

Gel Permeation and Thin-Layer Chromatographic Characterization and Solution Properties of Butadiene and Styrene Homopolymers and Copolymers

JAMES L. WHITE, DAVID G. SALLADAY,* DAVID O. QUISENBERRY, and DONALD L. MACLEAN,† *Department of Chemical and Metallurgical Engineering, University of Tennessee, Knoxville, Tennessee 37916*

Synopsis

Gel permeation chromatographic (GPC) and thin-layer chromatographic (TLC) studies of polystyrene, polybutadienes (BR), and their copolymers (SBR) have been carried out. GPC primarily separates them on the basis of molecular size, and TLC, on the basis of composition. Methods of obtaining absolute molecular weight distributions for BR and SBR based upon variations of the Strasbourg Universal Calibration procedure are described. In particular, $[\eta]$ - M relationships in both the GPC solvent (THF) and in a second solvent (toluene) were used; in addition, results of statistical mechanical calculations for \bar{s}^2 (based on the assumption of negligible steric hindrance and freely rotating bonds) were applied. An experimental comparison of these methods was carried out, and use of the $[\eta]$ - M relationships for both solvents was found to give satisfactory results. The predictions of the statistical theory were too low. A detailed study of polymer-solvent-gel interaction in the GPC unit was made through investigation of ternary phase equilibrium in the (polystyrene)-THF-(polymer) system. The polymers studied included BR and SBR with varying styrene contents. Experimental techniques for TLC separations of BR, SBR, and polystyrene according to the composition are described.

INTRODUCTION

Polybutadiene and its styrene copolymers are among the most important of industrial polymers, being the major synthetic rubbers. Determination of the structure of unknown polymers and the maintenance of control of structure are thus of special concern for this homo- and copolymer system. Variations in molecular weight distributions for these elastomer strongly influence rheological properties and processability.¹ The application of chromatographic techniques should be of great use in this effort.

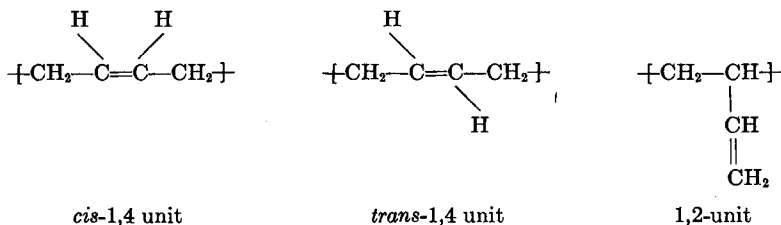
The determination of molecular weight distributions of elastomers was for many years carried out by fractional precipitation and precipitation-

* Present address: Amoco, Decatur, Alabama.

† Present address: Monsanto Company, Chemstrand Research Center, Durham, North Carolina.

chromatographic techniques.²⁻⁴ It was a difficult and tedious task. Such measurements have been greatly simplified through the development of the gel permeation chromatograph, where dilute solutions of unknown polymer are fractionated by percolation through special gels.⁵ Harmon⁶ has discussed applications of this instrument to practical studies of elastomer systems. However, there are difficulties in the quantitative as opposed to qualitative interpretation of the data obtained in the GPC instrument. The major problem in quantitative interpretation of such data is the lack of absolute calibration standards.

The GPC instrument is generally calibrated with narrow molecular weight-distribution polystyrene standards. However, if, as is generally believed, separation occurs on the basis of size, then a different calibration will be needed for each species investigated. Indeed, failure to do this and reliance on polystyrene standards can lead in our experience to errors of the order of 50% to 100%. It would be difficult and tedious to do this for each different polydiene and copolymer, for polydienes, unlike vinyl polymers, do not have structural units uniquely determined from its monomers, and there is an infinite variety of possible structures. Homopolymers alone formed from butadiene may have as many as three different units:



There has been some attempt to develop calibration curves for specific butadiene polymers. Adams, Farhat, and Johnson⁷ and Ura-neck and Burleigh⁸ constructed a calibration curve for alkyllithium-polymerized polybutadiene in a particular column, as have Iwama, Abe, and Homma⁹ for high *cis*-1,4 polybutadiene. The first step toward a general calibration procedure was made by Moore and Hendrickson¹⁰ who did much of the early work on the instrument. These authors suggested that a correlation could be developed by presuming that elution volume is determined by extended chain length and correcting the polystyrene calibration curve on this basis. Some experimental studies support this.¹⁰ However, results of most experimenters¹¹ are in disagreement. More recently Benoit et al.^{12,13} of the Strasbourg Center for Research on Macromolecules have proposed an alternative procedure based upon the Einstein-Kuhn-Flory theory of dilute polymer solutions.¹⁴ This procedure utilizes the relation

$$[\eta] = \Phi' \frac{(\bar{s}^2)^{3/2}}{M} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, \bar{s}^2 is the mean square radius of gyration, and Φ' is a universal constant. They argue that

if molecules separate on the basis of size, then the product $[\eta]M$ should be a unique function of the GPC elution volume. Such a plot is called a Universal Calibration Curve. For polymers with backbones consisting of single carbon-carbon bonds and similar steric interactions to polystyrene, this argument becomes equivalent to that of Moore and Hendrickson when polymer flexibility and solvent interaction are the same. Intrinsic viscosity-molecular weight data are needed for each polymer studied in the GPC solvent at the appropriate temperature, which is a severe limitation, as such data, especially in common GPC solvents such as THF, is rather limited. There has been some criticism of this method of GPC analysis, especially with regard to the interpretation of data for branched molecules.⁹ Indeed, one may say that very little is known of polymer-solvent-gel interaction in typical GPC systems.

In recent years there has been increased interest in the application of a classical analytic chromatographic technique, namely, thin-layer chromatography, to polymer systems. The thin-layer-chromatographic (TLC) method since its origins during the late 1930s has been widely used by the organic chemist and biochemist. These applications have been summarized in various treatises and monographs.¹⁵ Applications to synthetic polymers were at first slow. In the late 1950s, Langford and Vaughn¹⁶ applied paper chromatography to separate various synthetic homopolymers of different composition. More recently, this type of separation has been taken up by Inagaki, Matsuda, and Kamiyama in studies of separation of heterogeneous styrene-methyl acrylate copolymers according to composition,¹⁷ polymethacrylates on the basis of tacticity,¹⁸ and polystyrene according to molecular weight distribution.¹⁹ Similar separations in the thin-layer mode have been accomplished by Belenkii and Gankina.²⁰

In this paper, we will describe three experimental studies related to chromatographic characterization of polybutadiene and its styrene copolymers: (1) methods of determination of absolute molecular weight distributions for polybutadienes and its styrene copolymers from GPC data and their comparison with experiment; (2) experimental study of ternary-phase equilibrium involving polystyrene (the uncrosslinked form of the GPC packing), tetrahydrofuran (GPC solvent), and various polymers including polybutadiene and butadiene-styrene copolymers; and (3) TLC studies of the separation of polymers including those in the butadiene-styrene system. This paper represents a continuation of our earlier studies of mechanisms of chromatographic fractionation.^{21,22}

GEL PERMEATION CHROMATOGRAPHY

Analysis

Universal Calibration Curve. The generally accepted method of analyzing experimental data from gel permeation chromatography is the Universal Calibration Curve technique of the Strasbourg research group.^{12,13}

TABLE I
 $[\eta]$ - M Relationships for Polystyrene and Polybutadiene in Tetrahydrofuran

Polymer	Temp., °C	$K \times 10^6$	a	Reference
Polystyrene	25	14.1	0.700	12
Polystyrene	35	12.3	0.703	9
Polystyrene	25	16.0	0.700	23
<i>cis</i> -1,4-Polybutadiene	35	21.2	0.739	9
Alkyl lithium polybutadiene (35% <i>cis</i> , 55% <i>trans</i> , 10% 1,2)	40	39.6	0.697	24

According to their argument for any elution volume, the product of the intrinsic viscosity and molecular weight of an arbitrary diene polymer or copolymer and the polystyrene calibration standards will be the same. Then,

$$[\eta]_{\text{PS}}M_{\text{PS}} = [\eta]_{\text{PD}}M_{\text{PD}} \quad (2)$$

If the intrinsic viscosity is fitted to molecular weight data through the Kuhn-Mark-Houwink-Sakurada¹⁴ relation,

$$[\eta] = KM^a \quad (3)$$

where K and a are constants. Substitution of eq. (3) into eq. (2), after distinguishing K and a with suitable subscripts, gives upon solving for M_{PD} , the molecular weight of the polydiene of the suitable microstructure:

$$M_{\text{PD}} = fM_{\text{PS}} \quad (4)$$

with

$$f = \left(\frac{K_{\text{PS}}}{K_{\text{PD}}} \right)^{\frac{1}{1+a_{\text{PD}}}} M_{\text{PS}}^{\frac{a_{\text{PS}}-a_{\text{PD}}}{1+a_{\text{PD}}}} \quad (5)$$

When the a exponents are the same ($a_{\text{PS}} = a_{\text{PD}}$), we find that the factor f is independent of molecular weight.

In order to use eq. (5) to correct the polystyrene calibration curve to give molecular weights for polybutadiene and its copolymers, intrinsic viscosity-molecular weight relationships are required for both polystyrene and the polymer under consideration. As tetrahydrofuran (THF) in the range of 25°C to 40°C is the most widely used solvent system in this instrument, several $[\eta]$ - M relationships for polystyrene under these conditions have been experimentally determined^{9,12,23} and are summarized in Table I. It is equally necessary to have an $[\eta]$ - M relationship for each polybutadiene of different microstructure and copolymer in order to apply eq. (5) to obtain quantitative molecular weight distributions. Data of this sort seem limited, and only two sets of data on such polymers have been found in the literature or by correspondence.^{9,24} These are also summarized in Table I. Obviously, this paucity of experimental data suggests that room

TABLE II
 $[\eta]$ - M Relationships for Polystyrene, Polybutadiene, and Copolymers in Toluene

Polymer	Temp., °C	$K \times 10^5$	a	Reference
Polystyrene	30	9.2	0.720	25
	30	12.0	0.710	
	30	11.0	0.725	
	25	17.0	0.690	
	25	44.0	0.650	
<i>cis</i> -Polybutadiene	30	30.5	0.725	26
	30	33.9	0.688	
Emulsion polybutadiene (10% <i>cis</i> , 70% <i>trans</i> , 20% 1,2)*	26	65.0	0.67	2
Butyllithium polybutadiene (35% <i>cis</i> , 55% <i>trans</i> , 10% 1,2)	25	21.7	0.76	27
25% Styrene-butadiene copolymer (10% <i>cis</i> , 70% <i>trans</i> , 20% 1,2)	30	37.9	0.71	28
	25	52.5	0.66	

* Correlation based upon minimum branching has been used.

is open for developing approximate procedures for evaluating the f factor of eq. (5).

Toluene Data. An alternative procedure is to attempt to use $[\eta]$ - M data obtained in a different solvent in place of the required THF data. This would only be valid should the polymer-solvent interaction for the two systems be the same. A search of the literature for solvents in which plentiful $[\eta]$ - M data for polystyrene, polybutadiene, and copolymers indicates that the most extensive experimental work has been carried out perhaps in toluene.^{2,25-28} Table II summarizes such data for these systems.

As we have pointed out, the validity of the approximate procedure recommended above depends upon the assumption of equivalent polymer-solvent interaction. Substantial data on this point, of course, do not exist, but it may be noted that the Mark-Houwink exponents for both polystyrene and polybutadiene in THF and toluene are similar.

Predictions of Statistical Calculations. If molecular theories of dilute polymer solutions are of value, we should be able to apply the methods of statistical mechanics to the mean square radius of gyration of both polystyrene and polybutadiene (as well as its copolymers) to obtain an a priori calibration procedure. In developing our ideas in this direction, it should first be noted that the shape of an isolated molecule in dilute solution is strongly affected by the rigidity of the double bond in the *cis*-1,4 and *trans*-1,4 structures. Furthermore, the *cis*-1,4 and *trans*-1,4 structures themselves cause differences in chain characteristics; in particular, *trans*-1,4 chains will have a much more extended structure. The uniquely different characteristics of the chain statistics of polydiene chains was first recognized by Wall,²⁹ who computed the mean square end-to-end

distance \bar{r}^2 for 100% *cis*-1,4 and 100% *trans*-1,4 chains presuming rigid double bonds and freely rotating carbon-carbon single bonds. This work was extended by Markovitz³⁰ to include chains which contained mixtures of *cis*-1,4 and *trans*-1,4, as well as 1,2 and 3,4 units. Again with the free rotation hypothesis, Markovitz showed that generally

$$\bar{s}^2 = \frac{\bar{r}^2}{6}. \quad (6)$$

The free-rotation assumption has been relaxed in work by Christorazum,³¹ Au Chin-Tang and Ju Chuang-Lui,³² and, most recently, Mark³³ and Abe and Flory.³⁴

If we may presume that the elution volume in a GPC experiment is a unique function of molecular size or radius of gyration, then a polydiene chain will be eluted at the same volume as a polystyrene chain of the same size. Now the mean square radius of gyration \bar{s}^2 of a chain of single carbon-carbon bonds may be expressed as the product of the number of structural units N_{PS} in the chain, multiplied by a factor C_{PS} dependent upon the length of the carbon-carbon bond, the nature of the bond rotation hypothesis used, and steric hindrance. (C_{PS} is approximately twice the bond length squared, $2b^2$, in the freely rotating polyethylene model.) Now for a polydiene, \bar{s}^2 may be expressed by a similar product $N_{PD}C_{PD}$. At any elution volume, the number of structural units N_{PD} in a polydiene molecule and the number N_{PS} in a polystyrene chain will be related by

$$\bar{s}^2 = N_{PS}C_{PS} = N_{PD}C_{PD}. \quad (7)$$

If m_S is the molecular weight of a polystyrene unit and m_D the weight of a diene unit, then the molecular weight N_{PD} of the polydiene chain eluted at the same volume as a polystyrene of molecular weight M_{PS} is

$$M_{PD} = m_D N_{PD} = \frac{C_{PS} m_D}{C_{PD} m_S} M_{PS} = f M_{PS}. \quad (8)$$

The term m_D/m_S is simply computed from the known chemical formulae, being, say, 56/104 for polyisobutylene, 54/104 for polybutadiene, and 68/104 for polyisoprene.

It remains to compute the ratio C_{PS}/C_{PD} . If it is remembered that this is a ratio of factors and not the factors themselves, then it may not be as sensitive to the type of model used in its evaluation. Consideration of hindered rotation and steric hindrance increases the values of both C_{PS} and C_{PD} computed from simple free-rotation models.

The only extensive series of calculations of C_{PD} available for a variety of microstructures are those of Markovitz,³⁰ which unfortunately do contain both a free rotation and no steric hindrance assumptions. The f factors calculated for a series of polybutadienes and polyisoprenes of varying microstructure are summarized in Table III. It is to be noted that as C_{PD} is greater than C_{PS} , the f factors are much smaller than unity. We also include in this table predictions of f from eq. (5) for both THF and

TABLE III
f Factors for Different Polybutadienes and Copolymers

Polymer	<i>f</i> Factor		
	Calculated from eqs. (8) and (9) using Markovitz results	Calculated from eq. (5) for THF, $[\eta]$ - M data	Calculated from eq. (5) for toluene, $[\eta]$ - M data
Polystyrene	1.000	1.000	1.000
1,2-Polybutadiene	0.519	—	—
<i>trans</i> -1,4-Polybutadiene	0.158	—	—
<i>cis</i> -1,4-Polybutadiene	0.330	0.602	0.550
Alkyl lithium polybutadiene (35% <i>cis</i> , 55% <i>trans</i> , 10% 1,2)	0.217	0.611	0.5–0.6
Emulsion polybutadiene (10% <i>cis</i> , 70% <i>trans</i> , 20% 1,2)	0.208	—	0.65
Alkyl lithium SBR-1 (25% styrene, 27% 1,2, 25% <i>cis</i> , 48% <i>trans</i>)	0.325	—	—
Emulsion SBR (23.5% styrene and emulsion BR butadiene microstructure)	0.349	—	0.5–0.8 ~0.65
Alkyl lithium SBR-2 (48% styrene and alkyl lithium SBR butadiene microstructure)	0.436	—	—

toluene. The factors predicted from Markovitz statistics are considerably lower, approximately $1/3$ to $1/2$ of the $[\eta]$ predictions.

The above arguments may be readily extended to styrene copolymers of polydienes which possess a (mole) fraction κ of styrene units. It may be seen that if we again write s^2 as $N_{PD}C_{PD}$, then

$$M_{PD} = [\kappa m_S + (1 - \kappa)m_D]N_{PD} = \frac{C_{PS}}{C_{PD}} \frac{\kappa m_S + (1 - \kappa)m_D}{m_S} M_{PS} = fM_{PS}. \quad (9)$$

The factor in parenthesis is easily computed, and the problem again becomes one of evaluating C_{PS}/C_{PD} . The Markovitz theory may again be used with styrene units being considered equivalent to 1,2-addition diene units. Typical values of the *f* factor of eq. (9) for styrene–butadiene copolymers are given in Table III. The above argument may also be applied to copolymers with acrylonitrile or other monomers. These arguments are questionable in their application to block copolymers, for such polymer molecules probably do not form simple random coils in dilute solution.

While eqs. (8) and (9) are probably correct, difficulties arise in the above treatment because of the above-mentioned presumptions of the Markovitz

chain statistics results. Use of more sophisticated analyses such as those of Mark, Abe, and Flory^{33,34} would be desirable. Unfortunately, detailed calculations are not available. Even these would, however, be limited to theta solvents, i.e., solutions on the verge of precipitation, and the relative solvent quality will vary both from polydiene to polydiene and with the polydiene-styrene system.

Experimental

Introductory. The above-described methods of GPC calibration were contrasted by applying them to several commercial polymers and comparing the predicted number-average molecular weights with directly measured number-average molecular weights obtained on the same polymer with osmotic pressure measurements.

Materials. The polymers studied (see Table IV) included (1) commercial polystyrenes (Dow Styron 666 and Styron 678), investigated for the purpose of showing the validity of the instrument and calculational procedures to the study of polymers on which the calibration is based; (2) two commercial types of polybutadiene: (i) Phillips Cis-4 with a 93% *cis*-1,4 microstructure and (ii) alkyllithium-polymerized Firestone Diene 35 NF, 10% 1,2, 35% *cis*-1,4, 55% *trans*-1,4 microstructure polymer; (3) a series of styrene-butadiene copolymers with 23.5%-25% styrene (Texas-U.S. Chemical Synpol 1500, Phillips Solprene 300, Phillips Solprene 301); (4) 48% styrene SBR (Phillips Solprene 303).

Procedure. GPC refractive index-elution volume curves were obtained for the indicated solutions in tetrahydrofuran (THF) at 25°C. A bank of four Styragel columns of 10^6 , 10^5 , 10^4 , and 10^3 Å was used. Absolute molecular weights were computed by (1) using the polystyrene standard calibration curve, (2) using the THF $[\eta]$ - M data available, (3) using

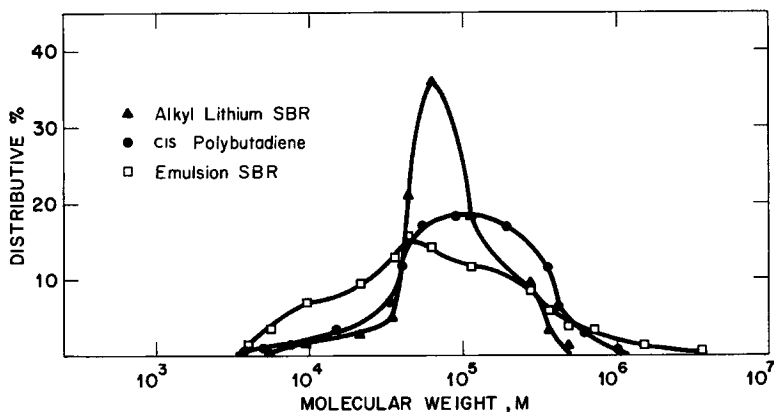


Fig. 1. Differential molecular weight distribution curves for three polymers: alkyl-lithium SBR (Phillips Solprene 301), emulsion SBR (Texas-U.S. Synpol 1500), and *cis*-polybutadiene (Phillips Cis-4).

TABLE IV
Molecular Weights for Polymers Determined by GPC and Membrane Osmometers

Polymer	M_w/M_n (GPC)	M_n (GPC polystyrene basis)	M_n (from eq. (8) or (9))	M_n (from eq. (5), toluene)	M_n (from eq. (5), THF)	M_n (osmom- eter)
Polystyrene (Dow Styron 666)	2.54	90,000	90,000	90,000	90,000	93,500
Polystyrene (Dow Styron 678)	3.08	76,340	76,340	76,340	76,340	78,800
<i>cis</i> -Polybutadiene (Phillips Cis 4)	3.36	191,000	63,000	105,000	115,000	118,500
Alkyl lithium polybutadiene (Firestone Diene 35 NF)	2.79	139,000	30,100	76,500	84,900	90,000
25% Styrene-butadiene copolymer (Phillips Solprene 300)	2.38	159,900	52,000	104,000	—	104,000
25% Styrene-butadiene copolymer (Phillips Solprene 301)	1.68	190,900	62,000	124,000	—	122,000
23.5% Styrene-butadiene copolymer (Texas-U.S. Synpol 1500)	5.40	106,000	37,000	69,000	—	72,000
48% Styrene-butadiene copolymer (Solprene 303)	1.45	113,600	49,500	—	—	102,000

toluene $[\eta]$ - M data as outlined, and (4) using the Markovitz statistical mechanical theory. These are summarized in Table IV.

Number-average molecular weights M_n were obtained directly from measurements with our Hallikainen Instruments membrane osmometer. The experiments were carried out in decalin at 25°C and the values of M_n computed from van't Hoff's law:

$$\lim_{c \rightarrow 0} \frac{\Pi}{cRT} = \frac{1}{M_n}. \quad (10)$$

The results are summarized in Table IV and Figure 1.

Discussion

Several observations may be made on the molecular weight distributions. Many of these are implicit in the earlier literature. The emulsion-polymerized butadiene-styrene (SBR) has a rather broad distribution compared to the alkylolithium-polymerized SBRs. The relative molecular weight distributions of the commercial polystyrene samples are of interest, as the breadths of their distribution are intermediate between those of the narrower alkylolithium SBR and the broad emulsion free-radical-polymerized SBR. The number-average molecular weights of the polybutadienes are in the same range as those reported by Bahary, Sapper, and Lane⁴ and by Ura-neck and Burleigh⁸ on similar commercial samples some years back, but there are differences.

With regard to the relative validity of the different GPC calibration procedures, as evaluated by comparing predicted and measured M_n , the Universal Calibration curve calculations from THF data does a rather good job with the polybutadienes. The toluene $[\eta]$ - M data also yield reasonably satisfactory predictions, but there are some individual discrepancies. The predictions from the simple Markovitz model are in considerable disagreement. It would seem from inspections of Tables III and IV, that an f factor of about 0.6 would be about correct for the polybutadienes or low-styrene SBRs studied.

One weakness in the above analysis approaches is the neglect of branching, particularly long-chain branching. It is well known that not only emulsion polymers are branched,^{2,4} but so also are commercial high-cis polybutadienes.⁹ The effect of introducing branching while not varying the degree of polymerization is to decrease the radius of gyration and intrinsic viscosity of a macromolecule.³⁵ Thus, if a GPC calibration curve is based upon linear polymer molecules, a branched macromolecule will be eluted at a lower elution volume than expected and its molecular weight underestimated. If, however, the calibration curve is based upon polymers with similar degrees of branching, this type of errors will be automatically compensated for. Hopefully, this will be the case for our $[\eta]$ - M based correlations. However, one would expect that branching differences might lead to different correlations for branched emulsion poly-

mers as opposed to linear alkylolithium polymers, though there is no evidence of this in our results. For further discussion, see Iwama, Abe, and Homma.⁹

TERNARY PHASE EQUILIBRIUM

Rationale

An experimental study of solubility of different polymers in THF and the phase separation in ternary solutions involving polystyrene, THF and a second polymer including polybutadiene and SBR has been carried out. These experiments resemble those of Dobry and Boyer-Kawenoki.³⁶ The purpose was two-fold, one from a purely scientific point of view, (1) to understand the physical chemistry of phase separation in polymer solutions and (2) to look at the conditions of phase separation and phase equilibrium in a system containing the same constituents as exists in a GPC column. It is the second application which is of the most interest to us here.

Experimental

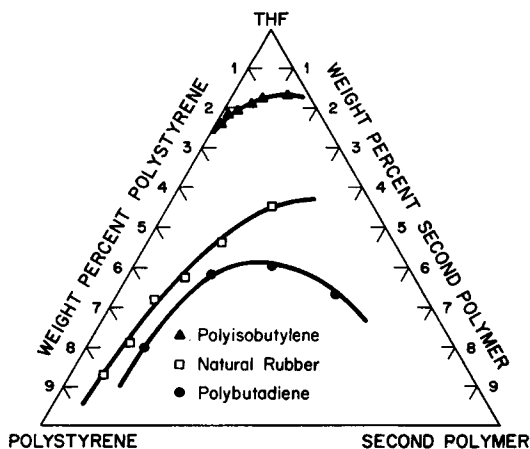
Materials. The polymers studied were (1) polyisobutylene; (2) 100% *cis*-polyisoprene (natural rubber); (3) 10% 1,2, 35% *cis*-1,4, 55% *trans* 1,4 alkyl lithium polymerized polybutadiene (Firestone Diene); (4) 25% styrene random butadiene-styrene copolymer (Phillips Solprene 301); (5) 48% styrene random butadiene-styrene copolymer (Phillips Solprene 303); (6) 25% styrene simple block styrene-butadiene (SB) (Phillips Solprene 1205); (7) 30% styrene mixed block styrene-butadiene-styrene (SBS) copolymer (Shell Kraton 1101). Dow Styron 678 was the polystyrene and reagent grade THF the solvent used. The polyisobutylene- and polyisoprene-polystyrene-THF systems were also studied for purposes of comparison.

Procedure. The solubilities of the individual polymers in THF was first studied. Mixtures of known concentrations were prepared from stock solutions and THF solvent. They were maintained at 25°C and examined about one week later for distinct layers or phase separation. Gradual variations in concentration were carried out until phase separation was observed. Ternary phase equilibrium diagrams were constructed for the different three component systems. These are summarized in Figures 2a and 2b.

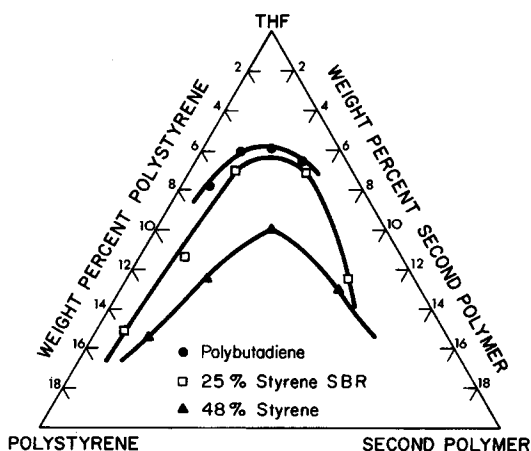
Discussion

The solubilities of the different polymers in THF could be nicely correlated with difference in solubility parameter.³⁷ This is summarized in Table V. The polystyrene had the greatest solubility, followed (in order of decreasing solubility) by polybutadiene, polyisoprene, and polyisobutylene. This is also the order of decreasing aromatic character.

The results of the ternary-phase equilibrium study showed the following (see Figs. 2a and b):



(a)



(b)

Fig. 2. Ternary-phase diagrams for polystyrene-THF-second polymer system. The polybutadiene and SBRs are commercial alkyl lithium-polymerized polymers and random copolymers.

1. Greater incompatibility of polymers with the polystyrene-THF system that have the greatest difference in solubility parameter, or lack of saturated or aromatic character. Thus, polyisobutylene is most incompatible, followed by polyisoprene, polybutadiene and butadiene-styrene copolymer. Copolymerization thus did increase the compatibility of one polymer in solution of THF with a homopolymer. For example, definite phase separation was observed with the 2% polystyrene-polybutadiene solution while for the 25% SBR-polystyrene, the total polymer concentration had to be equal or greater than 7%; and for 48% styrene SBR-polystyrene, total polymer concentration had to be equal or greater than 10%.

2. Blocking in the 25% showed little or no effect on phase separation.

TABLE V
Solubility of Polymers in Tetrahydrofuran

Polymer	Solubility parameter δ , (cal/cc) ^{1/2}	Solubility
Polyisobutylene	7.8-8.1	~2.5%
Natural rubber	7.9-8.1	~3.5%
Polybutadiene	8.3-8.6	~10.%
25% Styrene-butadiene copolymer (similar to Solprene 301)	8.4-8.7	—
48% Styrene-butadiene copolymer (similar to Solprene 303)	8.6-8.7	—
Polystyrene	9.1-9.15	large (>20%)
Tetrahydrofuran	9.1	100%

3. A mixture of any two copolymers in the THF showed no phase separation up to and including 9.5% of both copolymers.

These phase equilibria studies are valuable in understanding the interaction between polymer, polystyrene gel, and THF, which has been neglected in prior studies of GPC. Considerable differences were observed in phase equilibrium behavior involving polystyrene and THF with polybutadiene and with the copolymers. One interesting aspect is that phase equilibria in ternary polymer solutions can be related to the size of the polymer molecules in dilute solution. This comes about through the idea of the "theta temperature."¹⁴ The more incompatible a system, the less swollen a macromolecule will be and the smaller its radius of gyration in such an environment. One can see that as the amount of butadiene in the copolymer increases, the ternary system becomes increasingly incompatible. This means that the polybutadiene or copolymers of a given molecular weight will elute later in actuality than in theory. The magnitude of such effects is not known.

THIN-LAYER CHROMATOGRAPHY

Rationale

The heterogeneity of copolymers has received increasing attention in recent years, and butadiene-styrene copolymers have been among those studied.^{38,39} The experiments of Inagaki, Matsuda, and Kamiyama¹⁷⁻¹⁹ suggest that this is a useful technique for such studies. We report the results of some of our early experiments here (compare Quisenberry⁴⁰).

Experimental

Materials. Several polymers were studied in this experiment. These included poly(methyl methacrylate), polystyrene, 48% styrene-butadiene-

styrene copolymer (Phillips Solprene 303), 25% styrene SBR (Phillips Solprene 301), two polybutadienes (high *cis*-1,4, Phillips; *Cis*-4 and alkyl-lithium mixed microstructure, Firestone Diene 35 NF) and a polyisobutylene (Enjay Vistanex).

Procedure. Merck silica gel G (containing gypsum) was applied as the stationary phase on a 20 cm \times 10 cm thick glass plate. The thickness of the layer was adjusted to 250 microns. The plate was activated by heating in an oven at 60°C for 1 hr. Stock solutions for TLC tests were 1% toluene solutions. With the aid of a microsyringe, spots containing about 25 micrograms of each polymer were formed on the layer at a point 2 cm from the edge of the glass. Then the plate was placed in a sandwich chamber allowing a 5-cm solvent migration. After the plate was removed from the solvent and allowed to dry, a 1% methanol solution of iodine was sprayed onto the silica gel, marking the position of the polymer as brown spots. Guided by published rules¹² for the selection of eluotropic series, several reagent-grade solvents with different dielectric constants were chosen. Among these were acetone, methylethyl ketone, ethyl acetate, pyridine, THF, toluene, diethyl ether, and cyclohexane. Initially mixed solvents and mixed solvents produced by solvent gradients during elution were also studied.

In the case of the diene-containing polymers, two spots were observed, one generally lighter always located at zero. Since the diene polymers dissolve in several of the solvents used, it is very unlikely that the polymers always remain at the starting position. It was also found that extracting out all of the antioxidants and other additives did not affect the spots at the origin. However, premasticating the diene polymers was found to lighten these spots. It was concluded that they were crosslinked polydiene gel.

Results and Discussion

The reduced distances moved by the spots are designated by R_f . The R_f values of the above listed polymers in some of the different solvents cited above are given in Table VI. The fact that different solvents develop the particular polymers to different extents is striking. It is seen that poly(methyl methacrylate) may readily be separated from polystyrene and both of these from polybutadiene and polyisobutylene. The butadiene-styrene copolymer may be separated from either the polystyrene or the polybutadiene. Ethyl acetate and to a lesser extent methylethyl ketone and diethyl ether would seem to be starting points worthy of further study. Some effort was made using ethyl acetate as a basis. Mixtures of ethyl acetate and other solvents were evaluated as well as gradient elution-produced mixtures. The ethyl acetate-toluene elution gradient results show promise in their separation ability. Only the polybutadienes of different microstructure seem too difficult to separate.

TABLE VI
 R_f Values for Different Polymers in a Eluotropic Series of Solvents

Solvent	Poly(methyl methacrylate) (du Pont Lucite)	Polystyrene (Dow Styron 678)	48% Styrene-butadiene copolymer (Phillips Solprene 303)	25% Styrene-butadiene copolymer (Phillips Solprene 301)	Polybutadiene (Firestone Diene)	Polybutadiene (Phillips Cis-4)	Polyisobutylene (Enjay Vistanex)
Acetone	0.80-1.00	0	0	0	0	0	0
Methylethyl Ketone	0.90-1.00	0.50-0.54	0.30-0.40 ^a	—	0	0	0
Ethyl acetate	0.86-1.00	0.88-1.00	0.22-0.32 ^a	0	0	0	0
Pyridine	0.74-1.00	0.78-0.86	0.68-0.80 ^a	—	0.54-0.66 ^a	0.54-0.66 ^a	0
THF	0.82-1.00	0.76-0.90	0.64-0.80 ^a	—	0.44-0.70 ^a	0.50-0.74 ^a	0.38-0.56
Toluene	0	0.86-1.00	0.80-1.00 ^a	0.89-1.00 ^a	0.52-1.00 ^a	0.70-1.00 ^a	0
Diethyl ether	0	0	0.88-1.00 ^a	0.81-1.00 ^a	0.80-1.00 ^a	0.80-1.00 ^a	0
Cyclohexane	0	0	0	0	0	0	0.94-1.00
50% Ethyl acetate-50% diethyl ether	—	0.88-1.00	0.88-1.00 ^a	0.82-1.00 ^a	0.95-1.00 ^a	0.95-1.00 ^a	—
50% Ethyl acetate-50% toluene	—	0.86-1.00	0.89-1.00 ^a	0.84-1.00 ^a	0.76-1.00 ^a	0.71-1.00 ^a	—
75% Ethyl acetate-25% toluene (elution gradient)	—	0.90-1.00	0.24-0.28	0.17-0.24 ^a	0.00-0.18 ^a	0.00-0.20 ^a	—
33% Ethyl acetate-67% toluene (elution gradient)	—	0.90-1.00	0.25-0.33 ^a	0.18-0.32 ^a	0.04-0.26 ^a	0.10-0.22 ^a	—

^a Also spots at zero.

CONCLUSIONS

1. An experimental study of the application of the GPC Universal Calibration Curve philosophy to determine the molecular weight distribution of polybutadienes and butadiene-styrene copolymers was carried out. It was found that computations based upon statistical mechanical considerations led to considerable error. The procedure explicitly recommended by the Strasbourg group works rather well. It was also found that utility of toluene $[\eta]$ - M data in place of the system solvent (THF) works well. For polybutadiene and low-styrene SBRs, the correct molecular weights are about 60% of the values found from the polystyrene calibration curve.

2. In carrying out the above study, molecular weight distributions of several commercial polymers were reported.

3. Ternary-phase equilibrium studies of the system THF-polystyrene-arbitrary polymer have been reported and phase diagrams constructed. The results are used to suggest possible three-component interactions in the GPC crosslinked polystyrene gel support. Possible implications to GPC operation are indicated.

4. TLC studies have been made of the butadiene-styrene system and other polymers. Several solvents and solvent mixtures have been reported. Several solvents and solvent mixtures have been reported. Preliminary experiments indicate the possible utility of the ethyl acetate-toluene system proceeding via gradient elution.

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