

# Phase Equilibra of Polystyrene/Polybutadiene/ Tetrahydrofuran Using Gel Permeation Chromatography

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## Synopsis

Gel permeation chromatography using sequential differential refractive index and ultraviolet detectors has been successfully used to give the compositional analysis of conjugate phases in the incompatible system of polystyrene and polybutadiene with tetrahydrofuran as solvent. Application of this method to equilibrated samples yields tie lines, binodal curves, and plait points. The effects of molecular weights and molecular weight ratios on the slopes of the tie lines, the location of the binodal curve, and the depletion of second polymers from phases are discussed.

## INTRODUCTION

Phase separation between the two incompatible polymers polystyrene (PS) and polybutadiene (PBD) is of considerable industrial importance and has been studied in both solution<sup>1-8</sup> and the solid state.<sup>9-13</sup> In solution, the binodal equilibrium curve on the triangular diagram has frequently been approximated by cloud point isotherms determined by turbidimetric titration. Rigorous determination of the binodal curve, including tie lines and the plait point, requires lengthy equilibration and subsequent analysis of the conjugate phases. The method of analysis is severely restricted, however, by the necessity of maintaining an antioxidant in the solution to inhibit the crosslinking of the polybutadiene. The antioxidant frequently used, 2,6-di-*tert*-butyl-4-methylphenol, would mask the ultraviolet analysis of a solution of the two polymers.

In order to overcome these problems of analysis, we have used a gel permeation chromatograph (GPC) equipped with both differential refractive index (RI) and ultraviolet (UV) detectors. The sequence of operations is such that the antioxidant is separated from the two polymers by the columns before the polymers enter the detectors. The two detectors provide two pieces of information about the mixed polymers so that the concentration of each polymer can be determined.

The use of GPC for the determination of composition in PS/PBD systems is not new, although it has not been extensively reported in the past.<sup>14-16</sup> Previous studies involving the use of GPC for determining the binodal curves have not led to tie lines and plait points.<sup>16</sup> The novelty of the present approach is that, in addition to the equilibrium binodal curve, it also provides the tie lines and the plait points.

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## EXPERIMENTAL

### Choice of System

The system polystyrene (PS) and polybutadiene (PBD) was selected because of its importance in the areas of thermoplastic elastomers, high-impact polystyrenes, and ABS plastics. In addition, these polymers are the only two polymers commercially available in suitable quantities with narrow molecular weight distributions.

The characteristics of the commercial PS (Pressure Chemical Co.) and PBD (Phillips Petroleum Co.) samples are given in Table I. Included are data both provided by the suppliers and experimentally determined in our laboratory using gel permeation chromatography (Waters 301) plus, in the case of the PBD samples, the Mark-Houwink equation with constants found in the literature.<sup>17,18</sup>

The solvent employed throughout the study, both as the mutual solvent in the ternary system and as the carrier solvent in the GPC, was practical-grade tetrahydrofuran (THF) supplied by Fisher Scientific Co. and distilled prior to use.

### Analysis of Samples

The quantitative analysis of the samples was done on a Waters 200 GPC equipped with an ultraviolet (UV) unit using a monochromatic light of wavelength 254 nm and a differential refractive index (RI) unit using white light. The detectors were positioned in series along the eluant path and their outputs were recorded on a dual-channel Texas Instruments recorder. The GPC was used

TABLE I  
Characteristics of Polymer Samples

| Sample                   | Manufacturer's data <sup>a</sup> |                            |                       | Experimental data          |                            |                       |
|--------------------------|----------------------------------|----------------------------|-----------------------|----------------------------|----------------------------|-----------------------|
|                          | $\bar{M}_w \times 10^{-3}$       | $\bar{M}_n \times 10^{-3}$ | $\bar{M}_w/\bar{M}_n$ | $\bar{M}_w \times 10^{-3}$ | $\bar{M}_n \times 10^{-3}$ | $\bar{M}_w/\bar{M}_n$ |
| PS 9,000                 | 9.18                             | 9.17                       | <1.06                 | —                          | —                          | —                     |
| PS 37,000                | 36.0                             | 33.0                       | <1.06                 | 36.6                       | 33.7                       | 1.09                  |
| PS 110,000               | 110.0                            | 110.0                      | <1.06                 | 123.6                      | 107.8                      | 1.15                  |
| PBD 17,000 <sup>b</sup>  | 17.0 ± 1.7                       | 16.0 ± 1.6                 | 1.06                  | —                          | —                          | —                     |
| PBD 170,000 <sup>c</sup> | 170.0 ± 17                       | 135.0 ± 13                 | 1.26                  | 161.3                      | 119.5                      | 1.35                  |

<sup>a</sup> Manufacturer's data supplied by Pressure Chemical Co. (PS samples) and Phillips Petroleum Co. (PBD samples).

<sup>b</sup> 43.5% cis, 49.1% trans, 7.4% vinyl, 0.04% antioxidant.

<sup>c</sup> 47.1% cis, 44.5% trans, 8.4% vinyl, 0.04% antioxidant.

TABLE II  
Extinction Coefficients<sup>a</sup> from the GPC Calibrations

| Polymer     | Ultraviolet | Refractive index |
|-------------|-------------|------------------|
| PS 110,000  | 4.50        | 3.16             |
| PS 37,000   | 4.55        | 3.19             |
| PS 9,000    | 4.55        | 3.17             |
| PBD 170,000 | —           | 2.30             |
| PBD 17,000  | —           | 2.30             |

<sup>a</sup> Units are in<sup>2</sup> ml/mg.

with four columns containing Styragel packing of the following size designations: 2000–5000 Å, 15,000–50,000 Å, 150,000–700,000 Å, and 5,000,000 Å. The flow rate was 1 ml/min and the injected sample size was 2.0 ml.

In order to obtain quantitative results from the GPC output, it was necessary to calibrate the machine in a unique fashion. A series of samples of each PS in THF covering the concentration range of 0.4 to 2.0 mg/ml was passed through the GPC, and the UV and RI outputs for each sample were recorded. The areas under each of these chromatograms was calculated using a polar planimeter, and a plot of area versus concentration of polymer was made. The resulting plots were linear over the complete range of concentration studied. An identical procedure was followed for a series of PBD samples where the UV response at 254 nm was found to be zero<sup>14,19</sup> and the RI response was found to be a linear function of concentration. The extinction coefficients are given in Table II.

In order to analyze a sample containing PS and PBD, the UV output was used to determine the PS concentration. By using the RI area–PS concentration plot, the PS contribution to the total RI peak was calculated. By subtracting this area from the total RI area and by using the RI area–PBD concentration plot, the concentration of PBD present was calculated. Through the use of dilution factors, the concentrations of these two polymers in the phase sampled were determined. The validity of the procedure was checked by analyzing prepared samples containing known amounts of PS, PBD, and THF. The analysis was accurate to within 1% of the expected value of any of the components over the complete range of concentrations, PS/PBD ratios, and PS and PBD molecular weights. Typical results of such tests to determine the accuracy and precision of the method are given in Figure 1. By doing repetitive runs with prepared mixtures, the method proved to yield results reproducible to within 1%. A slight influence of the second polymer in solution on the location of the peak was observed, as has been reported earlier in Berek's laboratory.<sup>20</sup> As can be seen from the figure, however, the areas remain unaffected.

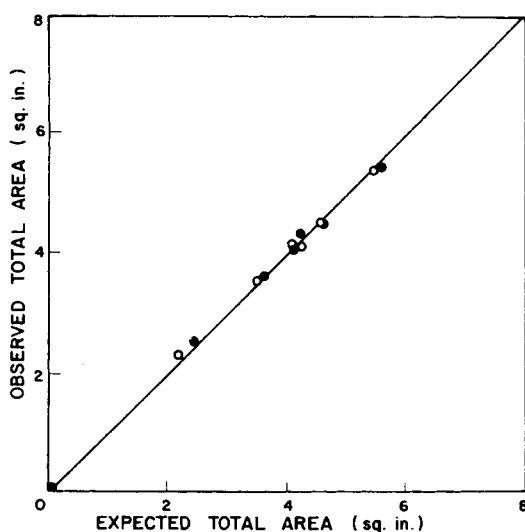


Fig. 1. Verification of RI areas of mixtures of polymers. Test points are expected to fall along the 45° line: (●) PS 37,000/PBD 17,000; (○) PS 37,000/PBD 170,000.

### Preparation of Mixtures and Sampling of Phases

Predetermined amounts of the two polymers to be studied were weighed into a sample bottle, a predetermined amount of THF was then weighed in, and the sample bottle stoppered. The polymers were employed as received without further purification, while the THF was freshly distilled. Following manual shaking of the bottle, it was allowed to equilibrate at 23°C until the solution became clear or separated into two phases partitioned by a distinct interface.

The top phase was sampled using a micrometer syringe with disposable needle, weighed into a 100-ml volumetric flask, and diluted to 100 ml with THF. The interface was carefully removed and discarded. Using a clean syringe and needle, the bottom phase was likewise removed, weighed into a 100-ml volumetric flask, and diluted.

### RESULTS AND DISCUSSION

The results for three pairs of polymers of different molecular weights are presented in Figure 2. A number of experimental observations can now be made, many of which would not be possible without the complete determination of the tie lines and plait points for the binodal curves.

Comparing curves 1 and 3, we see that increasing the molecular weights of the two polymers decreases the compatibility or mutual solubility of the two polymers as represented by both the binodal curves and the plait points moving in the direction of the solvent apex. Interestingly for these two pairs of polymers, where the ratios of the molecular weights of PS and PBD remain approximately the same while the molecular weights in absolute values are changing by a factor of 10, the two plait points are aligned with the solvent apex of the triangular di-

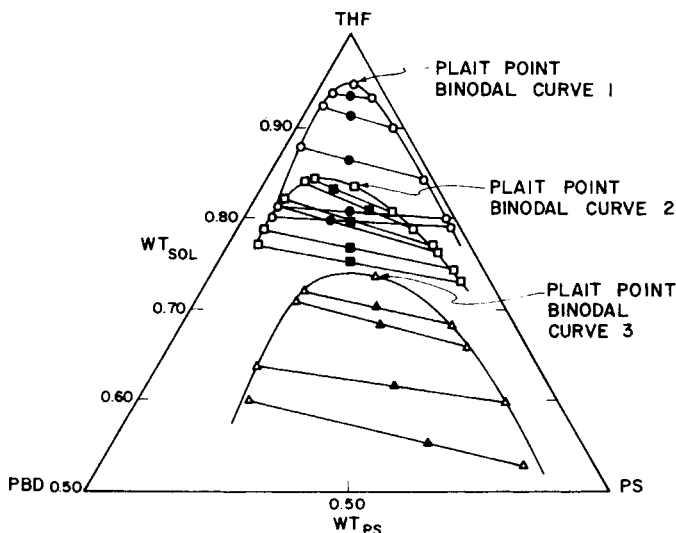


Fig. 2. Phase diagram for ternary systems at  $23 \pm 0.4^\circ\text{C}$ . Solid symbols represent mix point compositions, open symbols represent equilibrium phase compositions: (O) binodal curve 1, PS 110,000/PBD 170,000; (□) binodal curve 2, PS 37,000/PBD 17,000; (▲) binodal curve 3, PS 9,000/PBD 17,000. Tie lines are shown connecting conjugate phases via mix points.  $WT_{PS}$  is the weight fraction of PS in the total polymer.  $WT_{SOL}$  is the weight fraction of solvent THF in the total polymer-solvent mixture.

agram. Besides the plait point for the higher molecular weight polymers being closer to the solvent apex of the triangular diagram, this decreased compatibility at higher molecular weight is also manifested by the PBD-rich segment of the binodal curve being closer to the PBD-THF axis and the PS-rich segment of the binodal curve being closer to the PS-THF axis, that is, each conjugate phase contains a lower weight fraction of the alternate polymer at higher molecular weights.

The tie lines generally are not parallel to the PBD-PS axis but have a slope toward the PS axis. This slope indicates that at equilibrium between conjugate phases there is less solvent in the PS-rich phase than in the PBD-rich phase. The tie lines of curves 1 and 3 are approximately parallel to each other, while the tie lines of curve 2 are significantly steeper, indicating a strong dependence of the slope on the relative molecular weights of the two polymers.

Comparing curves 2 and 3, we see that increasing the molecular weight of just the polystyrene causes the entire binodal to shift in the direction of decreased mutual solubility. The PBD-rich segment of curve 2 shifts significantly toward the PBD-THF axis, indicating that the increase in the molecular weight of the polystyrene has a greater effect in depleting the PBD-rich phase of polystyrene than in depleting the PS-rich phase of polybutadiene. The steeper slope of the tie lines in curve 2 reflects the fact that, although a greater concentration of solvent is now present in both phases, the increase in the concentration of solvent is greater in the PBD-rich phase than in the PS-rich phase. Accordingly, the plait point is shifted both toward the solvent apex and toward the PBD-THF axis.

## SUMMARY

The quantitative use of gel permeation chromatography in the dual detection mode for the study of ternary phase equilibria has been established. Its advantage is that the method yields tie lines and plait points, a fact that was apparently overlooked in previous phase studies done using gel permeation chromatography. The present method of establishing tie lines has proved to be more convenient in our case than the methods employed by Kern,<sup>21</sup> Bristow,<sup>22</sup> and Berek, Lath, and Durdovic.<sup>23</sup> In addition, because of the ability to separate molecules according to size, any impurities such as antioxidants (2,6-di-*tert*-butyl-4-methylphenol in the present case) are removed prior to the UV and RI analysis.

A Rotary International Fellowship awarded to one of the authors (V.N.) is gratefully acknowledged. The authors also wish to thank the National Research Council of Canada for partial support and Professor R. Y. M. Huang for the use and dedication of the Waters 200 GPC in his laboratory.

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Received December 8, 1977