

Reexamination of Cloud Point Isotherms for the System Polystyrene/Polybutadiene/Tetralin

Bimodal cloud point isotherms had been found in our laboratory for the ternary system polystyrene (PS)/polybutadiene (PBD)/tetrahydronaphthalene (tetralin) when the polymers were of narrow molecular weight distribution.^{1,2} Further studies were made on this system because the unexpected bimodality suggested an unusual behavior of the anticipated tie lines in this region and because the method of determining the composition of the heterogeneous system was thought to be a source of experimental error in the observations.

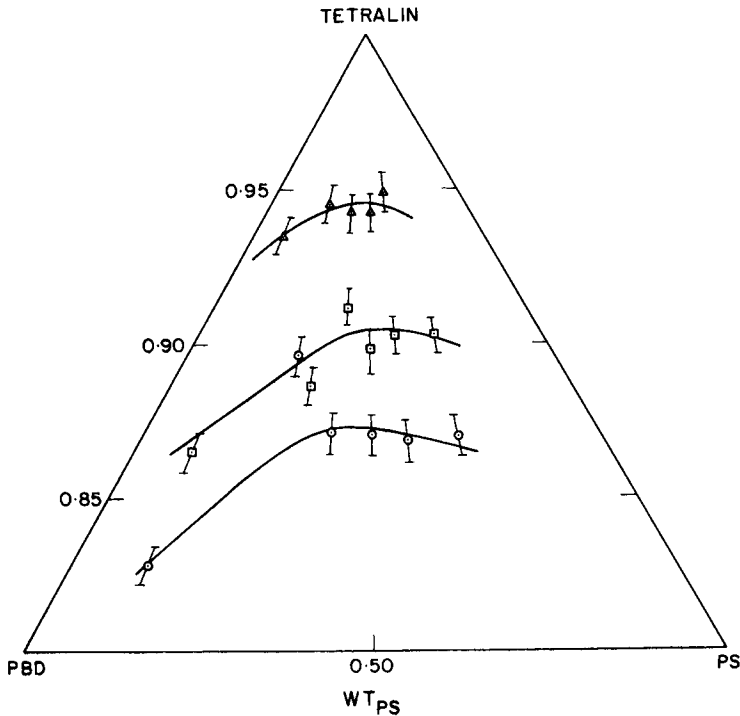


Fig. 1. Cloud point isotherms for different molecular weights of polystyrene, with polybutadiene of \bar{M}_w 170,000, $T = 29^\circ\text{C}$ (revised from ref. 2): (Δ) PS4-PBD2; (\square) PS2-PBD2; (\circ) PS1-PBD2.

TABLE I
Characteristics of Polystyrene Samples

Sample	Supplier's data ^a			Experimental data		
	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n
PS1	$20.8 \pm .8$	$20.2 \pm .8$	<1.06	—	—	—
PS2	36.0	33.0	<1.06	36.6	33.7	1.09
PS4	111.0	111.0	<1.06	123.6	107.8	1.15

^a Data for samples supplied by Pressure Chemical Co.

TABLE II
Characteristics of Polybutadiene Samples

Sample	Supplier's data ^a			Experimental data		
	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n
PBD1 ^b	17.0 ± 1.7	16.0 ± 1.6	1.06	—	—	—
PBD2 ^c	170.0 ± 17	135.0 ± 13.5	1.26	161.3	119.5	1.35

^a Data supplied by Phillips Petroleum.

^b 43.5% Cis, 49.1% trans, 7.4% vinyl; 0.4% 2,6-di-*tert*-butyl-4-methylphenol antioxidant.

^c 47.1% Cis, 44.5% trans, 8.4% vinyl; 0.4% 2,6-di-*tert*-butyl-4-methylphenol antioxidant.

EXPERIMENTAL

As an alternative to our method of sampling of the heterogeneous mixture to determine the weight percent concentrations of the total polymer in the ternary system,² known weights of the two polymers were mixed in a known weight of tetralin in the two-phase region of the diagram based on our previous findings. The cloud points were then determined from the amounts of tetralin added to bring about clarity. When these cloud points were found to occur at lower total polymer concentration and the bimodality had been diminished appreciably, the two methods were examined more closely.

The original method used was the addition of a known weight of the polystyrene and polybutadiene to the solvent tetralin and, if necessary, the evaporation of solvent until the mixture became turbid. A portion of the sample was titrated in a Spectronic 20 colorimeter with its cell thermostatically controlled at 29°C. The remaining portion of the turbid mixture was weighed, dried in a vacuum oven at 80°C and 29 in. Hg to "complete dryness" (defined to be a rate of weight loss of less than 0.002 g/h for an initial sample weight of about 1.4 g), and weighed again, and the composition of the initial turbid mixture was calculated by difference. By then adding to this composition the amount of tetralin employed in the titration, the composition at the cloud point was calculated. The method of drying to determine the amount of solids had been used in phase studies of a multicomponent system by Dobry and Boyer-Kawenoki as early as 1947 and by others more recently.³

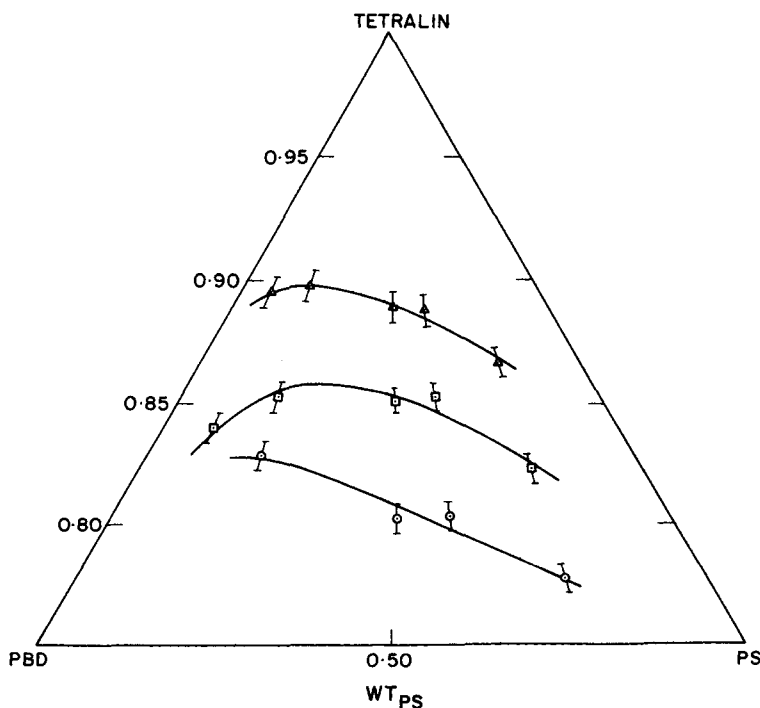


Fig. 2. Cloud point isotherms for different molecular weights of polystyrene with polybutadiene of \bar{M}_w 17,000, $T = 29^\circ\text{C}$ (revised from ref. 2): (Δ) PS4-PBD1; (\square) PS2-PBD1; (\circ) PS1-PBD1.

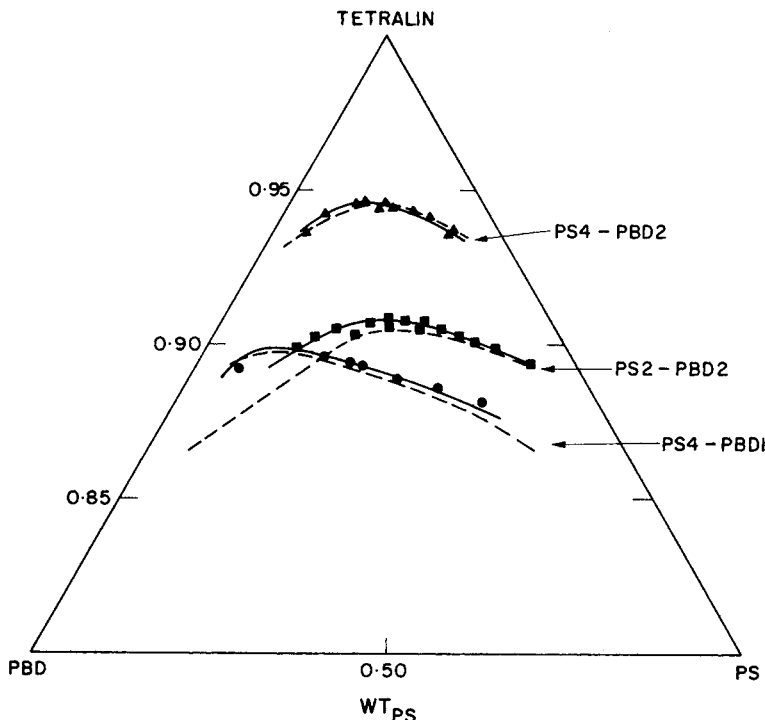


Fig. 3. Comparison of present results with revised results from literature,² $T = 29^{\circ}\text{C}$. Solid symbols and solid lines represent results of the present study. Broken lines represent revised results of reference 2, taken from Figures 1 and 2.

In order to compare the compositions determined by the two methods, a detailed study of the drying was carried out.⁴ Using a variety of polystyrene and polybutadiene samples (see Tables I and II) in tetralin, with samples of 2.4 g, and redefining complete dryness as a rate of weight loss of less than 0.0002 g/hr, it was found that the concentration of solvent calculated by our original method differed from the actual composition by values in the range of +0.897% to -1.725% tetralin, with a standard deviation of 0.654% tetralin. This experimental error was found to be systematic rather than random. In addition, the error is not constant but varies with the molecular weights and molecular weight distribution of the polymers as well as the composition, being greatest in the region of weight of polystyrene/weight of total polymer of 0.50–0.65 (i.e., $0.50 \leq \text{WT}_{\text{PS}} \leq 0.65$), that is, the region of bimodality.

The error in the turbidimetric titration itself was found to be much less, with a deviation of $\pm 0.135\%$ tetralin.

RESULTS

When the original data are corrected according to these new drying curves, the resulting cloud points are as shown in Figures 1 and 2, where the size of the symbol employed reflects the random error in the turbidimetric determination of the concentration of the cloud point, while the strokes represent the 90% confidence limits from the drying studies, and WT_{SOL} represents the weight of solvent/total weight of the system. Through these corrected data have been drawn revised cloud point isotherms.

Studies recently completed using the improved technique of fixing the total polymer composition directly yield the same general shape of the cloud point isotherms as the original curves corrected for the drying error, as can be seen in Figure 3. Any dip or valley is now within experimental error, contrary to the results published previously in references 1 and 2.

The improved technique, then, eliminates any possible errors in drying. It is limited in its applicability, however, by the necessity for some prior knowledge of the approximate location of the cloud point curve. The earlier evaporation technique, on the other hand, must be used with caution, especially with solvents of low volatility.

References

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