

The Effect of Molecular Weight and Temperature on Phase Separation in the Ternary System Polystyrene/Polybutadiene/Tetralin

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Synopsis

The phase diagram and cloud point surface for the ternary system polystyrene/polybutadiene/tetralin were determined at 29°, 87°, and 143°C. Polystyrenes and polybutadienes of narrow molecular weight distribution were used to study the effect of molecular weight on the cloud point concentration. The phase diagram obtained was bimodal. This unusual shape was more pronounced at higher molecular weights. A model describing the molecular weight dependence of the cloud point concentration was tested and found to hold over a wide composition and temperature range.

INTRODUCTION

Previous work by the authors¹ on phase separation in the system polystyrene/polybutadiene/tetralin (tetrahydronaphthalene) showed a unique bimodal solubility (cloud point) isotherm using narrow molecular weight distribution (MWD) polymers. The usual unimodal shape was obtained using similar polymers of broad MWD.

An explanation for the bimodal shape of the cloud point isotherm is still lacking, although Koningsveld² has observed a similar shape in the system polyethylene/polypropylene/diphenyl ether of unreported MWD, but only at elevated temperatures and in the vicinity of the maximum of the cloud point surface.

Our studies of polystyrene/polybutadiene/tetralin have now been extended to examine the effect of molecular weight and temperature in order to gain further information on this phase separation.

EXPERIMENTAL

A modified spectrophotometric technique³ was used in a turbidimetric titration to obtain the incipient cloud point under isothermal conditions. A high-temperature cell jacket was designed for use in an Arthur H. Thomas thermostated cell assembly in the spectrophotometer (Bausch and Lomb, Model 20). Titrant was added with a microsyringe. Temperature, using a thermocouple probe, and absorbance at 520 m μ were recorded simulta-

TABLE I
 Characterization Data^a of Polymers of Narrow Molecular Weight Distribution

	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
PS	10,000	9,600	≤ 1.10
PS	20,400	20,200	≤ 1.06
PS	37,000	36,000	≤ 1.06
PS	111,000	111,000	≤ 1.06
PBD ^b	17,000	16,000	1.06
PBD ^c	170,000	135,000	1.26

^a Provided by Pressure Chemical Co. and Phillips Petroleum, Special Products Division; PS = polystyrene; PBD = polybutadiene.

^b 43.5% Cis, 49.1% trans, 7.4% vinyl; contains approximately 0.4% Ionol antioxidant.

^c 47.1% Cis, 44.5% trans, 8.4% vinyl; contains approximately 0.4% Ionol antioxidant.

neously on a dual-channel recorder. Mechanical mixing was provided with a low-speed stirrer immersed in the solution. Preliminary study had shown the losses of the tetralin solvent due to evaporation to be negligible over the temperatures and time intervals studied.

Narrow MWD polystyrene and polybutadiene were purchased from Pressure Chemical Co. and Phillips Petroleum Co., respectively. Characterization data are given in Table I as supplied by the manufacturer.

Arbitrary but convenient weight fractions of the polymers in solutions were prepared. The solvent was evaporated from the solutions until they were turbid. The turbid mixtures were put in the spectrophotometer and were titrated isothermally with tetralin. The incipient cloud point composition was determined from the spectrophotometric data by the usual method.³

Possible oxidative degradation, especially at the higher temperatures, was shown to be negligible by intrinsic viscosity measurements on the polymers before and after the experiments.

RESULTS

The weight-average molecular weights of the polymers were used to correlate the molecular weight dependence since a better correlation had been found with the weight average in our earlier studies. The solubility (cloud point) isotherm as a function of composition for different molecular weights of polystyrene at a fixed molecular weight of polybutadiene is shown in Figure 1. The solubility is seen to increase with decreasing molecular weight as expected. The bimodal shape is less pronounced with a lower molecular weight of polystyrene. This trend is also evident in Figure 2, which examines the same effects with a polybutadiene of lower molecular weight. With low molecular weight polymers, the conformational restriction in solution would be reduced and interactive effects reduced. If the bimodal effect were strictly a reflection of molecular weight, then with

reduced chain length the effect should decrease or disappear. The presence of the effect still exists at the lower molecular weights.

When the solubility at the two molecular weights of polybutadiene was plotted at constant molecular weights of polystyrene (Figs. 3, 4, and 5), it

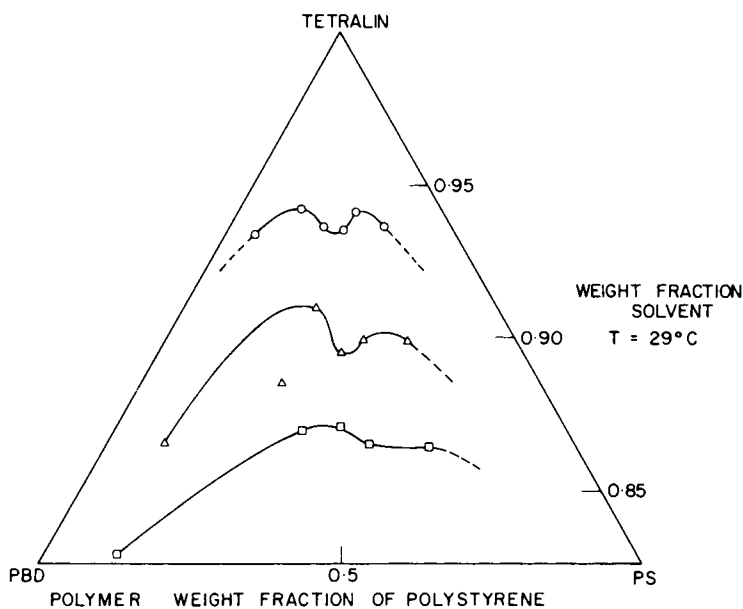


Fig. 1. Cloud point isotherms as a function of molecular weight of polystyrene at constant molecular weight (170,000) of polybutadiene. Polystyrene: (○) 110,000; (Δ) 37,000; (□) 20,400.

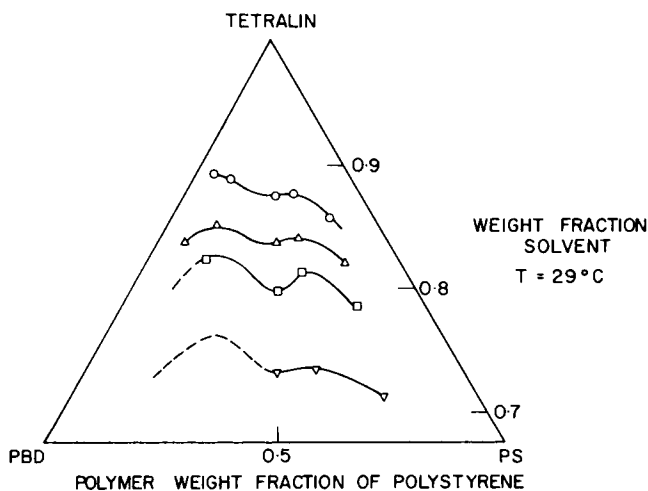


Fig. 2. Cloud point isotherms as a function of molecular weight of polystyrene at constant molecular weight (17,000) of polybutadiene. Polystyrene: (○) 110,000; (Δ) 37,000; (□) 20,400; (▽) 10,000.

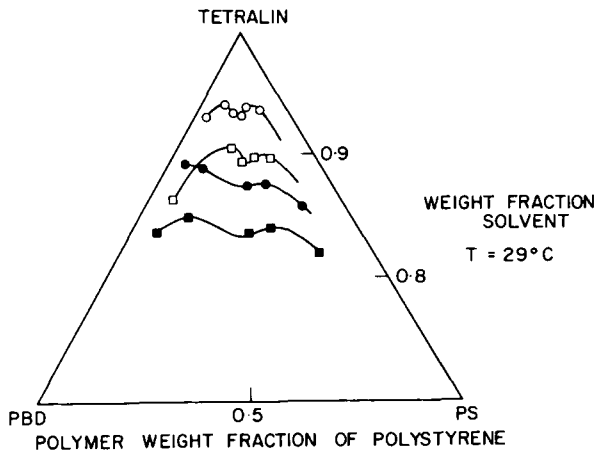


Fig. 3. Cloud point isotherms as a function of molecular weight of polybutadiene at constant molecular weight of polystyrene. Polystyrene: (O) 110,000; (□) 37,000. Solid points, polybutadiene 17,000; open points, polybutadiene 170,000.

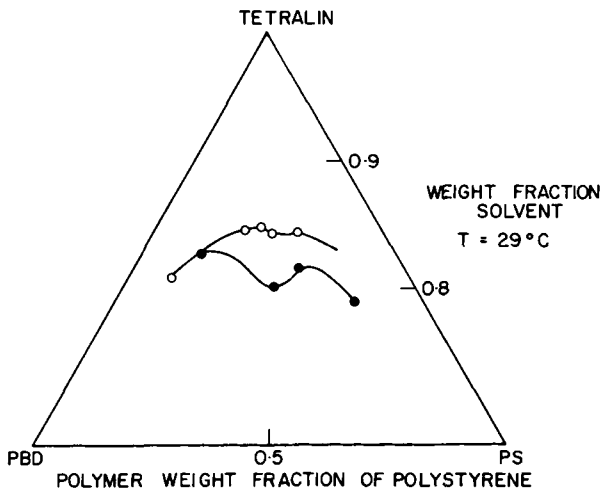


Fig. 4. Cloud point isotherms as a function of molecular weight of polybutadiene at constant molecular weight (20,400) of polystyrene. Polybutadiene: (O) 170,000; (●) 17,000.

appeared that the polybutadiene controlled the shape of the cloud point isotherm more strongly than did the polystyrene component. The local minimum in the curve (i.e., the local maximum in solubility) also appears to be shifted towards increasing polystyrene compositions as the molecular weight of polybutadiene is lowered.

Figures 6 and 7 show the effect of temperature on the system. Increasing the temperature increases polymer solubility. Increasing the temperature does not drastically affect the shape of the isotherm, but the minimum is shifted in favor of a more polystyrene-rich composition. The cloud point

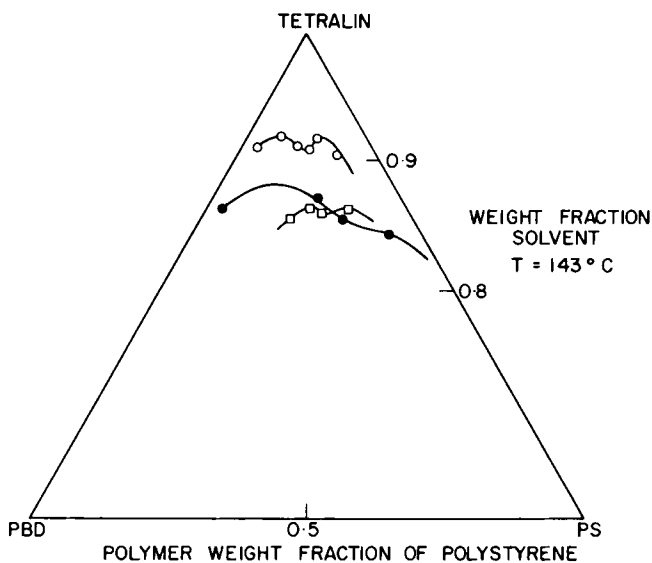


Fig. 5. Cloud point isotherm as a function of molecular weight of polybutadiene at constant molecular weight of polystyrene at 143°C. Polystyrene: (O) 110,000; (\square) 37,000. Solid points, polybutadiene 17,000; open points, polybutadiene 170,000.

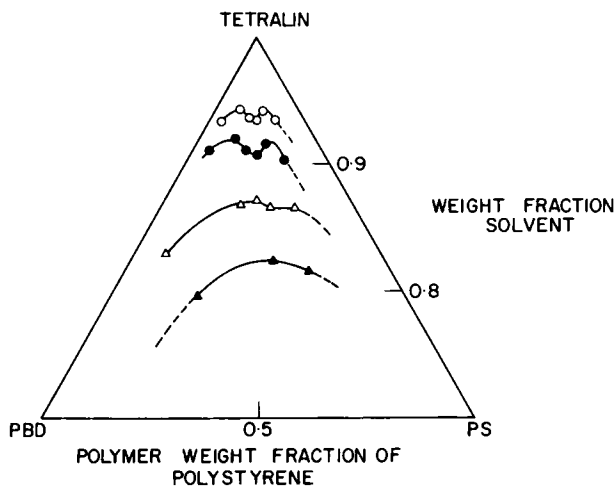


Fig. 6. Cloud point isotherms as a function of temperature for various polystyrene-polybutadiene molecular weight combinations: (O) polystyrene 110,000, polybutadiene 170,000; (Δ) polystyrene 20,400, polybutadiene 170,000. Solid points, $T = 143^\circ\text{C}$; open points, $T = 29^\circ\text{C}$.

surface for the system polystyrene/polybutadiene/tetralin is represented in Figure 8. The occurrence of the trough or furrow in the cloud point surface over the wide temperature range studied indicates its stability. Temperatures much higher than 143°C were not feasible because evaporation losses became significant using our apparatus at atmospheric pressure.

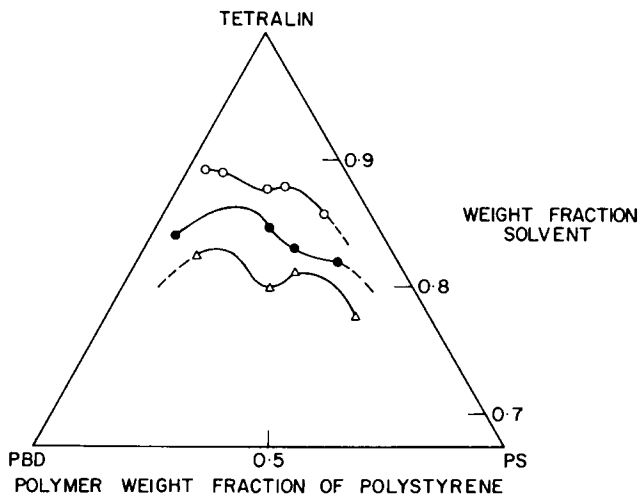


Fig. 7. Cloud point isotherms as a function of temperature for various polystyrene-polybutadiene molecular weight combinations: (○) polystyrene 110,000, polybutadiene 17,000; (△) polystyrene 20,400, polybutadiene 17,000. Solid points, $T = 143^{\circ}\text{C}$, open points, $T = 29^{\circ}\text{C}$.

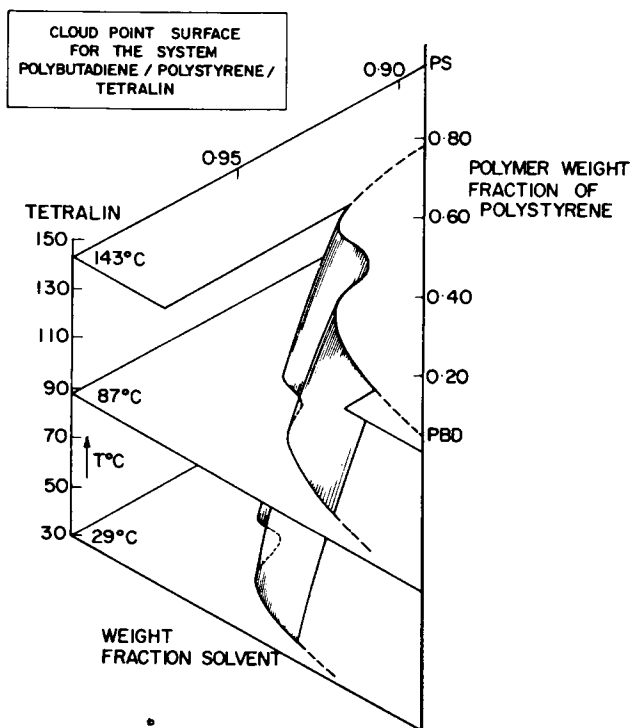


Fig. 8. Cloud point surface for system polybutadiene (170,000), polystyrene (110,000), tetralin.

Experimental techniques become much more difficult at more elevated temperatures, subsequently reducing the accuracy of the data expected and the likelihood of equilibrium existing between the phases.

It was previously mentioned that Koningsveld² had observed a similar dip in the cloud point surface for the system diphenyl ether/polyethylene/atactic polypropylene at elevated temperatures approaching its upper critical solution temperature. However, when the atactic polypropylene was replaced by isotactic polypropylene, the resultant cloud point surface did not exhibit the previous bimodal shape. This result tends to emphasize the effect of geometric structure on the incompatibility of polymers. The polybutadienes used in the present study were approximately 50% *cis* and 50% *trans*. An interesting investigation would be a study of the cloud point surface of the highly *cis* or *trans* form of the polymers.

A tentative explanation of the phenomenon implies two or more interacting forces which balance to give the increased solubility or the minimum in the bimodal cloud point isotherm at a particular composition. It is more pronounced with the high molecular weight polybutadiene/high molecular weight polystyrene combination than with their low molecular weight counterparts. This decreased sharpness at lower molecular weights may be due to the general increased solubility of the lower molecular weight species. The minimum occurs at about 50% (by weight) polymer composition for both low and high molecular weight polybutadiene. There does seem to be a slight shifting of the minimum toward increasing polystyrene composition as the molecular weight of the polystyrene is decreased at constant molecular weight of polybutadiene.

An attempt to correlate the molecular weight dependence of the polymers with the cloud point concentration was made.

An initial treatment by Hong and Burns³ indicated that the effect of molecular weight on polymer incompatibility might be described by the following type of model:

$$\frac{\beta_1}{M_1} + \frac{\beta_2}{M_2} + \gamma = C_p \quad (1)$$

where β_1 , β_2 , and γ are constants characteristic for a particular system, M_1 = weight-average molecular weight of component 1, M_2 = weight-average molecular weight of component 2, and C_p = weight fraction total polymer at the incipient cloud point. (Hong used C_v , where C_v = volume fraction of polymers at the incipient cloud point.)

This model initially stemmed from work done by earlier authors^{4,5} who tried to correlate the effect of molecular weight on incompatibility by intrinsic viscosity. Equation (1) had been tested using the system fractionated polystyrene/poly(methyl methacrylate)/benzene for a fixed 1:1 weight ratio of the two polymers. A reasonable fit was obtained.

This type of treatment was extended to the system under study in order to test the validity of the model for different polymers and solvent and under a wide range of composition and temperature. A nonlinear least-

TABLE II
Parameters for the Cloud Point Equation

Polymer weight fraction of polystyrene	β_1 , mole/g	β_2 , mole/g	γ
$T = 29^\circ\text{C}$			
0.228	1839	863	0.0365
0.5	1419	1293	0.0332
0.607	1612	1097	0.0358
0.685	1633	1130	0.0338
$T = 143^\circ\text{C}$			
0.5	1815	1196	0.0200
0.607	1862	1345	0.0200

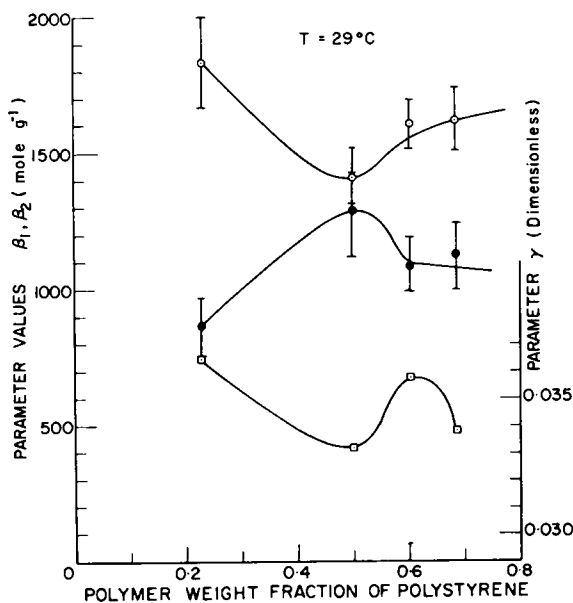


Fig. 9. Parameters for the solubility model $\beta_1/M_1 + \beta_2/M_2 + \gamma = C_p$, obtained from least-squares analysis of data: (O) β_1 ; (●) β_2 ; (□) γ .

squares computer optimization technique was used to analyze the data. Table II summarizes the parameters obtained. The fit of the data was reasonable with the limited points studied.

A plot of the parameters over the composition range studied is made in Figure 9. The parameter for polystyrene (β_1) decreases with increasing composition, reaching a minimum at the same composition that the minimum in the cloud point isotherm was found and then increases. The parameter for polybutadiene is exactly the opposite. It increases with increasing composition, reaching a maximum at the composition of the minimum in the cloud point isotherm. This result indicates the role of

interaction between the polymers. The resultant dip in the cloud point curve could be related to an enhanced influence of the polybutadiene and the decreasing control of polystyrene.

Attempts to predict cloud point concentrations at intermediate compositions using this equation showed deviations of 5% to 20%. The uncertainty could be attributed to the statistical error of the parameters from the least-squares analysis. More data points would be necessary in order to decrease the standard deviation of the fit.

In summary, the proposed model appears to hold over a wide range of molecular weight, composition, and temperature for the new polymer system studied. The model appears to hold well even in the anomalous region of increased solubility. An analysis of the parameters supports the interaction concept of the trough in the cloud point surface. The model also permits a rough calculation of cloud point concentration for interpolated polymer composition.

References

1. D. G. Welygan and C. M. Burns, *Polym. Lett.*, **11**, 339 (1973).
2. R. Koningsveld, H. A. G. Chermin, and M. Gordon, *Proc. Roy. Soc. (London)*, **A319**, 331 (1970).
3. S. D. Hong and C. M. Burns, *J. Appl. Polym. Sci.*, **15**, 1955 (1971).
4. O. Fuchs, *Makromol. Chem.*, **90**, 293 (1966).
5. R. Kuhn, H. J. Cantow, and W. Burchard, *Angew. Makromolek. Chem.*, **2**, 157 (1968).

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