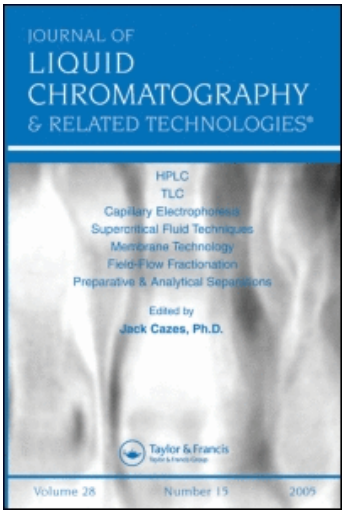

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Quantitative Analysis of Mixed Polymer Systems by the Use of Gel Permeation Chromatography

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QUANTITATIVE ANALYSIS OF MIXED POLYMER SYSTEMS BY THE USE OF GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

The use of gel permeation chromatography for the quantitative analysis of composition in mixed polymer systems is presented. The advantages of this method in determining the compositions of conjugate phases in polymer 1-polymer 2-solvent systems is discussed with typical examples.

INTRODUCTION

The phenomenon of phase separation in mixtures of two polymers in a mutual solvent or two polymers in the solid state is known as incompatibility and is of considerable practical importance. Limited miscibility plays a role in the preparative and analytical fractionation of polymers, in the preparation of plastic films, including paint and varnish coatings, and in the determination of service properties of certain systems such as high impact styrene-butadiene products. The analysis of the resulting separate phases is of critical importance in furthering the knowledge of this phenomenon. The purpose of the present paper is to introduce and demonstrate the simplicity,

versatility, and advantages of a new technique for analyzing ternary polymer-polymer-solvent systems. The technique is based on a quantitative application of gel permeation chromatography.

In order to represent graphically all of the possible mixtures and the situations resulting when two polymers are present in a mutual solvent the ternary phase diagram is employed. Figure 1 represents a typical ternary phase diagram for a polymer 1 - polymer 2- solvent (P1-P2-S) system. (At the risk of oversimplification the discussion to follow will omit any reference to metastable mixtures and the spinodal. For discussions of these aspects see, for example, the work of R. Koningsveld, reference 1). A mixture in the "unstable mixture" region will, if allowed to reach equilibrium, separate into

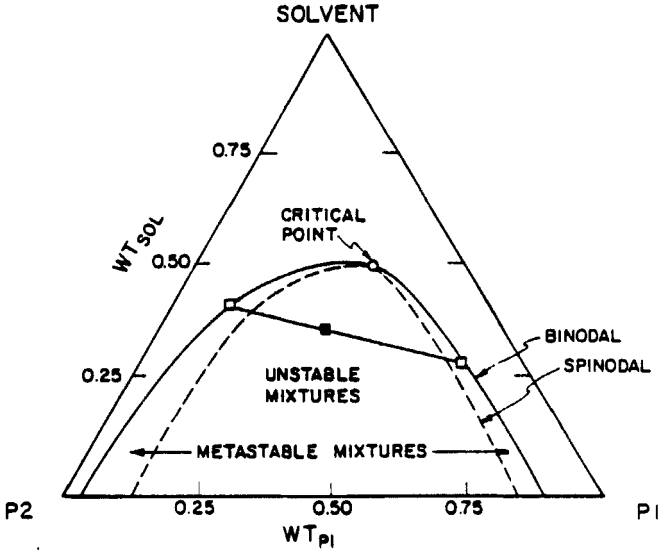

FIGURE 1 Equilibrium phase diagram for the ternary system P1-P2-S. WT_{P1} represents the weight fraction of P1 in the polymer mixture. WT_{SOL} represents the weight fraction of solvent in the total polymer-solvent mixture. □——■——□ represents the tie line joining the coexisting phases in equilibrium and passing through the compositional representation of the original mixture.

two coexisting phases in equilibrium. A line joining the compositional representation of these two phases will be a straight line, passing through the original mix point. Such lines are referred to as tie lines and are used extensively in chemical engineering calculations to determine the amount of the two phases. If a number of samples are allowed to equilibrate and each phase is analyzed to determine its composition, a curve can be traced through the compositions of these coexisting phases in equilibrium. This curve, alternatively known as the equilibrium phase curve, the coexistence curve, or the binodal, separates the region of unstable mixtures from the region in which mixtures form one homogeneous solution. A number of attempts have been made to predict the location of the binodal [2-8]. When a series of tie lines is drawn for a given system it is possible to determine the mid-point for each tie line and then join these mid-points by a line which when extrapolated intercepts the binodal. The point defined by this interception is known as the critical or plait point. The significance of this point is that the physical characteristics of the two coexisting phases become identical. Knowledge of this point also has theoretical significance since the critical composition is used in a number of theoretical treatments of compatibility [4,5].

A number of studies dealing with P1-P2-S incompatibility have been conducted in the past thirty years [1-21]. The original studies in this area were reported in 1947 and involved allowing mixtures to equilibrate, sampling, and analyzing each phase in order to establish the binodal [9]. The analytical technique employed varied for each system studied and often required elaborate procedures to completely remove solvent and other substances which might interfere with the analysis (for example, antioxidants). In 1956 Kern [10] advanced the studies by adding tie lines (but no critical point). Again a variety of elaborate techniques of chemical analysis was necessary. In 1963 Paxton [13] employed a technique of adding solvent to a mixture which was originally unstable and therefore turbid when agitated. In this way he was able to establish the composition of the mixture at the point at which the agitated

mixture becomes clear. A series of such experiments permits the establishment of the cloud point isotherm. However, the validity of using this cloud point isotherm to represent the binodal is in question [15]. In addition, the number of samples required to establish the isotherm is excessive and there is no information given concerning the composition of coexisting phases or the critical point. The technique described in this paper eliminates most of the complications encountered in the studies mentioned above.

QUANTITATIVE ANALYSIS USING GEL PERMEATION CHROMATOGRAPHY

From its inception in 1960 gel permeation chromatography (GPC) has contributed greatly to the study of polymers in solution by its ability to separate the polymer sample according to the size of the molecule in solution [22]. Initially the primary use of GPC was to determine molecular weight distributions of polymers by monitoring the effluent from the columns with a differential refractometer [23]. In recent years attempts have been made to use GPC in a more quantitative manner. Owens and Cobler [24] discussed the difficulties of obtaining good quantitative data on the distribution of size and the composition of mixtures or copolymers and suggested the use of multiple runs with different solvents or the use of multiple detectors. Bartosiewicz [25] has described the use of various analytical methods on fractions collected from GPC. Terry and Rodriguez [26] describe the use of infrared spectrometry for monitoring the concentration of various functional groups as a function of molecular size, using multiple runs with a monomeric material included to aid in relating the successive runs to each other quantitatively. Cantow and co-workers [27] as well as Runyon et al. [28] have described the use of an ultraviolet (UV) monochromator in series with a differential refractive index (RI) detector for simultaneously determining the composition and molecular size in styrene-butadiene copolymer rubbers. In this paper we extend and quantify this approach by establishing an experimental technique capable of analyzing a large variety of P1-P2-S systems.

PROCEDURE

A P1-P2-S system of interest is selected for study. A stock solution of P1-S is prepared. A stock solution of P2-S is prepared, usually at a concentration identical to the P1-S solution but this is not a necessary requirement. Using these stock solutions a series of ternary mixtures of varying compositions is prepared in test tubes with glass stoppers. Alternatively, the two solid polymers may be weighed and the solvent added. The mixtures are agitated and then placed in a temperature-controlled circulating water bath. The samples are allowed to equilibrate until the mixture either becomes one homogeneous solution or two phases separated by a distinct interface. The time required for this attainment of equilibrium may vary from minutes to weeks depending on the molecular weight of the polymers, the temperature, the total polymer concentration, and the proximity to the critical point.

When the mixture has equilibrated the top phase is carefully sampled using a syringe. The sample is weighed into a pre-weighed volumetric flask and the sample diluted with the eluent being used in the GPC. The size of the volumetric flask, and therefore the dilution factor, is selected such that the estimated polymer concentration of the final solution is within the range of the calibration of the instrument (to be discussed below). Using a clean syringe the bottom phase is sampled, weighed and diluted as was done for the sample of the top phase. This procedure is repeated for each equilibrated mixture used in the study of the system.

In order to analyze quantitatively the samples prepared above it is necessary to calibrate the GPC in a unique fashion. A series of solutions of P1 in the eluent E is prepared covering the concentration range of 0.1 to 2.0 mg/ml. The recorded GPC output representing individually the UV and RI for each sample is collected and the area between the baseline and the chromatogram determined using a polar planimeter. A plot of RI area versus polymer concentration and UV area versus polymer concentration is used

to establish RI and UV extinction coefficients for polymer P1. An identical procedure is followed for polymer P2. The result is a set of four extinction coefficients to be used in determining concentrations of ternary mixtures.

The sample to be analyzed is now injected into the GPC and the RI and UV chromatograms collected. Figure 2 represents a typical chromatogram illustrating the fact that in the usual situation the peaks for the two polymers typically show some overlap, and because of its ability to separate molecules based on size the solvent S has been removed from the polymers and emerges later as an impurity peak. The areas under the curves are determined and the resulting values used in the following equations.

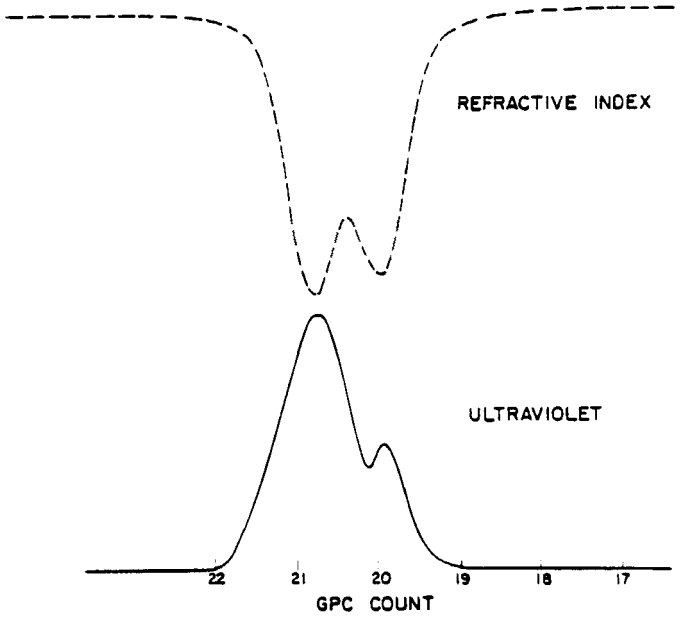

FIGURE 2 Typical GPC output for a mixture of two polymers. Both polymers show a response in differential refractive index and ultraviolet.

$$UV_T = UV_{P1} \times P_1 + UV_{P2} \times P_2$$

and

$$RI_T = RI_{P1} \times P_1 + RI_{P2} \times P_2$$

where

UV_T and RI_T represent the total enclosed area for the UV and RI outputs

UV_{PI} and RI_{PI} represent the UV and RI extinction coefficients for polymer PI

P_I represents the unknown concentration of polymer PI

These equations can be solved simultaneously to yield the concentration of P1 and P2 in the injected sample. The total mass of these polymers in the one phase is then calculated by using the dilution factor. Since the phase is weighed into the volumetric flask, the weight of solvent S can be calculated by mass balance. Therefore, the exact composition of the phase is established. By repeating the procedure for the sample prepared from the co-existing phase the tie line can be established. By repeating for a limited number of mixtures the binodal can be established and the critical point determined.

ADVANTAGES OF TECHNIQUE

The technique as outlined above has a number of advantages over the techniques previously reported in the literature.

(1) The technique may be employed for any polymer-polymer-solvent system provided the polymers are soluble in the eluent, the eluent does not cause interference in the UV and RI analysis, and the extinction coefficients of the polymers can be established over the range of molecular weights being considered. A list of eluents used in GPC in the past includes: methylene chloride, tetrahydrofuran, toluene, perchloroethylene, chloroform, m-cresol, dimethylformamide, benzene, o-chlorophenol, carbon tetrachloride, 1,2,4-trichlorobenzene, o-dichlorobenzene, water and others.

(2) Because of its ability to separate molecules according to size in solution no pre-analysis sample preparations are required other than filtration of the injected sample to remove dust. In most analytical techniques employed in the past it was necessary to remove any component which may interfere with the analysis. This often required drying the sample to remove solvent or more elaborate procedures to remove inhibitors, antioxidants, etc. which may accompany the polymers. The GPC automatically removes these components prior to passage through the detection device and eliminates any interference.

(3) A minimal number of samples are required to establish the binodal. In most systems studied in our laboratories five mixtures (i.e. ten phases) were sufficient to define the binodal. The length of time required to study one complete system is short in comparison to many of the chemical methods or the cloud point determination.

(4) While other techniques have demonstrated their ability to generate binodals, tie lines, and critical points no other technique matches the GPC in terms of certainty, ease and time. These advantages cannot be overemphasized. There has been some doubt expressed concerning the ability of the cloud point isotherm to represent the binodal [15], and the cloud point isotherm gives no information about tie lines or the critical point. Since it is the binodal which is of practical importance the ability to establish this curve positively is a necessity. Provided adequate time is allowed to establish equilibrium prior to sampling the validity of the binodal established by the GPC technique is certain. The ability to generate tie lines and critical points has recently gained additional importance. In the past theoretical treatments of incompatibility were limited because of the inability to experimentally generate the required data. One such treatment

by Hsu and Prausnitz [29] deals with the problem by predicting the compositions of the coexisting phases, establishing tie lines, and thereby tracing the binodal and determining the critical point. In their work they had no way of conveniently verifying their predictions experimentally. The technique outlined in this paper should solve this problem.

EXPERIMENTAL

For the purposes of illustration of the technique the system polystyrene (PS)-polybutadiene (PBD)-tetrahydrofuran (THF) is reported. The PS-PBD system has been studied and reported by many investigators both in the solid state and in solution [11-13,18-21]. The use of GPC is uniquely suited to this system because of the ability to eliminate the effect on the analysis of the antioxidant (2,6-ditertiarybutyl-4-methylphenol) which must be present to prevent crosslinking of the PBD.

MATERIALS AND METHODS

The characteristics of the commercial PS (Pressure Chemical Co.) and the PBD (Phillips Petroleum Co.) samples are given in Table 1. The polymers were employed as received with no further purification or pre-treatment.

TABLE 1

CHARACTERISTICS OF POLYMER SAMPLES

Sample	Manufacturer's Data $\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
PS 9,000	9.18	9.17	<1.06
PS 37,000	36.0	33.0	<1.06
PS 110,000	110.0	110.0	<1.06
PBS 17,000[a]	17.0 ± 1.7	16.0 ± 1.6	1.06
PBD 170,000[b]	170.0 ± 17	135.0 ± 13	1.26

a 43.5% cis, 49.1% trans, 7.4% vinyl, 0.04% antioxidant
b 47.1% cis, 44.5% trans, 8.4% vinyl, 0.04% antioxidant

In the majority of systems the solvent employed, both as the mutual solvent in the ternary system and as the eluent in the GPC was practical grade tetrahydrofuran (THF) supplied by Fisher Scientific Co., and distilled prior to use. For one ternary system the solvent employed was 1,2,3,4-tetrahydronaphthalene (Tetralin) supplied by Fisher Scientific Company and used as received.

The quantitative analysis of the samples was done using a Waters 200 GPC equipped with an ultraviolet unit using a monochromatic light of wave length 254 nm and a differential refractive index unit using white light. The detectors were positioned in series along the eluent path and their outputs were recorded on a two-channel Texas Instruments recorder. The GPC was used with four columns containing Styragel packing of the following size designations: 2000 - 5000Å, 15 000 - 50 000Å, 150 000 - 170 000Å and 5 000 000Å. The flow rate was 1 ml/min and the injected sample size was 2.0 ml.

A series of samples of each PS and each PBD in THF covering the concentration range 0.1 mg/ml to 2.0 mg/ml was passed through the GPC and the UV and the RI outputs for each sample recorded. The area under each chromatogram was determined using a polar planimeter, a plot made of area versus concentration of polymer, and extinction coefficients determined.

The ternary mixtures were prepared, sampled, and analyzed as outlined in the section PROCEDURE.

In order to verify the validity and accuracy of the technique a series of samples representing a variety of combinations of PS and PBD in THF, and a variety of concentrations of each component were prepared. The mixture of known composition was sampled (without allowing equilibrium to be established) and the mixture analyzed in the manner to be used to analyze unknown systems.

RESULTS AND DISCUSSION

In Figure 3 are presented typical results for the calibration of the GPC. Within the concentration range of study the UV and RI area varies linearly with concentration of polymer. The extinction coefficient for each system studied is listed in Table 2. In this

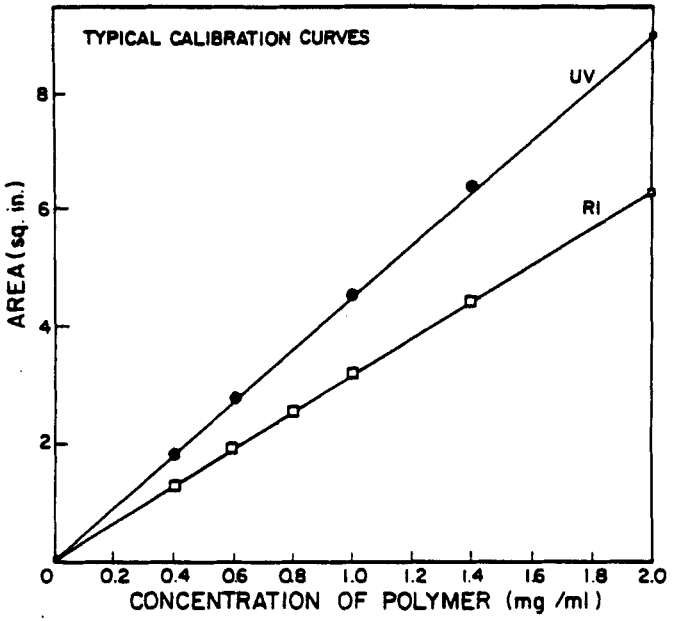

FIGURE 3 Typical calibration curves for the ultraviolet and differential refractive index response for one polymer.

TABLE 2

EXTINCTION COEFFICIENTS FROM THE GPC CALIBRATIONS

Polymer	Ultraviolet (in^2 ml/mg)	Refractive Index (in^2 ml/mg)
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

case the UV extinction coefficients for the polybutadiene samples are zero. This is to be expected since PBD shows no response in UV light of 254 nm [28]. Barrell et al. have predicted that the extinction coefficients of polymers will vary with molecular weight [30]. While the results do indicate a very slight variation of extinction coefficients with molecular weight no distinct trend is established.

The ability of the present technique to determine the composition of mixtures was verified by preparing ternary samples of precisely known compositions and sampling the agitated mixture. With these samples it was possible to predict the exact UV and RI total areas expected. When the sample was analyzed on the GPC the total areas were determined and compared to the predicted areas. Figure 4 presents typical results for the total RI area for two systems at various mass fractions of the two polymers. The experimentally determined results are in excellent agreement with the areas predicted.

The results for various PS-PBD-THF systems at 23°C are presented in Figures 5 through 7. A detailed discussion of these results and the implications of the tie lines (their location and slope), the location of the critical point, and the location and shape of the binodal is given in our recent publications [20,21].

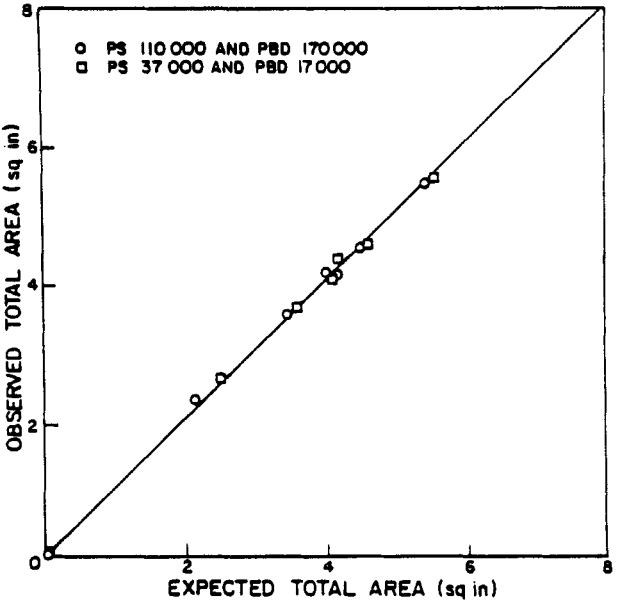

FIGURE 4 Comparison of observed and calculated total areas under RI chromatograms for mixed polymer systems.

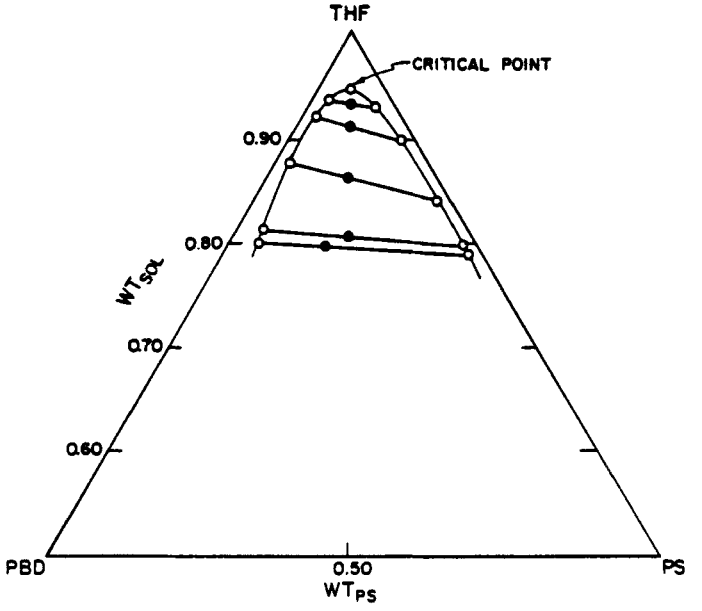

FIGURE 5 Phase diagram for PS110 000/ PBD 170 000/THF at 23 ± 0.4°C.

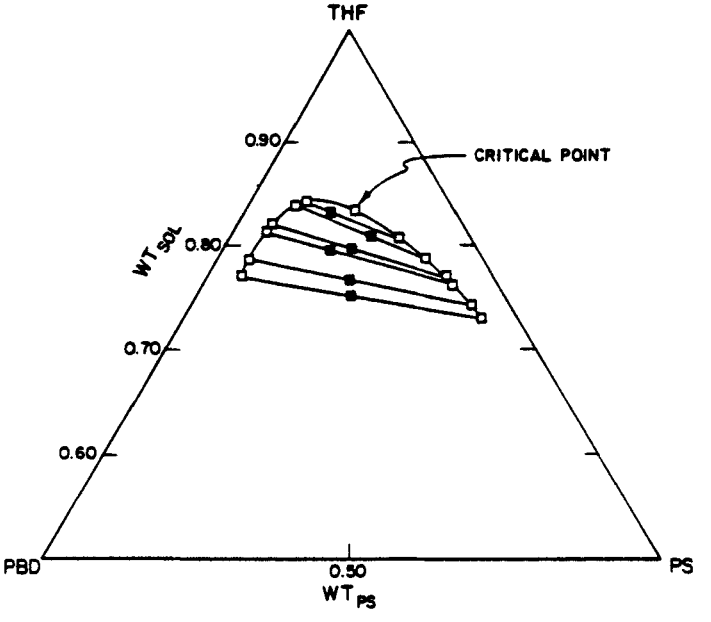

FIGURE 6 Phase diagram for PS37000/ PBD17000/THF at 23 ± 0.4°C.

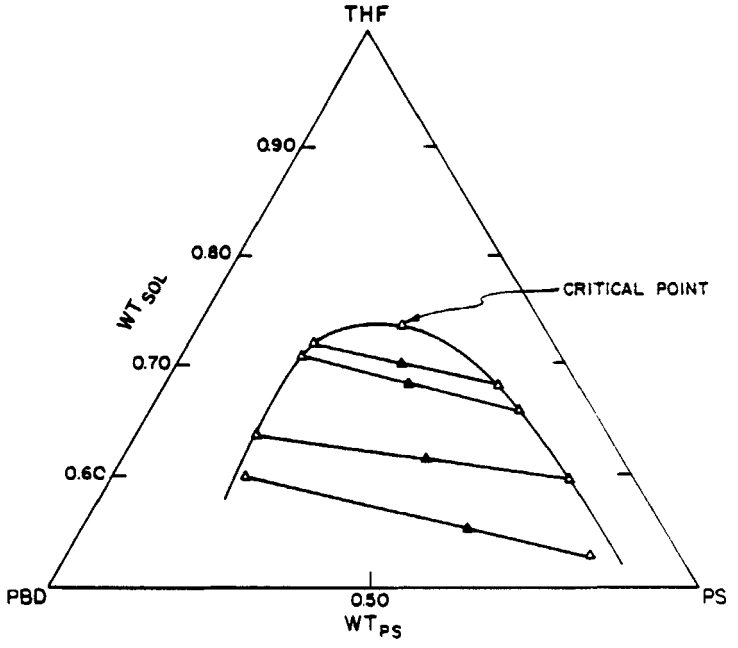

FIGURE 7 Phase diagram for PS9000/ PBD 17000/THF at 23 ± 0.4°C.

The present discussion deals with the technique and what results can be expected. In these figures it can be seen that the binodal is quickly and accurately established with between four and six tie lines. More tie lines than those shown were later determined and were found to show excellent agreement with the original samples. The bottom tie line in Figure 7 is of particular interest. This sample, which is approximately 40 to 50% by mass polymer was extremely slow to reach equilibrium. The phases were sampled early to determine what influence on the tie line this lack of equilibrium would have. The result is that the tie line does not extend fully to the binodal. Given further time the phases would become more concentrated in the appropriate component and the compositions of the phases fall on the binodal. The system PS-PBD-THF is a convenient simplification of the variety of possible systems that

could be analyzed by the GPC technique. In this system the ternary solvent S is identical to the eluent, and therefore, there is one less component to deal with in the total system. The PS-PBD-THF system does however present one potential problem and that is the anitoxidant 2,6-ditertiarybutyl-4-methylphenol (Ionol) present in the PBD. The GPC simply eliminates this low molecular weight contaminant prior to passage through the metering system. The Ionol emerges from the system as a low molecular weight impurity and has no influence on the compositional determinations. If we add the complicating factor of a different ternary solvent the capabilities and the limitations of the technique are put to a more demanding test. (Recall that with most conventional techniques the solvent had to be removed prior to sample analysis.) As a severe test we selected as the ternary system solvent 1,2,3,4-tetrahydronaphthalene (Tetralin) a viscous, high boiling point solvent with molecular weight of 132.31, viscosity of 2.202 cp (at 20°C), specific gravity of 0.970, and

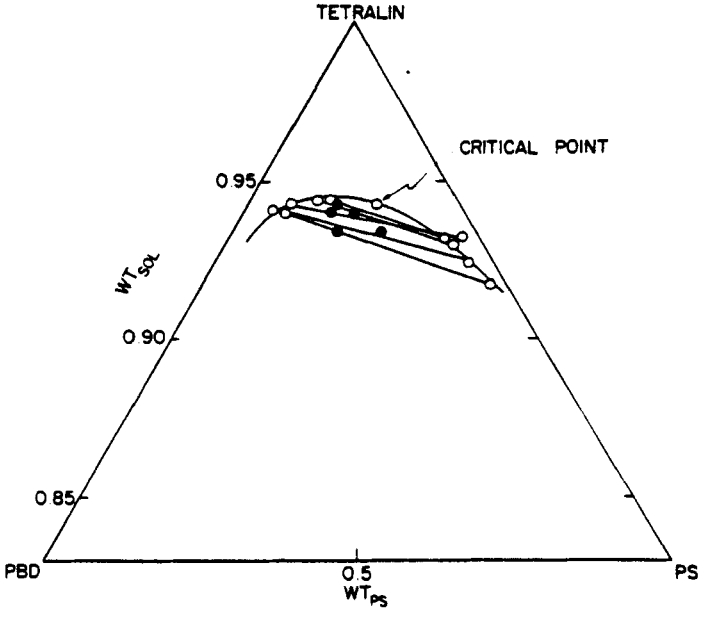

FIGURE 8 Phase diagram for PS110 000/ PBD 170 000/ Tetralin at 29 ± 0.4°C.

boiling point of 208°C, compared to a molecular weight of 72.11, viscosity of 0.486 cp (at 20°C), specific gravity of 0.889 and boiling of 65°C for the THF [31]. The results for one such system at 29°C are presented in Figure 8. Four of the five tie lines illustrate a definite trend and these points were used to establish the binodal. The apparent inaccuarcy of the fifth tie line results from the fact that Figure 8 is plotted on an extremely magnified scale, thereby exaggerating even the slightest inaccuracies. The results in Figure 8 illustrate that the technique easily produces an accurate representation of the binodal for systems of reasonable complexity (i.e. the presence of a solvent S different than eluent as well as the presence of antioxidant).

CONCLUSIONS

A convenient technique has been developed for analyzing solutions containing polymer 1, polymer 2, and solvent. The technique takes advantage of the ability of gel permeation chromatography to separate molecules according to size in solution, and requires dual detectors in series to monitor the GPC effluent. The technique has shown applicability in ternary phase studies yielding accurate representations of the binodal, tie lines, and critical point with a minimal number of samples. The presence of contaminants such as antioxidants or a second solvent presents little problem. It is expected that this chromatographic technique of studying mixed polymer solutions will find widespread use in the future as a means of experimentally verifying some of the latest theoretical treatments of incompatibility.

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