

## Analysis of a Living Polymer Mixture by Use of Small-Molecule Gel Permeation Chromatography

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### Synopsis

A procedure is presented for determining the concentration of polymer lithium, alkyl lithium, and monomer by use of small-molecule GPC. The system poly(styryllithium), butyllithium, styrene, and benzene are used to illustrate the method. The method as presented has a lower limit on the direct measurement of butyllithium concentration of 0.00005 molar. If the total carbon-bound lithium is to be determined, the limit can be appreciably lowered. The styrene-benzene separation was obtained for concentration ratios of 1:5 or greater. Several suggestions are presented for improving these analyses.

### INTRODUCTION

The concentration of *n*-butyllithium in a solvent may be determined by the titration methods of Uraneck et al.,<sup>1</sup> Kolthoff and Harris,<sup>2</sup> Gilman and Heubien,<sup>3</sup> or Gilman and Cartledge,<sup>4</sup> by UV absorption, or by terminating the mixture with water and determining by gas chromatography the amount of butane formed. Since titration methods measure the total carbon-bound lithium concentration, they cannot be used to determine the amount of unreacted alkyl-lithium in a polymerization mixture. Termination with water and subsequent analysis for *n*-butane has been used by Hsieh,<sup>5</sup> Landon and Anthony,<sup>6</sup> and Porter et al.,<sup>7</sup> and UV absorption has been used *in situ* in high-vacuum reaction systems to measure the polymer lithium or *n*-butyllithium concentration. The basic problem with the former method is the necessity of accurately weighing 20-30 mg of reference gas, usually isobutane, and injecting it into the sample to be analyzed. The difficulty with the use of UV absorption, except *in situ*, is that of obtaining a true sample in the UV detector since polymerization would occur in the sample line from the reactor to the detector. Hence, there existed a need for another method for analyzing for butyllithium in reacting systems.

The use of the disulfide cleavage reactions combined with small-molecule gel permeation chromatography (GPC) was, therefore, investigated for the reaction system of styrene, benzene, *n*-butyllithium, and poly(styryllithium). When this mixture is terminated with a disulfide, a thioether and an alkyl- or aryllithium mercaptide is formed by the reaction



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where R is an alkyl or aryl group and R'Li is either the poly(styryllithium) or *n*-butyllithium. In the proposed procedure, the concentration of the butyl thioether or the polymer thioether is measured instead of the concentration of mercaptide, which was measured in the titration method proposed by Uranek et al.<sup>1</sup> Hence, if the disulfide contains a suitable chromophore, the concentration of living polymer as well as that of the *n*-butyllithium can be determined by UV absorption.

### ANALYTICAL EQUIPMENT

A Water's Model 202/401 analytical liquid chromatograph equipped with UV and RI detectors was used with 4-ft columns and with a continuous flow of tetrahydrofuran (THF) through the reference side of both detectors. The GPC columns were packed with neutral styrene-divinylbenzene copolymer particles manufactured by the Hamilton Company. This gel was 8.25% crosslinked with an average pore size of 18 Å. The size distribution of the spherical gel particles, as evaluated by a Coulter Counter Model TA, was such that 80% were in the range of 20 to 40 microns in diameter. In order to pack a column with this gel without severe agglomeration, the gel was stirred in a hot, concentrated sodium hydroxide solution (approximately pH 13) for 10 hr. The excess sodium hydroxide was neutralized with hydrochloric acid and the resulting salt solution decanted from the gel. The gel was washed in an upflow of distilled water to remove the salt and then was batch washed on a frittered glass filter with distilled water. This procedure decreased the amount of agglomeration but did not eliminate it. Acetone washes were used to remove the water prior to suspending the gel in a solvent mixture whose density had been adjusted so as to maintain the suspension. Two columns were then packed with this gel.

### SELECTION OF A DISULFIDE

Three major criteria had to be satisfied in the selection of a disulfide reagent for determining the *n*-butyllithium and polymer lithium concentrations: (1) the disulfide has to have some property (refractive index or ultraviolet absorption) that permitted it to be detected in low concentrations; (2) the disulfide has to be sufficiently different in size from the thioether that would be formed; and (3) the disulfide could not participate in any side reactions with alkyl-lithium compounds. With these criteria in mind, the two Hamilton columns were calibrated with the compounds listed in Table I, and the calibration curve is presented in Figure 1. A linear least-squares analysis was used to provide the best straight line through the data, and the equation of the line is

$$\text{elution volume} = 88.6 - 32.6 \log (\text{carbon number}). \quad (2)$$

Of special interest is the fact that Hendrickson and Moore,<sup>8</sup> Hendrickson,<sup>9</sup> and this study found that branched molecules eluded at volumes which closely correspond to those which would have been predicted for linear isomers of the same chemical species.

### DETERMINATION OF THE POLYMER CONCENTRATION

Table II lists some disulfides, the derived thioethers, and the chromophores they contain. Of all the listed chromophores, the nitro (NO<sub>2</sub>) group is the most

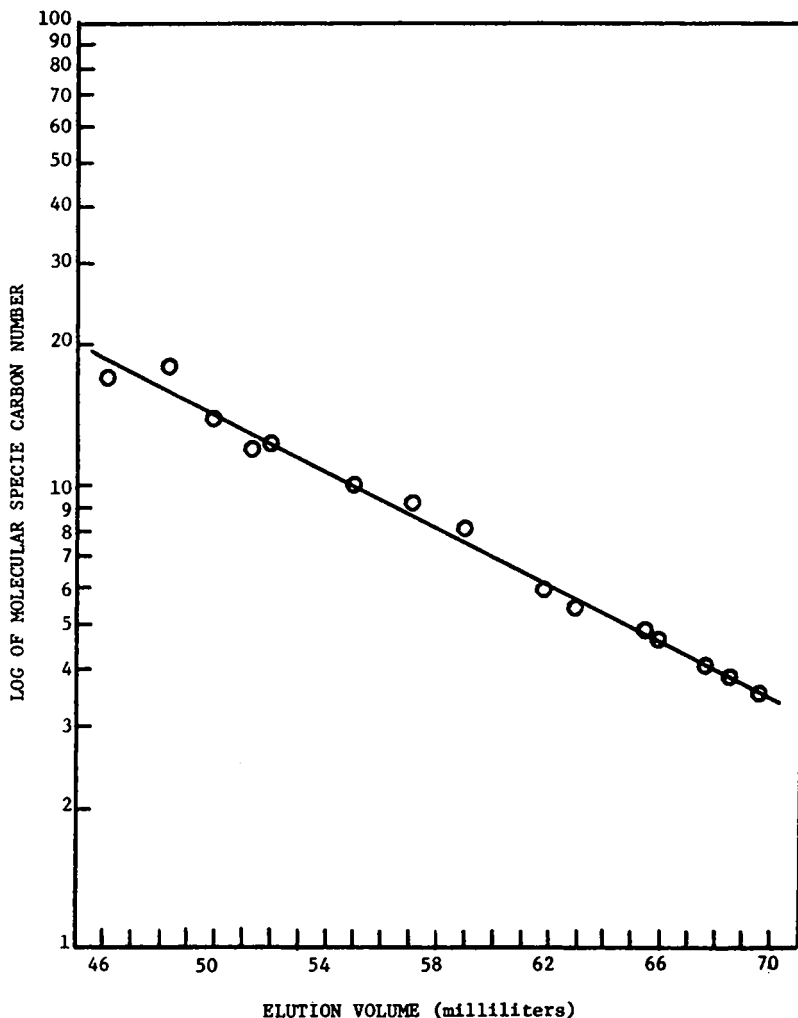


Fig. 1. Calibration curve of the Hamilton gel columns.

desirable in terms of detection by ultraviolet absorption. Unfortunately, nitro-substituted aryl disulfides are not suitable because of side reactions with *n*-butyllithium. Another satisfactory chromophore is the benzene ring since it absorbs ultraviolet light of 254 nm wavelength, but it cannot be used to selectively detect disulfide-terminated polymer molecules for polystyrene because it also contains the benzene ring structure. The last class of organic disulfides considered was the alkyl disulfides. Only compounds containing tertiary carbon atoms bonded to the sulfur-sulfur linkage were considered since the acidic nature of  $\alpha$ -hydrogen atoms can lead to lithium-hydrogen interconversions instead of the desired cleavage reaction. The sulfur atom in a thioether has a strong molar absorption ( $\epsilon_{\max} = 1600$ ) at 215 nm, but this wavelength is outside the range of the ultraviolet absorption detector for this instrument.

Because the Waters differential ultraviolet detector could not be easily modified to function at 215 nm, the following method which was not tested is proposed. By terminating two samples, one with water and one with disulfide, a nonflowing type of spectrophotometer could be utilized. Both samples would be passed

TABLE I  
GPC Results with 8.25% Crosslinked Hamilton Gel

Compound	Molecular size, carbon units	Peak elution volume, ml	Peak width, <sup>a</sup> ml	Plate Count, per ft
Benzene	3.55	70.6	5.35	348
Cyclohexane	3.92	69.6	5.54	316
Toluene	4.08	68.6	5.29	336
Isoprene	4.64	66.8	5.24	325
Styrene	4.85	66.4	5.29	314
Nitrobenzene	5.46	63.9	5.17	305
<i>n</i> -Hexane	6.0	62.8	4.86	333
<i>n</i> -Octane	8.0	59.9	4.86	303
<i>p</i> -Tolyl disulfide	9.26	58.0	4.8	292
Decane	10.0	55.9	4.18	357
Dodecane	12.0	52.9	3.94	361
3-Nitrophenyl disulfide	12.02	52.3	4.39	283
Tetradecane	14.0	50.8	4.01	321
<i>t</i> -Octyl disulfide	18.0	49.3	4.49	241
Bis(2,4-dinitrophenyl) disulfide	17.28	47.1	4.18	253

<sup>a</sup> Measured between the leading and trailing tangents which intercept the baseline.

TABLE II  
Comparative Sizes of Disulfides and Their Desired Thioether Derivatives

Disulfide	Estimated molecular size, carbon units	Desired thioether structure	Estimated thioether size, carbon units	Chromophores	
				Disulfide	Thioether
Phenyl disulfide	7.7	$\phi$ -S- <i>n</i> Bu	7.85	$\phi$ , S-S	$\phi$ , S-C
Naphthyl disulfide	8.98	$\phi\phi$ -S- <i>n</i> Bu	8.49	$\phi\phi$ , S-S	$\phi\phi$ , S-C
<i>p</i> -Totyl disulfide	9.26	CH <sub>3</sub> -S- <i>n</i> Bu	8.63	$\phi$ , S-S	$\phi$ , S-C
<i>t</i> -Butyl disulfide	10.0	<i>t</i> (C <sub>4</sub> H <sub>9</sub> )-S- <i>n</i> Bu	9.0	S-S	S-C
3-Nitrophenyl disulfide	12.02	NO <sub>2</sub> - $\phi$ -S- <i>n</i> Bu	10.1	NO <sub>2</sub> , $\phi$ , S-S	NO <sub>2</sub> , $\phi$ , S-C
Pentylphenyl disulfide	16.8	C <sub>5</sub> H <sub>11</sub> - $\phi$ -S- <i>n</i> Bu	12.4	S-S	S-C
Bis(2,4-dinitrophenyl) disulfide	17.28	(NO <sub>2</sub> ) <sub>2</sub> - $\phi$ -S- <i>n</i> Bu	12.64	NO <sub>2</sub> , $\phi$ , S-S	NO <sub>2</sub> , $\phi$ , S-C
<i>t</i> -Octyl disulfide	18.0	<i>t</i> (C <sub>8</sub> H <sub>17</sub> )-S- <i>n</i> Bu	13.0	S-S	S-C
<i>t</i> -Dodecyl disulfide	26.0	<i>t</i> (C <sub>12</sub> H <sub>25</sub> )-S- <i>n</i> Bu	17.0	S-S	S-C

through the columns and the polymer fractions collected. After evaporating the THF from both samples and dissolving them in a suitable solvent, e.g., isooctane, the optical densities at 215 nm could be measured. The difference in the two values would be proportional to the concentration of carbon-sulfur bonds.

### BUTYLLITHIUM AND TOTAL CARBON-LITHIUM ANALYSIS

On examination of Tables I and II, one observes that *p*-tolyl disulfide, which was used by Uranek et al.,<sup>1</sup> cannot be used with these columns since the thioether

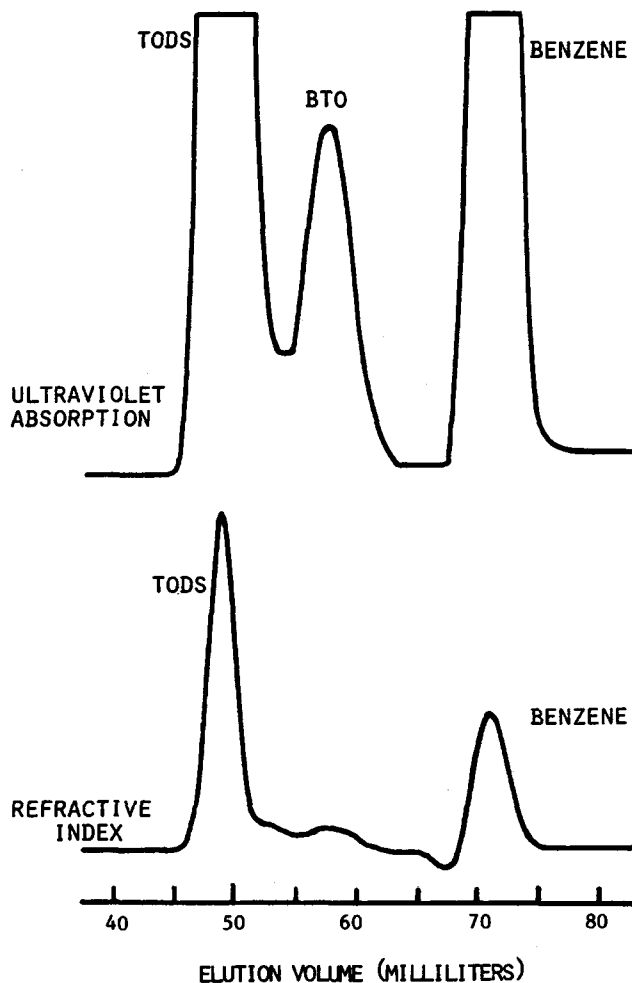


Fig. 2. Chromatogram of *n*-butyllithium terminated with TODS. Reaction conditions: reactants at 10°C. Analysis conditions: 2 4-ft Hamilton columns; 0.73 ml/min THF flow rate; ambient temperature; detector sensitivities RI-A64X, UV-R08.

and disulfide are approximately the same size. Pentylphenyl disulfide, *t*-octyl disulfide, or *t*-dodecyl disulfide, however, could be used. Of these three compounds, only *t*-octyl disulfide (TODS) and *t*-dodecyl disulfide are commercially available. TODS was chosen because the large number of isomers of *t*-dodecyl disulfide and its thioether could contribute to an excessive broadening of the GPC chromatogram.

Figure 2 illustrates a trace of butylthioether (BTO) and TODS. The absence of a differential refractive index (*DRI*) trace for the BTO and that the BTO trace is small at the 254 nm wavelength are particularly significant. This mixture was prepared by injecting 1 ml of 2.96 molar *n*-butyllithium (in benzene) into 1.5 ml of pure TODS. Both of the reactants had been chilled to 10°C. The resulting reaction mixture had a BTO concentration of 1.18 moles/l. Because the mercaptide is insoluble in THF, the mixture needs to be diluted with THF to precipitate the mercaptide prior to injecting the sample into the GPC. A 0.1-ml aliquot of the mixture was added to 10 ml THF, and approximately 1

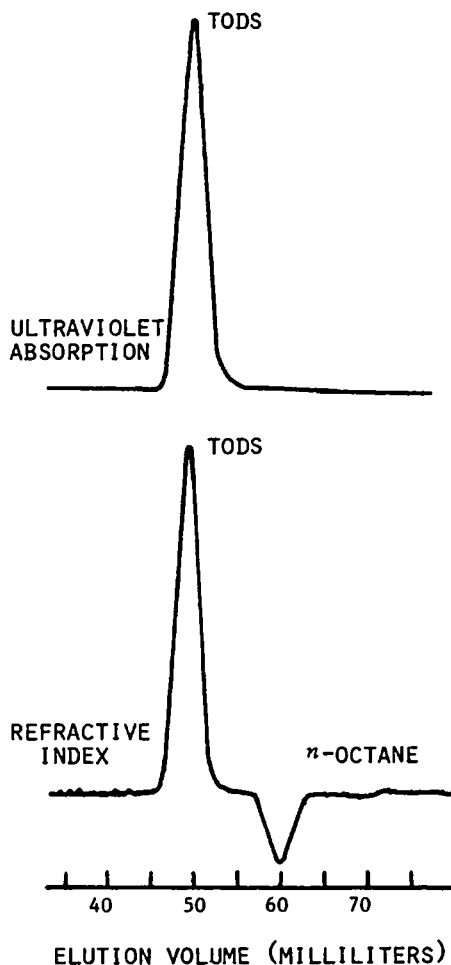


Fig. 3. Chromatogram of the TODS-*n*-octane mixture. Conditions: 2 4-ft Hamilton columns 1.04 ml/min THF flow rate; ambient temperature; detector sensitivities RI-A4X, UV-R04.

ml of this supernatant was injected via a 2-ml sample loop. Hence,  $1.3 \times 10^{-5}$  mole of BTO was injected into the GPC for analysis. Inspection of the resulting trace suggests that the minimum detection quantity of BTO would be approximately  $6.5 \times 10^{-6}$  mol. This is one half of the BTO which was present in the sample for the chromatogram illustrated in Figure 2. Hence, a lower limit for measurement of butyllithium in the original sample is of the order of  $5 \times 10^{-5}$  molar. This limit could be lowered by operating the UV detector at 215 nm wavelength or by selecting a disulfide that contains a nonreacting chromophore that absorbs more strongly at 254 nm.

The concentration of total carbon-bound lithium can be determined by measuring the reduction in the area of the TODS peak. This method would lower the minimum measurement level for butyllithium. Such a method could utilize the fact that TODS has a higher molar absorption at 254 nm than does BTO, or that a DRI trace is obtained for TODS. In order to permit relative decreases in the TODS concentration to be measured, *n*-octane was used as a reference

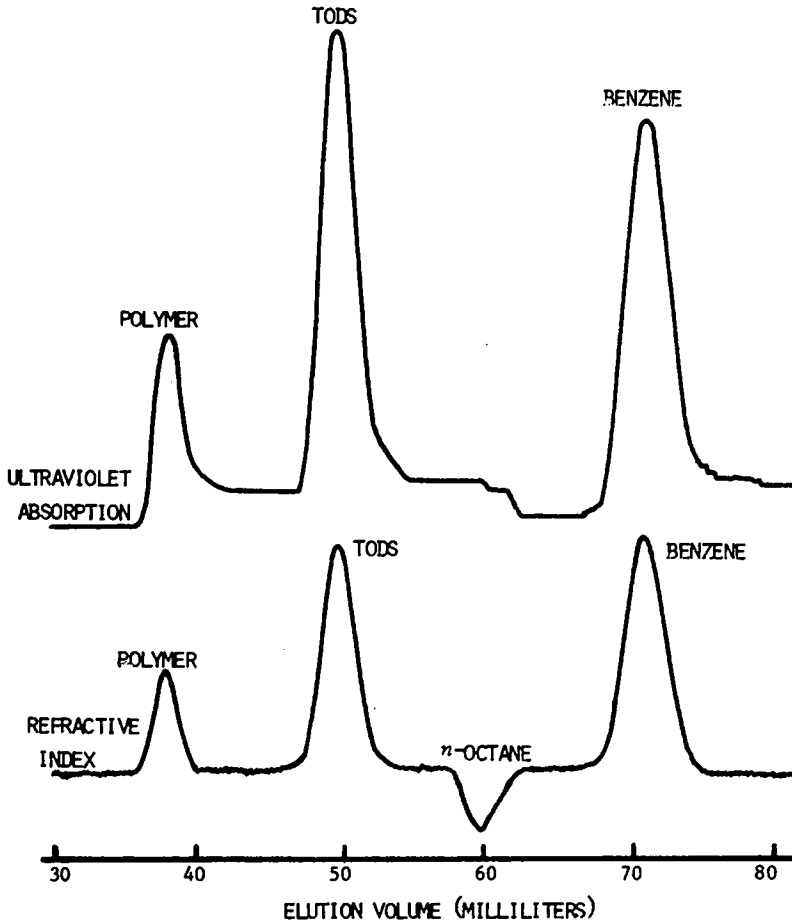


Fig. 4. Chromatogram of polymerization mixture. Conditions: 2 4-ft Hamilton columns; 0.77 ml/min THF flow rate; ambient temperature; detector sensitivities RI-A4X, UV-R16.

component. Figure 3 shows both the DRI and DUV traces for a standard mixture. Since *n*-octane has only a DRI trace, the DRI traces of both compounds were used to measure the decrease of TODS. The procedure then is as follows. Prepare a standard mixture of TODS and *n*-octane. Terminate the reaction mixture or a butyllithium solution by injection into the standard mixture. Analyze the resulting mixture. The decrease in the area ratios of the TODS/*n*-octane relative to the standard mixture gives the concentration of total carbon-bound lithium. A calibration curve would be generated by reacting known weights of *n*-butyllithium solution with the standard mixture of TODS and *n*-octane. A comparison of Figures 3 and 4 illustrates this analytical method. The concentration of BTO was too low for DUV detection, but there was a measurable decrease in the area ratio of TODS/*n*-octane.

If the BTO concentration is large enough, or if another butylthioether with a lower detection limit is used, then this technique could be used to determine the active polymer concentration in a reaction mixture. The method would consist of determining the decrease in the area of the disulfide chromatogram and subtracting the area of butyl thioether peak.

## STYRENE-BENZENE ANALYSIS

To determine the monomer conversion by small-molecule GPC, the benzene-styrene separation for an equimolar mixture is shown in Figure 5. Since one of the desired results was a single-pass determination of all pertinent experimental values, the two Hamilton gel columns were placed in series with three 4-ft linear columns with exclusion limits of  $10^6$  Å. Figure 6 illustrates the results

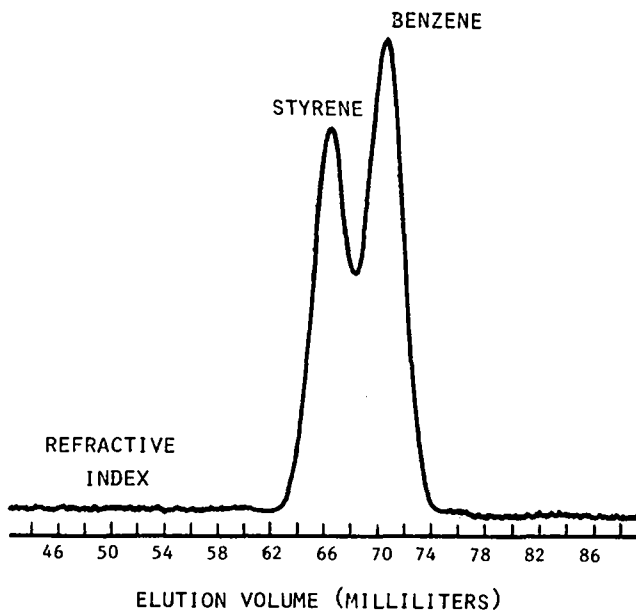


Fig. 5. Chromatogram of benzene-styrene separation on Hamilton gel columns. Conditions: 2 4-ft Hamilton columns; 1.03 ml/min THF flow rate; ambient temperature; RI detector sensitivity A4X.

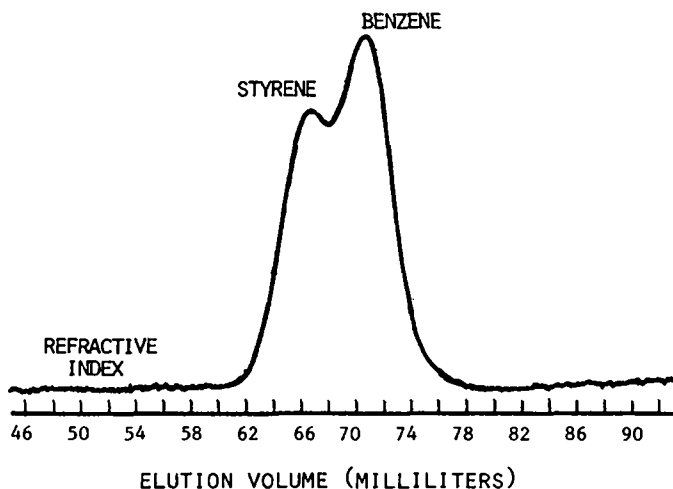


Fig. 6. Chromatogram of benzene-styrene separation on Hamilton and Waters columns. Conditions: 2 4-ft Hamilton columns and 3 4-ft Waters columns in series; 1.03 ml/min THF flow rate; ambient temperature; RI detector sensitivity A4X.



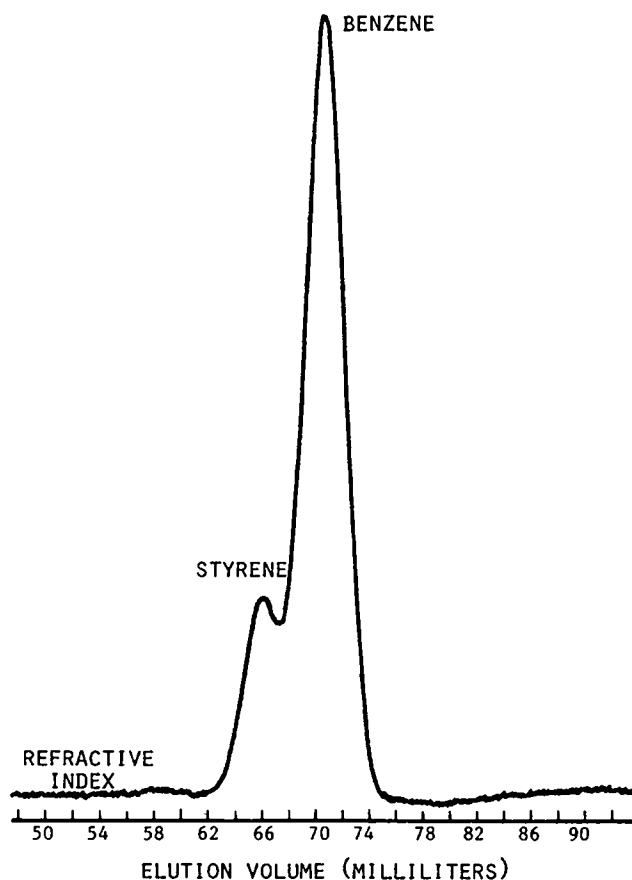


Fig. 7. Chromatogram of 1.5 molar styrene in benzene. Conditions: 2 4-ft Hamilton columns; 0.98 ml/min THF flow rate; ambient temperature; RI detector sensitivity A4X.

obtained for the same mixture as was used to obtain Figure 5. It is apparent that axial dispersion in the  $10^6$  columns is excessive for the smaller molecules. For mixtures with styrene concentrations of 1.5 molar or less, as illustrated in Figure 7, considerable interference is obtained between the DRI trace of styrene and benzene. A better resolution in the benzene-styrene separation could be obtained by columns with higher efficiencies, more columns with the same plate count, lower THF flow rates, and/or recycle analyses. Some of these methods are discussed in more detail by Cox.<sup>10</sup>

## CONCLUSIONS

A method has been presented for determining the concentrations of an alkyl-lithium, polymer lithium, and monomer in a reaction mixture by use of the butyllithium, poly(styryllithium), benzene, and styrene system. Due to physical limitation of the instruments in this laboratory, this analysis was done by analyzing for the butyllithium and total lithium concentration and then analyzing the styrene concentration by use of benzene as a reference component. However, chromophores and equipment modifications are recommended which would extend the range of this basic technique.

The authors particularly appreciate the assistance of Mr. Matt C. Arrington of Dow Chemical Co., Texas Div., who packed the GPC columns. The support of the Department of Chemical Engineering, Graduate College, and Texas Engineering Experiment Station are also appreciated.

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Received May 23, 1974

Revised July 18, 1974