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Synthesis and Characterization of Styrene-Isoprene Diblock Copolymers

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ABSTRACT

A simple reusable apparatus for the synthesis of up to 40 g quantities of poly(styrene-*b*-isoprene) diblock copolymers of reasonably low (1.2 to 1.5) polydispersity has been described. The diblock copolymers synthesized were characterized by gel permeation chromatography (GPC), membrane osmometry, viscosimetry, and nuclear magnetic resonance (NMR) spectroscopy. Number-average molecular weights (\bar{M}_n) calculated from the raw GPC chromatographs of the diblock copolymers using the summation method and \bar{M} versus elution volume plots for polystyrene and polyisoprene standards agree well with those measured experimentally with osmometry. It is suggested that for polydisperse block copolymers this method is simpler than the use of a universal calibration curve. Mark-Houwink constants K and α for polyisoprene having 18% (1,2-), 66% (3,4-), and 16% (1,4-) microstructure were found to be 3.2×10^{-4} dL/g and 0.67, respectively, in THF at 25°C. In toluene at 30°C, $K = 2.0 \times 10^{-4}$ dL/g and $\alpha = 0.7$ were obtained. The diblock copolymers had 26% (1,2-), 60% (3,4-), and 14% (1,4-) microstructure in the isoprene segments, and the values of K and α for these copolymers ($PS > 50\%$, $\bar{M} > 20.0 \times 10^3$) in THF at 25°C were 9.0×10^{-5} dL/g and 0.75. For $\bar{M} < 20.0 \times 10^3$ the value of α was 0.5. The experimental values of $[\eta]$ were

found to be lower than those calculated theoretically, presumably due to the polydisperse nature and the biellipsoidal configuration of the diblock copolymers.

INTRODUCTION

The synthesis and characterization of poly(styrene-*b*-isoprene) diblock copolymers has been the subject of numerous review articles and books [1-5]. It is well established that living anionic sequential addition polymerizations allow synthesis of predetermined and well-controlled structures. In spite of the apparent simplicity of the living polymer technique, the preparation of block copolymers is extremely difficult in practice as it generally involves rigorous purification of reagents using special reaction flasks under high vacuum [6, 7]. In this communication we describe a simple reusable apparatus which allows the syntheses of poly(styrene-*b*-isoprene) diblock copolymers of reasonable polydispersity (\bar{M}_w/\bar{M}_n) ratios.

EXPERIMENTAL

Materials

Styrene (Fisher Chemical Co.) and isoprene (Aldrich Chemical Co.) were stored over calcium hydride (CaH_2) and degassed on a vacuum line for 1 week. These were then distilled under vacuum, the head and tail fractions being discarded.

Tetrahydrofuran (THF; BDH Omnisolv) was kept over CaH_2 and degassed for 1 week. It was refluxed with and distilled over a sodium mirror prior to use.

n-BuLi solution in hexane (1.6 M, Aldrich Chemical Co.) was used as received. Polystyrene standards of molecular weights ranging between 900 and 1.8×10^6 were purchased from Pressure Chemical Co.

Polyisoprene samples of different molecular weights were prepared by polymerizing isoprene at 25°C in THF with *n*-BuLi as initiator.

Poly(styrene-*b*-isoprene)

Block copolymers were synthesized via anionic living polymerization by employing the sequential monomer addition technique. The apparatus used in these polymerizations is shown in Fig. 1. Initially it was washed sequentially with sulfochromic acid, water, and methanol and dried in an oven at 150°C. Prior to its use it was rinsed with an *n*-BuLi solution (excess). Addition of monomers, solvent,

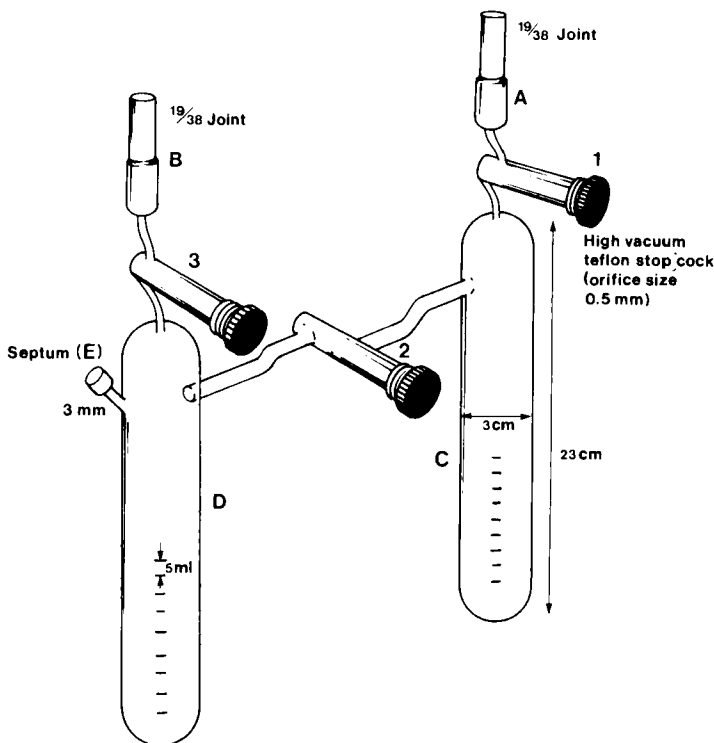


FIG. 1. Schematics of the polymerization apparatus.

and *n*-BuLi to the apparatus was achieved as follows. With Stopcocks 2 and 3 closed and Stopcock 1 in the open position, the apparatus was connected to the vacuum line at Joint A. Isoprene monomer (10 to 60 mL) was distilled through A into Ampule C which was immersed in liquid nitrogen. After closing Stopcock 1, the apparatus was disconnected from the vacuum line. With Stopcocks 1 and 2 closed, and Stopcock 3 open, the apparatus was connected to the vacuum line at Joint B. Styrene (10 to 40 mL) and then THF (25 to 40 mL) were distilled into Ampule D which was immersed in liquid nitrogen. Stopcock 3 was then closed and the apparatus was removed from the vacuum line. Once the contents of Ampule D had reached room temperature, they were thoroughly mixed. The resultant styrene solution in THF was now brought to -100°C and the desired amount of *n*-BuLi was added to it through the septum at E. Polymerization of the red solution was carried out at -100°C for about 30 min while maintaining Ampule D at -100°C . Isoprene monomer in Ampule C was then transferred to Ampule D by opening Stopcock 2. When all the isoprene had been trans-

ferred to Ampule D, Stopcock 2 was closed. A color change from red to yellow in the contents of Ampule D indicated that cross-initiation of isoprene had been completed. The yellow solution was removed from the cooling bath and polymerization was allowed to proceed at ambient conditions for 1 h. The reaction was terminated by adding methanol till the yellow color disappeared. The solution was quantitatively removed from Exit E and methanol was added to precipitate the polymer. The precipitated polymer was filtered through a weighed sintered glass filter, thoroughly washed with methanol, and dried in a vacuum oven at 60°C to a constant weight. Twenty to 40 g of block copolymers could be easily synthesized using this apparatus.

Polymer Characterization

Nuclear Magnetic Resonance (NMR)

Proton NMR spectra of the products were measured at 80 and 250 MHz using Bruker WP80/54 and WM 250 instruments. The 80 MHz spectra in deuteriochloroform were used for the determination of polymer composition. Proton spectra in deuterated benzene at 250 MHz were used in establishing the microstructure of the isoprene segments; carbon-13 spectra was also useful in this regard. Tetramethylsilane was used as the internal standard in all cases.

Osmometry (OSM)

Number-average molecular weights \bar{M}_n of polyisoprene as well as of poly(styrene-*b*-isoprene) were determined at 37°C in toluene using osmometry. A Knauer vapor-pressure osmometer (Type 11.00) was used for samples with $\bar{M}_n < 20,000$ g/mol. The instrument was calibrated with ultrapure benzil solution as well as with a polystyrene standard ($\bar{M} = 9000$). Molecular weights higher than 20,000 were obtained with a Knauer membrane osmometer (Type 01.00) using gel cellophane membranes (Type 0-8).

Viscosimetry

A high precision automatic capillary viscometer [8] was used for all viscosity measurements. A kinetic energy correction was necessary since the unit gave solvent and solution flow times shorter than 100 s. Constants for the viscometer were determined by measuring the efflux times of liquids with known viscosity and density.

Intrinsic viscosities $[\eta]$ were determined by extrapolating the reduced viscosity (η_{sp}/c) to zero concentration (c) using the well-known Huggins equation

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \quad (1)$$

where k_H is the Huggins constant.

Gel Permeation Chromatography (GPC)

Molecular weight distributions of polymers were measured using a Waters Associates GPC equipped with a high pressure solvent delivery system (Model 6000A), ultraviolet absorbance detector (Model 440), and a differential refractometer (Model R401) operated at 25°C. The separating system consisted of six μ -Styragel columns connected in series, each packed with cross-linked polystyrene gel (by the Waters method) having pore sizes of 100, 500, 1×10^3 , 1×10^4 , 1×10^5 , and 1×10^6 Å, respectively. The flow of solvent was maintained at 1 mL/min while the concentration of polymer solution was limited to 0.2% in order to render negligible the "concentration effects" on the peak position in the chromatograms. Calibration of the instrument was performed with PS standards as well as with polyisoprene samples of predetermined molecular weights.

Weight-average (\bar{M}_w) and number-average (\bar{M}_n) molecular weights of the block copolymers were computed from the uncorrected GPC chromatograms using the summation method [9]. The molecular weights of the copolymer were assumed to be weighted averages of the log molecular weights of the homopolymers of the constituent comonomers [10-12].

RESULTS AND DISCUSSION

Molecular weights of poly(styrene-*b*-isoprene) can be determined with the help of direct methods such as light scattering (\bar{M}_w) and osmometry (\bar{M}_n) or using an indirect method, i.e., gel permeation chromatography (GPC) alone [10-12] or in combination with intrinsic viscosity data using the universal calibration curve [13]. In the present work these three approaches have been tested and compared.

Solution Properties of Polyisoprene

In order to use GPC alone for molecular weight determinations of diblock copolymers, calibration curves of molecular weight \bar{M} versus elution volume, V_e are required. As in our case, PS standards of narrow polydispersity are readily available. Polyisoprene samples of different molecular weights were synthesized and characterized by viscosity, GPC, and osmometry. These data are shown in Table 1. Due to the polydisperse nature of polyisoprene samples (Fig. 2), the GPC calibration curve of \bar{M} versus V_e was prepared indirectly using the basic definitions (Eqs. 2 and 3) of weight- (\bar{M}_w) and number- (\bar{M}_n) average molecular weights:

TABLE 1. Solution Properties of Poly(isoprene)

Sample	Intrinsic viscosity [η]		$\bar{M}_n \times 10^{-3}$ osmometry	GPC molecular weights		
	THF, 25°C	Toluene, 30°C		$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n
X-432	0.054	0.041	1.78	1.6	1.4	1.10
X-422	0.087	0.074	3.60	4.2	3.3	1.27
X-440	0.115	-	5.05	7.9	5.57	1.40
X-441	0.184	-	14.05	18.0	14.6	1.23
X-425	0.513	0.468	53.0	77.5	63.0	1.23
X-428	0.887	0.807	97.3	161.0	109.3	1.47
X-430	2.170	1.964	304.5	554.0	268.0	2.07
X-409	4.690	4.510	580.0	2240.0	935.0	2.40

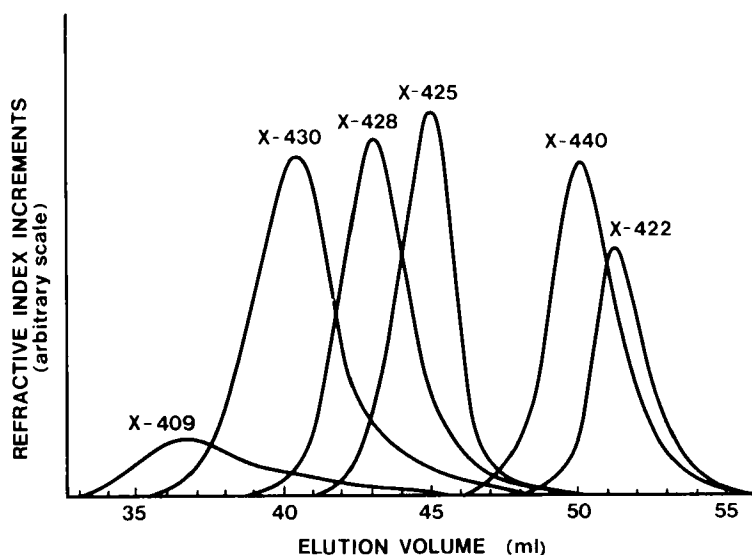


FIG. 2. GPC chromatograms of polyisoprene samples.

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i} \quad (2)$$

$$\bar{M}_n = \frac{\sum w_i}{[\sum w_i / M_i]} \quad (3)$$

where w_i is the weight of species i of molecular weight M_i and can be obtained from the GPC chromatogram. Assuming that the variation of \bar{M} versus V_e is linear, one can optimize a calibration curve which, when used in combination with Eqs. (3) and (4), yields \bar{M}_w and \bar{M}_n values similar to those obtained by the classical methods of light scattering and osmometry. One such curve is shown in Fig. 3. One notes that between the molecular weight range of 10.0×10^3 to 100.0×10^3 , M_{PS}/M_{PI} varies from 1.33 to 0.68 and is not constant at 1.35 as pointed out by the work of Tung [12].

Correcting for polydispersity using the Schulz-Zimm [14, 15] molecular weight distribution functions, the $[\eta]$ values for polyisoprene listed in Table 1 were related to \bar{M} (Fig. 4), yielding $K = 2.3 \times 10^{-4}$ dL/g, $\alpha = 0.67$ in THF at 25°C and $K = 2.0 \times 10^{-4}$ dL/g, $\alpha = 0.7$ in toluene at 30°C. Our values of K and α for polyisoprene in THF at 25°C are different than the values of $K = 1.251 \times 10^{-4}$ dL/g, $\alpha = 0.717$ reported by Kraus and Stacy [16]. It is quite possible that these variations arise due to the differences in microstructures of polyisoprene samples prepared in the two laboratories.

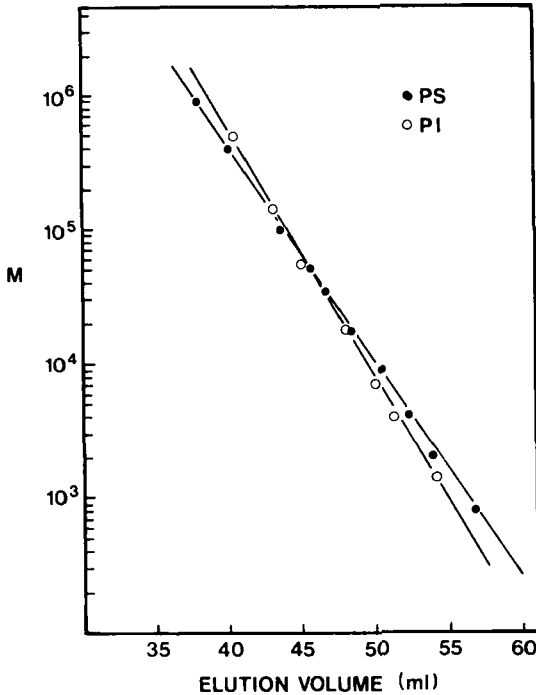


FIG. 3. Plot of $\log \bar{M}$ versus elution volume for polystyrene and polyisoprene.

Microstructure of Polyisoprene

Isoprene can undergo polymerization to give four isomeric structural units, 1,2-, 3,4-, and cis- and trans-1,4. Since the properties of diene polymers are affected by the type and distribution of these units in the chains, it was important to determine the microstructure of the present series of block copolymers.

The microstructure of polyisoprenes using NMR spectroscopy has been extensively studied [17-27]. Tanaka et al. [17-21] studied both proton and carbon-13 spectra of an extensive range of diene polymers and used deuteration techniques to interpret the spectra. Pham et al. [22-27] have studied the microstructure and the mechanistic aspects of the anionic polymerization of dienes. The anionic polymerization of isoprene was found to be most strongly dependent on the solvent; hydrocarbons give predominantly 1,4-addition while ethers and donor solvents lead to 1,2- and 3,4-addition. The reaction temperature and type of catalyst or metal have a less pronounced effect on the microstructure.

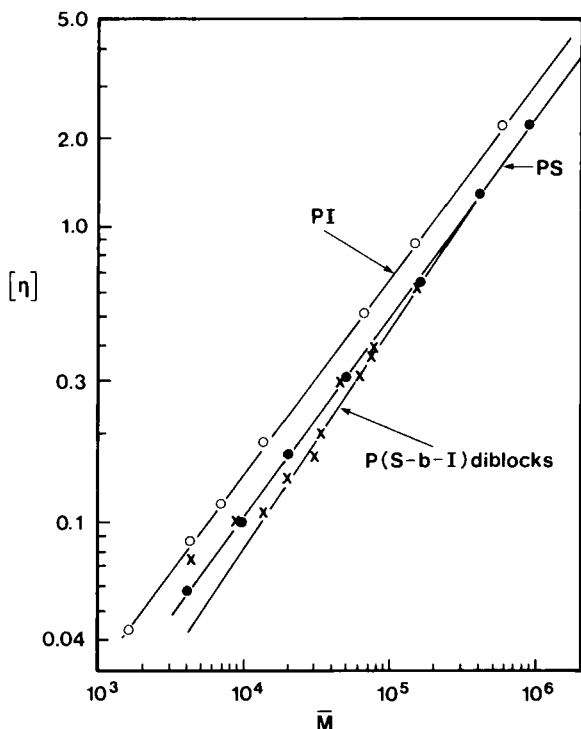


FIG. 4. Log-log plot of $[\eta]$ versus \bar{M} ; (\circ) \bar{M}_v polyisoprene, (\bullet) \bar{M}_w polystyrene, and (\times) \bar{M} poly(styrene-*b*-isoprene).

In Figs. 5 and 6 are shown 20 MHz carbon-13 spectra of polyisoprene X-441 (Fig. 5) and a typical block copolymer X-434 (Fig. 6). The peaks centered at 111 and 143 ppm are attributed to the terminal and internal vinyl carbons, respectively, of the 1,2- and 3,4-units. The two sets of peaks at 120-130 and 130-140 ppm are assigned to the 3- and 2-carbons, respectively, of the 1,4-units. The complexity of the carbon-13 spectrum is due to a combination of sequence distribution, *cis-trans* isomerism, and tacticity effects. We have made no attempt to interpret these effects. However, we have observed that the pattern of these peaks was closely reproduced from batch to batch, which confirms the reproducibility of the synthetic procedure.

The structural units were measured quantitatively using proton NMR spectra. Many conditions were tried and we found that the original method described by Pham [22], deuterated benzene solvent at 65°C, offered the best resolution of the vinyl proton region. In the 250 MHz spectra shown in Figs. 7 and 8 the internal vinyl protons of the 1,2- (a)

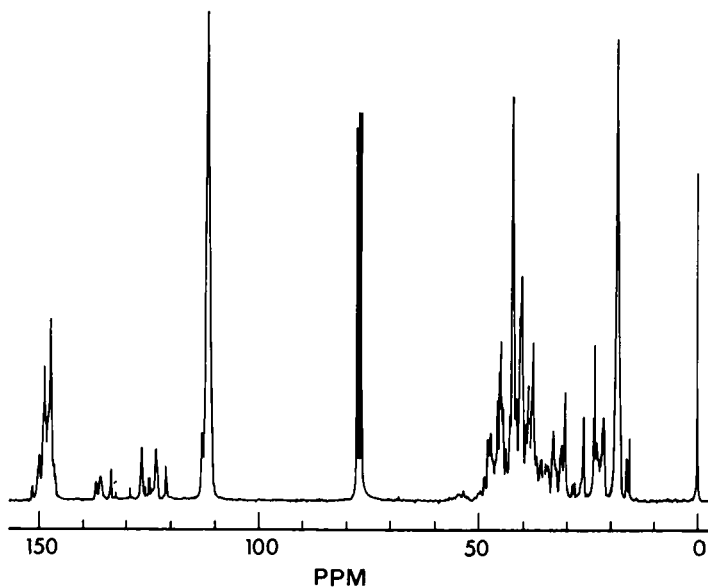


FIG. 5. 20 MHz ^{13}C spectrum of polyisoprene sample X-441.

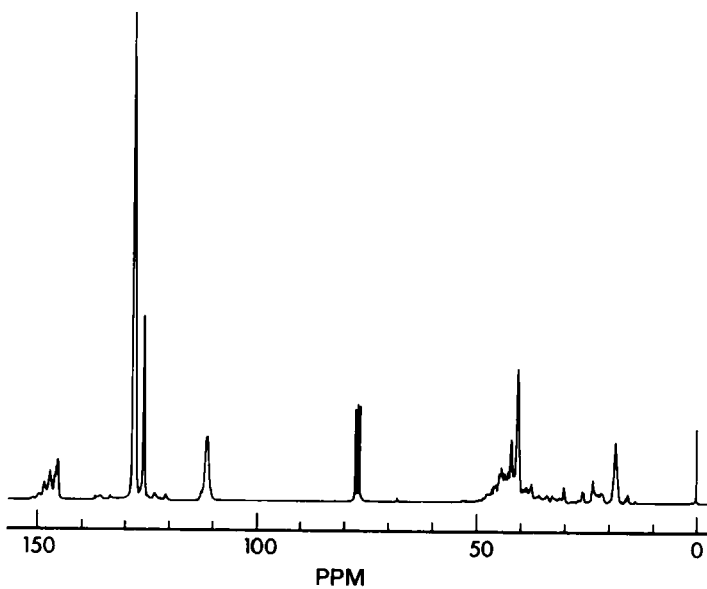


FIG. 6. 20 MHz ^{13}C spectrum of poly(styrene-b-isoprene) sample X-434.

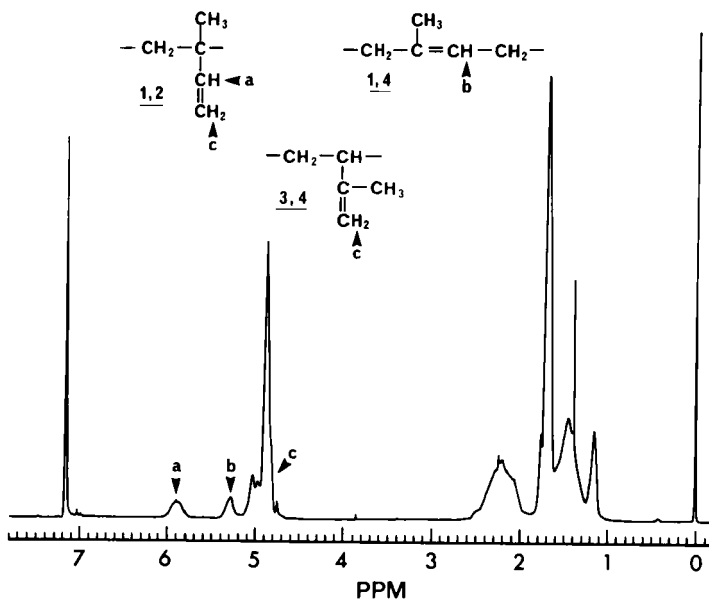


FIG. 7. 250 MHz proton NMR spectrum of polyisoprene sample X-441.

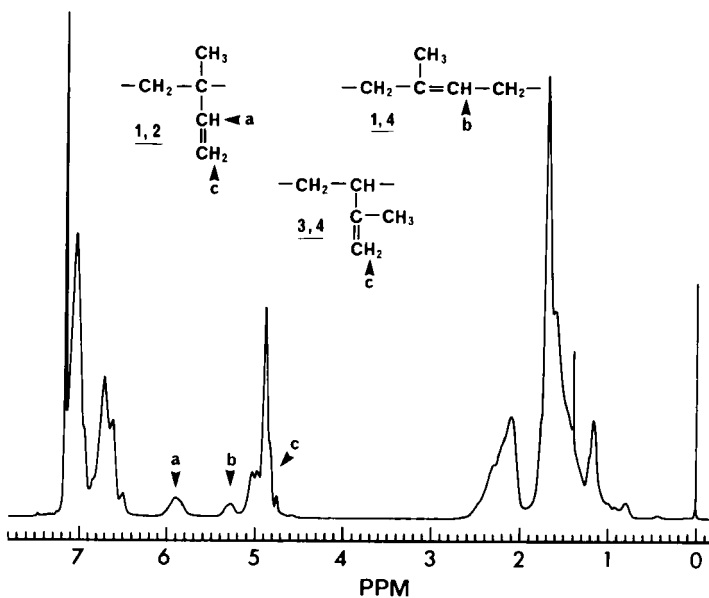


FIG. 8. 250 MHz proton NMR spectrum of poly(styrene-b-isoprene) sample X-434.

TABLE 2. Microstructure of Polyisoprene

Microstructure (% addition)	Polyisoprene	Poly(styrene-b-isoprene)
1,2-	18	26
3,4-	66	60
1,4-	16	14

and 1,4-isomer (b) are well resolved and separate from the peak due to the terminal methylene protons (c). The microstructure of isoprene in polyisoprene X-441 (Fig. 7) as well as in the block copolymer X-434 (Fig. 8) is presented in Table 2. The differences in the microstructure of the polyisoprene homopolymers and the diblock copolymers arise, in all probability, from the different thermal conditions used in their synthesis. For the block copolymer, isoprene was added to living polystyrene at -100°C and the polymerization was allowed to proceed at ambient conditions. In the case of polyisoprene, initiation as well as polymerization were carried out at ambient temperature. It is believed that due to the exothermic nature of the isoprene polymerization reaction, the temperature within the ampule during the homopolymerization of isoprene is higher than that during the block copolymer synthesis.

Solution Properties of Block Copolymers

In Table 3 are presented the molecular weights \bar{M}_v , viscosity $[\eta]$, and GPC elution volumes (V_e) for polystyrene and polyisoprene samples. Using these data, a universal calibration curve of $[\eta]M$ versus elution volume V_e , was prepared and is shown in Fig. 9. One notes that polyisoprene samples of high molecular weight ($\bar{M}_v > 10^5$) deviate slightly from the universal calibration curve.

In Fig. 10 is shown a typical GPC chromatogram of a poly(styrene-b-isoprene) sample, X-437. One notes that the polydispersity of the sample is not large, suggesting that block copolymers (up to 40 g in weight) and of reasonable polydispersity can be synthesized with the reusable apparatus described in this paper. Molecular weights of the block copolymer synthesized were computed as follows.

Considering block copolymer poly(styrene-b-isoprene) as homopolymers PS and PI, $(\bar{M}_w \text{ and } \bar{M}_n)_{\text{PS}}$ -molecular weights of the block copolymer using PS calibration curve (Fig. 3); $(\bar{M}_w \text{ and } \bar{M}_n)_{\text{PI}}$ -molecular weights of the block copolymer using polyisoprene calibration curve (Fig. 3) were computed by the summation method [9] using Eqs. (2) and

TABLE 3. Molecular Weights (\bar{M}_v), Viscosity $[\eta]$, and GPC Elution Volumes for Polystyrene and Polyisoprene Samples

Polymer	$\bar{M} \times 10^{-3}$	$[\eta]$ in THF at 25°C	$[\eta]\bar{M}_v$	Elution volume V_e (mL)
PS	0.8	0.043	34	56.7
PS	2.0	0.044	88	53.8
PS	4.0	0.058	232	52.3
PS	9.0	0.100	900	50.5
PS	17.5	0.170	2,975	48.3
PS	50.0	0.300	15,000	45.5
PS	100.0	0.480	48,000	43.3
PS	390.0	1.320	514,800	41.2
PS	900.0	2.300	2,070,000	37.8
X-432	2.1	0.054	113	54.1
X-422	4.3	0.087	375	51.3
X-440	6.5	0.115	750	50.0
X-441	13.2	0.184	2,430	47.9
X-425	60.7	0.513	31,140	45.0
X-428	137.7	0.887	122,140	43.0
X-430	522.5	2.170	1,133,825	40.5

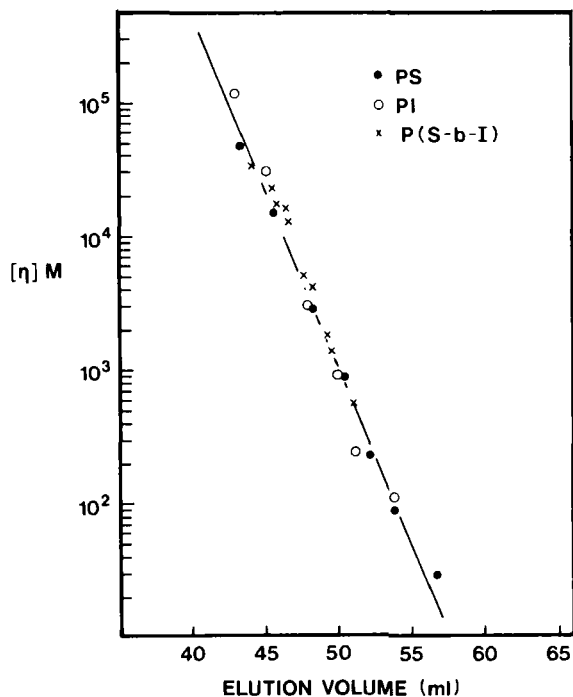


FIG. 9. Plot of $\log [\eta] M$ versus elution volume for polystyrene, polyisoprene, and poly(styrene-b-isoprene) samples.

(3). With the knowledge of the composition of the block copolymer, i.e., % PS (W_{PS}) and % PI (W_{PI}), weighted average molecular weights were computed [10-12] using

$$\log \bar{M}_{\text{block}} = W_{PS} \log \bar{M}_{PS} + W_{PI} \log \bar{M}_{PI} \quad (4)$$

Molecular weights \bar{M}_w and \bar{M}_n of all block copolymers are listed in Table 4, which also carries their GPC peak elution volumes, and \bar{M}_n from osmometry and viscosity (experimental as well as calculated) data. One notes that \bar{M}_n (GPC) values computed using the summation method [9] and Eq. (4) agree well with those obtained from osmometric measurements. This would suggest that for poly(styrene-b-isoprene) with polydispersity ratios between 1.2 and higher, our method of computing \bar{M}_w and \bar{M}_n is valid.

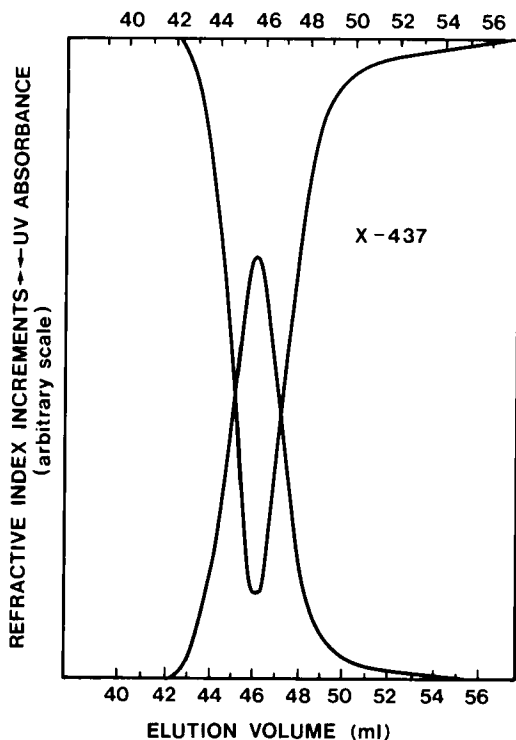


FIG. 10. A typical GPC chromatogram of poly(styrene-*b*-isoprene) sample X-437.

Alternatively, one may use the universal calibration curve for calculating molecular weights if the intrinsic viscosity and the GPC elution volume of the block copolymer are known. This method gives precise values for block copolymers only if the polydispersity of the samples is low. For block copolymers of polydispersity ratios greater than 1.2, one can simply compute peak elution molecular weights which are in most cases close to the \bar{M}_n of the polymer as is evident from Table 4.

$[\eta]M$ versus uncorrected peak elution volume V_e for block copolymers is shown in Fig. 9, and one notes that for most block copolymers these fit the universal calibration reasonably well.

In Table 4 are also presented the experimental as well as calculated intrinsic viscosities $[\eta]$ for the block copolymers in THF at 25°C. The calculated values were obtained using

$$[\eta]_{\text{calc}} = W_{\text{PS}}[\eta]_{\text{PS}} + W_{\text{PI}}[\eta]_{\text{PI}} \quad (5)$$

TABLE 4. Molecular Characteristics of Poly(styrene-*b*-isoprene) Diblock Copolymers

No.	% Styrene by weight	Peak elution volume (mL)	Molecular weights ($\times 10^{-3}$)					[η] THF, 25°C	
			\bar{M}_{peak} (GPC)	\bar{M}_{w} (GPC)	\bar{M}_{n} (GPC)	\bar{M}_{n} (OSM)	Exptl	Calc	
X-421	41	-	-	4.5	3.6	3.6	3.6 ^a	0.076	0.075
X-452	50	50.75	6.15	8.75	5.0	-	-	0.101	0.113
X-414	31	-	-	12.3	8.8	7.65 ^a	7.65 ^a	-	0.164
X-420	72	49.5	11.2	13.5	7.3	7.7 ^a	7.7 ^a	0.110	0.143
X-434	51	49.0	12.3	19.5	10.75	-	-	0.142	0.197
X-413	45	-	-	29.6	9.3	9.35 ^a	9.35 ^a	0.168	0.266
X-435	55	48.0	20.0	32.5	18.35	-	-	0.204	0.275
X-446	46	47.5	24.0	33.3	22.0	23.0 ^b	23.0 ^b	0.210	0.290
X-437	55	46.0	43.5	47.3	33.8	34.0 ^b	34.0 ^b	0.298	0.358
X-447	62	45.6	53.0	60.0	36.8	-	-	0.314	0.405
X-449	25	45.8	45.7	59.8	40.3	-	-	0.360	0.456
X-439	62	45.3	58.3	72.0	41.7	-	-	0.375	0.452
X-448	47	44.3	81.4	77.0	50.7	50.1 ^b	50.1 ^b	0.393	0.494
X-438	77	42.2	-	147.0	62.5	-	-	0.622	0.657

^aVapor pressure.^bMembrane.

One notes that the calculated values, using \overline{M}_w data of each segment of the block copolymers, are higher than the experimental values due to the polydisperse nature of these materials. A plot of $[\eta]_{\text{exp}}$ versus \overline{M} ($\overline{M} > 2.0 \times 10^4$) for the block copolymers (Fig. 4) yielded $K = 9.0 \times 10^{-5}$ dL/g and $\alpha = 0.75$. One notes that α for the block copolymers (styrene > 50% by weight) is higher than those of the constituent comonomers, due in all probability to the extended nature of the copolymer coil. For block copolymers with \overline{M} lower than 2.0×10^4 , the α values were lower than 0.75. This may be explained on the basis that the high molecular weight block copolymers exist in the form of a dumbbell whose two biellipsoids are only partly merged together. As the molecular weights of these block copolymers decrease, the two biellipsoids of the dumbbell merge together completely and the block copolymer behaves as if it were a mixture of two homopolymers, thereby yielding lower α (0.5) values.

CONCLUSIONS

The principal conclusions to be drawn from this study may be summed up as follows.

1. The reusable polymerization apparatus for the synthesis of diblock copolymers discussed in this report presents considerable advantages over the conventional techniques, especially in industrial laboratories where relatively large quantities are required for testing in various applications.

2. Molecular weight computations using GPC and membrane osmometry have shown that the polydispersity ($\overline{M}_w/\overline{M}_n$) ratios of these diblock copolymers is generally around 1.5 which is acceptable for most operations. Furthermore, once a GPC system has been calibrated for polystyrene and polyisoprene samples of low polydispersity, molecular weights can be obtained precisely, knowing the composition of the block copolymers, using the summation method [9], and assuming that the molecular weights are the weighted averages of the log molecular weights of the homopolymers [10-12].

3. The slight differences in the microstructure of polyisoprene in the homopolymer and the diblock copolymer result from the differences in their temperature of polymerization. Furthermore, due to the different microstructure of the polyisoprene prepared in this lab, $K = 3.2 \times 10^{-4}$ dL/g and $\alpha = 0.67$ for this polymer in THF at 25°C, are different than those ($K = 1.25 \times 10^{-4}$ dL/g, $\alpha = 0.717$) reported by Kraus and Stacy [16]. The K and α values of our diblock copolymers ($\overline{M} > 20.0 \times 10^3$) are 9.0×10^{-5} dL/g and 0.75, respectively. Higher values of α for the block copolymers, as compared to those of the two homopolymers, suggest that the copolymer coil is in extended form.

X-ray studies are in progress on the micelle formation of styrene-isoprene diblock copolymers in heptane. The results of these studies will be published as they become available.

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