS100K+PMMA29K+toluene,
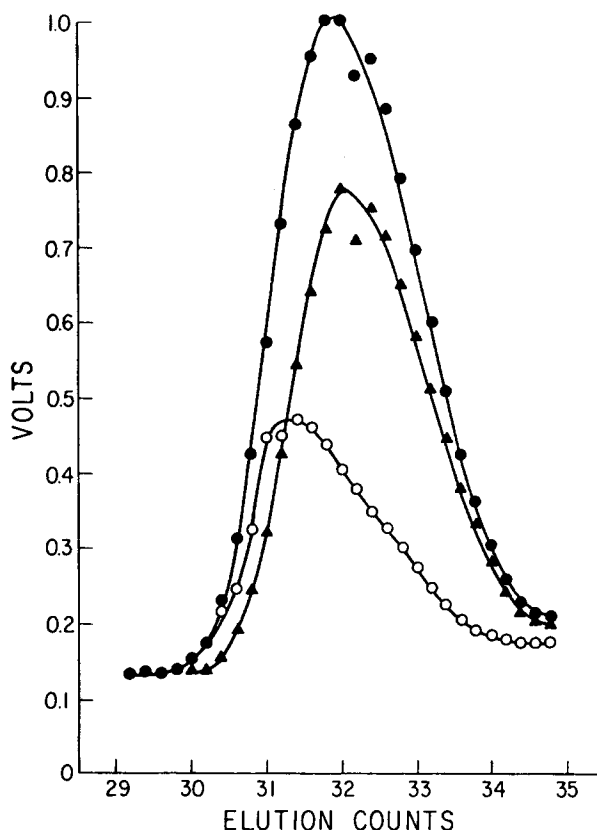
Fig. 4. Composite GPC chromatogram of PS and PMMA mixture and its resolved component chromatograms of PS and PMMA in the bottom phase in equilibrium with the top phase shown in Figure 3. Symbols same as in Figure 3.

PS37K+PMMA180K+toluene, PS37K+PMMA69K+toluene, and PS37K+PMMA29K+toluene. Compositions of the conjugate phases were analyzed by the use of GPC and molecular weight distributions of the polymers in them by the method detailed above.

TABLE I
Characteristics of Polymer Samples

| | Given by supplier | | Measured by our GPC | | |
	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	Code
Polystyrene	37,000	<1.05	35,220	1.29	PS37K
Polystyrene	100,000	<1.05	86,792	1.43	PS100K
PMMA	29,000	1.10	27,013	1.16	PMMA2-9K
PMMA	180,000	1.10	150,798	1.68	PMMA18-0K
PMMA (Industrial grade)	—	—	69,850	2.00	PMMA6-9K

TABLE II
Molecular Weight of Polystyrene in Conjugate Phases

	Top Phase (TP)		Bottom Phase (BP)		
Tie line	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$(\overline{M}_w)$ TP/$(\overline{M}_w)$BP
	System PS37K + PMMA29K + toluene				
1	27,339	13,968	27,797	22,187	0.98
2(C)	34,120	19,198	28,434	19,285	1.20
3(B)	28,223	13,858	27,763	19,563	1.02
4(A)	28,920	17,769	28,523	20,088	1.01
	System PS37K + PMMA69K + toluene				
1	32,798	22,015	22,719	20,147	1.44
2	34,454	16,612	27,040	19,985	1.27
3(D)	31,406	21,368	25,830	16,176	1.22
	System PS37K + PMMA180KI + toluene				
1(E)	33,276	22,142	24,994	15,927	1.33
2	27,600	13,210	22,381	14,415	1.23
3	28,160	13,959	21,687	15,735	1.30
4	26,387	13,677	14,193	11,131	1.86
	System PS100K + PMMA29K + toluene				
1	74,434	46,785	56,803	32,300	1.31
2	72,348	43,515	50,330	29,805	1.44
3	69,620	35,300	61,411	30,913	1.13
	System PS100K + PMMA69K + toluene				
1	73,790	57,651	65,848	42,600	1.12
2(G)	71,667	33,552	61,308	54,424	1.17
3(F)	77,638	57,006	61,675	45,705	1.26
	System PS100K + PMMA180K + toluene				
1	72,860	56,862	63,053	56,868	1.16
2	72,666	54,059	65,326	56,406	1.11
3	70,844	61,640	59,337	50,120	1.19
4	71,076	60,905	59,646	48,657	1.19
5	75,373	59,890	59,102	45,539	1.28

DISTRIBUTION OF PS MOLECULES IN THE CONJUGATE PHASES

In our study PS was directly detected by a UV detector; hence its $\overline{M}_w$ and $\overline{M}_n$ can be calculated from its UV chromatograms. $\overline{M}_w$ and $\overline{M}_n$ values in Tables II and III were calculated from GPC chromatograms to which a Chang-Huang correction[6] had been applied. In order to cut down computer time for this correction calculation, five data points per elution count along the chromatogram curve were used. Table II shows the corrected $\overline{M}_w$ and $\overline{M}_n$ values of all samples examined in this study. It can be noted that when the molecular weights of PS are low, as in the PS37K + PMMA29K + toluene combination, the molecular weights of PS in the top phase do not appear to be significantly different from those in the bottom phase. However, when the molecular weights of the starting PS were increased, the molecular weights of PS in the top phase (TP) and those in the bottom phase (BP) show a difference, as indicated by their $(\overline{M}_w)$TP/$(\overline{M}_w)$BP ratios, which appears to show an overall trend that when the starting PS contains some very large molecules, the large PS molecules tend to accumulate in the top phase where PS concentration is high, and smaller PS molecules

TABLE III
Molecular Weight of PMMA in Conjugate Phases

Tie line[a]	Top Phase (TP)		Bottom Phase (BP)		$(\overline{M}_w)$BP/$(\overline{M}_w)$TP
	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	
(A)	28,954	23,260	24,511	20,040	0.85
(B)	32,786	27,162	25,750	20,028	0.79
(C)	39,868	32,805	24,685	18,419	0.62
(D)	45,970	23,852	83,085	34,474	1.81
(E)	36,739	34,827	152,295	98,085	4.15
(F)	75,661	50,796	82,216	38,280	1.09
(G)	84,125	63,560	102,745	63,849	1.22

[a] Same tie lines as in Table II.

tend to stay in the bottom phase where PMMA concentration is high. This observation suggests that there is a tendency of the smaller PS molecules to move across the interface to interact with PMMA molecules in the bottom phase.

DISTRIBUTION OF PMMA MOLECULES IN THE CONJUGATE PHASES

The RI extinction coefficient of PMMA was much smaller than that of PS (see Fig. 1). To preserve a high accuracy in the calculated results only those phases in which PMMA accounts for over 10% of the RI area were treated for $\overline{M}_w$ and $\overline{M}_n$ evaluation. This degree of accuracy was checked by a close agreement of the resolved PMMA area/PS area ratio with that calculated by the microcomputer using 30 data points per elution count in both the RI and UV chromatograms. As a result of these constraints only 22 phase samples were so treated. Fourteen of them were conjugated phases joined by tie lines A, B, C, D, E, F, and G in Tables II and III.

In Table III tie lines D, E, F, and G indicate that PMMA molecules show a similar trend as noted in Table II, i.e., larger PMMA molecules tend to stay in the bottom phase and smaller PMMA molecules tend to stay in the top phase to interact with PS molecules. Tie lines A, B, and C in the same low molecular weight combination, however, appear to behave otherwise. When a null hypothesis that the $(\overline{M}_w)$TP/$(\overline{M}_w)$BP ratios in Table II together with the $(\overline{M}_w)$BP/$(\overline{M}_w)$TP ratios in Table III are in fact not significantly different from unity is tested statistically, this null hypothesis must be rejected and the alternative that these ratios are larger than unity must be accepted. Acceptance of this alternative hypothesis lends support to the inference that the smaller molecules of one polymer show a stronger tendency to interact with molecules of the other polymer.

We had pointed out in an earlier article[2] that our experimental results indicated that the compatibility between PS and PMMA tends to increase as their molecular weights decrease. In the same communication we reported calculated PS-PMMA interaction parameters at the plait points, χ_{23C}, which appear to show a trend of increasing in value as the molecular weights of PS and PMMA decrease. We attributed this trend to be a result of stronger

interaction with smaller polymer molecules in a mixture. This interpretation of the χ_{23C} values appears to agree well with data presented in Tables II and III.

CONCLUSION

The composite GPC chromatogram of a mixture of polystyrene and poly(methyl methacrylate) has been successfully resolved into its component chromatograms by using a newly developed technique. This technique has made possible the calculation of $\overline{M}_w$ and $\overline{M}_n$ values of PS and PMMA in the conjugate phases of PS-PMMA-toluene systems. Calculated molecular weights of the polymers in the conjugate phases indicate that the larger PS molecules tend to stay in the top phase while smaller PS molecules show an affinity to interact with PMMA molecules in the bottom phase. The reverse is also true with PMMA molecules. Such an observation strongly suggests that interaction and hence the partial miscibility between PS and PMMA molecules in this PS-PMMA-toluene system are accomplished mainly by their smaller molecules.

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