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Application of GPC in the Study of Stereospecific Block Copolymers*

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Summary

Three different techniques involved in the preparation of stereospecific block copolymers were studied using gel permeation chromatography (GPC). These techniques involved the use of a monofunctional organolithium catalyst, a difunctional organolithium catalyst, and a combination of a monofunctional organolithium catalyst and a coupling technique. GPC curves were obtained on the block copolymers using two different column sequences and solvents. The ABA block copolymers studied contained styrene, vinyl toluene, or α-methyl styrene as thermoplastic monomers and butadiene as the elastomeric monomer. The results obtained showed that block copolymers prepared using monomers and catalyst systems free of impurities generally exhibited single peaked GPC curves. In systems where impurities were found to be present, small amounts of A block homopolymer and AB block copolymer were formed. In such cases, the GPC curves were observed to have two or three peaks.

INTRODUCTION

A new class of block copolymers, called the "thermoplastic elastomers," has recently achieved commercial importance. These block copolymers have been receiving considerable interest recently (*1–3*). The "thermoplastic elastomers" consist of ordered, block copolymers of the general structure ABA, where A is a thermoplastic block

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polymer and B is an elastomeric block polymer. A typical example of an ABA block copolymer is polystyrene–polybutadiene–polystyrene. However, other monomers such as vinyl toluene and α-methyl styrene have been used in the A block segment and isoprene has been used in the B block segment. These copolymers exhibit rubberlike properties similar to vulcanized elastomers, but without vulcanization (*4–6*). They may be formed into useful mechanical goods by modern, rapid, thermoplastic processing techniques. Furthermore, if the polymerization is carried out properly, the resultant block copolymer will have a very narrow molecular-weight distribution with a predictable and controllable molecular weight.

Techniques for the anionic polymerization of block copolymers have been adequately described (*1*). Hence, mechanisms of polymerization will not be discussed here. However, reference will be made to three different techniques involved in preparing block copolymers to help illustrate the usefulness of gel permeation chromatography. The several techniques involved the use of (a) a monofunctional organolithium catalyst, (b) a difunctional organolithium catalyst, and (c) a combination of a monofunctional organolithium catalyst and a coupling technique.

EXPERIMENTAL

The block copolymers were analyzed using Waters Associates' Model 100 and Model 200 Gel Permeation Chromatographs. The Model 100 instrument contained a combination of four columns of cross-linked polystyrene gels with pore sizes of 10^6, 10^5, 10^4, and 10^2 Å. Operating conditions for this instrument were: solvent, tetrahydrofuran at room temperature; pumping rate 1 ml/min. The Model 200 instrument contained five columns of crosslinked polystyrene gels with pore size of 10^7, 10^6, 10^5, 10^4, and 10^2 Å. Operating conditions for this instrument were: solvent, toluene at 70°C; pumping rate, 1 ml/min.

Reference will be made in the discussion of this paper to certain multiple peaks in the gel permeation chromatography (GPC) curves as being related to homopolymer and block copolymer peaks. Identification of these peaks was made by first fractionating and isolating the individual peaks using GPC, followed by IR spectrophotometric analyses of each fraction. Some samples known to have two or three peaks were injected into the GPC, and fractions representing each peak were collected for analysis using an IR spectrophotometer. The

IR interpretations provided the necessary information for labeling the various peaks in the GPC scans.

DISCUSSION

It is known that the strength of the thermoplastic elastomer is markedly dependent upon the perfection of the ABA block structure comprising the network and the purity of the final system (*2*, *3*, *7*). A primary prerequisite to the synthesis of pure block copolymers is rigorous purification of monomers and initiator systems. However, it is often difficult to obtain systems that are entirely free of reactive im-

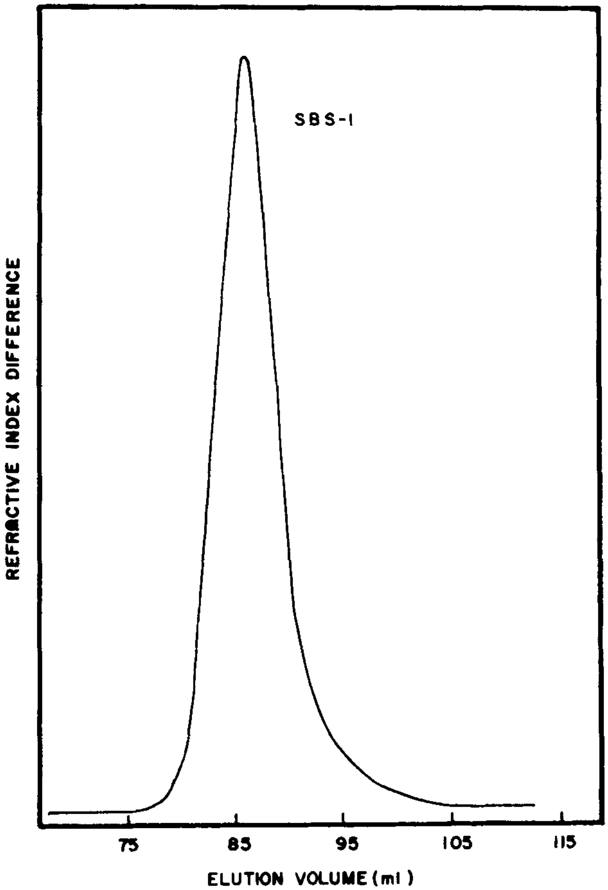

FIG. 1. Gel permeation chromatogram of sample SBS-1 block copolymer.

purities. Since, ideally, a pure ABA block copolymer is expected to have a very narrow molecular-weight distribution, its distribution curve should also be single peaked. In systems where impurities are present or side reactions occur, such as chain transfer with the solvent, small amounts of A block homopolymer and AB block copolymer may be formed. In such cases, the molecular-weight distribution curves could have two or three peaks. GPC has been used successfully in characterization studies with ABA block copolymers (*7–10*). The GPC chromatograms alone can provide valuable information on the synthesis of ABA block copolymers.

Figure 1 shows a chromatogram (Model 100 instrument) of a poly(styrene–butadiene–styrene) block copolymer prepared from a monofunctional organolithium catalyst. As is evident, the distribution curve is very narrow and has a single peak. The chromatogram (Model 100 instrument) of another poly(styrene–butadiene–styrene) block copolymer prepared from a monofunctional organolithium catalyst is shown in Fig. 2. In contrast to the single peaked curve for the other block copolymer, this SBS-2 sample has two peaks in its distribution curve. The first peak eluting at about 110 ml is the ABA

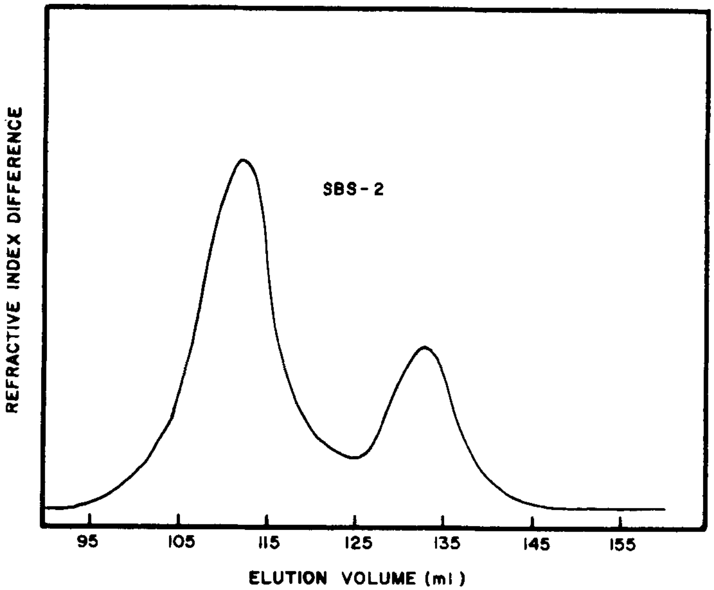

FIG. 2. Gel permeation chromatogram of sample SBS-2 block copolymer.

block copolymer, while the other peak is the A block homopolymer, which in this case is polystyrene. The polymerization of the SBS-2 sample was believed to have occurred normally, until the chromatogram was viewed. It was found later that a small amount of impurity in the butadiene had been sufficient to terminate some of the polystyryllithium anions formed initially. Hence, the final ABA block copolymer contained some polystyrene.

The following examples will serve to illustrate other situations which can arise in preparing SBS block copolymers. These GPC analyses were made using the Model 200 instrument. The chromatogram of Sample SBS-3, again prepared using a monofunctional organolithium catalyst, is shown in Fig. 3. Notice the two somewhat obscured and smaller peaks eluting at about 167 and 180 ml. The first peak is the poly(styrene–butadiene–styrene) block copolymer, while the last two peaks right after it are the poly(styrene–butadiene) block copolymer and polystyrene homopolymer, respectively. Figure 4 shows that the distribution curve for SBS-4 appears to be very broad and skewed in comparison to the SBS-3 block copolymer sample. These samples were run consecutively so this broadness for SBS-4

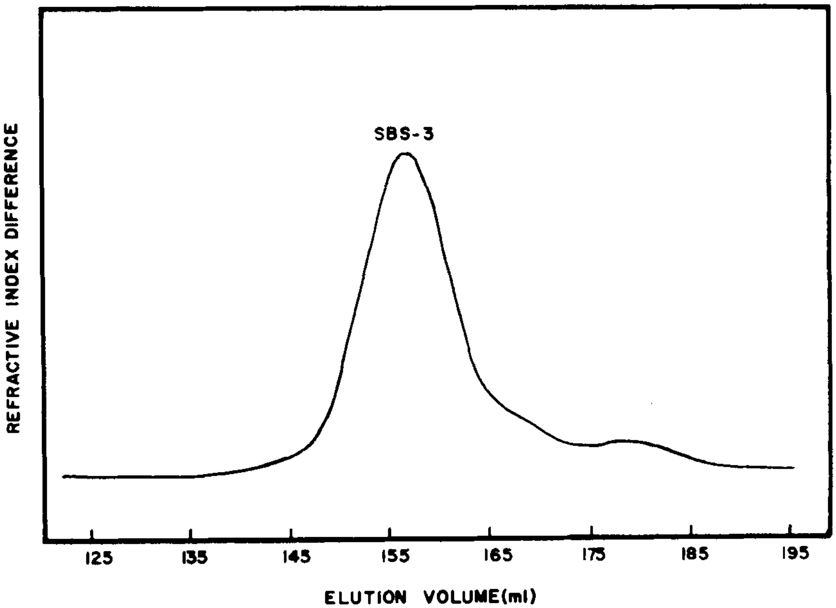

FIG. 3. Gel permeation chromatogram of sample SBS-3 block copolymer.

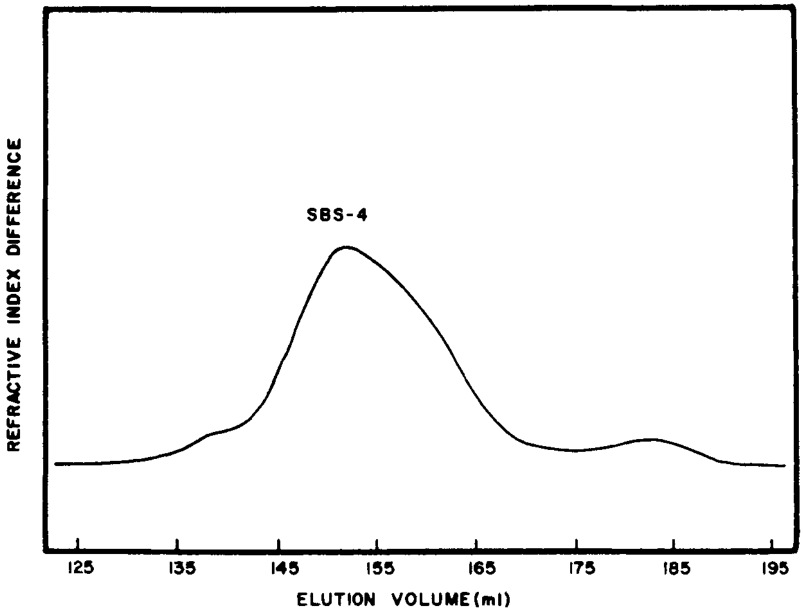

FIG. 4. Gel permeation chromatogram of sample SBS-4 block copolymer.

is believed to be due to a higher level of AB block copolymer content hidden under the trailing end of the distribution curve. The poly(styrene–butadiene–styrene) block copolymer peak in Sample SBS-4 eluted at a lower elution volume than did that for SBS-3. A similar effect was also observed for the AB block copolymer peak. However, the original intention of the synthesis work was that the monomer compositions be the same. About the only observable similarity between these two samples is the small polystyrene homopolymer peak appearing at about 180 ml.

Considering a different monomer combination, the chromatogram for a poly(vinyl toluene–butadiene–vinyl toluene) block copolymer is shown in Fig. 5. This block copolymer contained about 34% vinyl toluene and was also prepared using a monofunctional organolithium catalyst. As seen from the curve, the VBV-5 sample had three observable peaks. The main ABA peak eluted at about 160 ml, and there was a tailing polyvinyltoluene peak at about 180–185 ml. There also was an unknown component eluting at about 145–150 ml. This component is believed to be a higher molecular-weight fraction of the same composition as the main VBV material. Although the chromato-

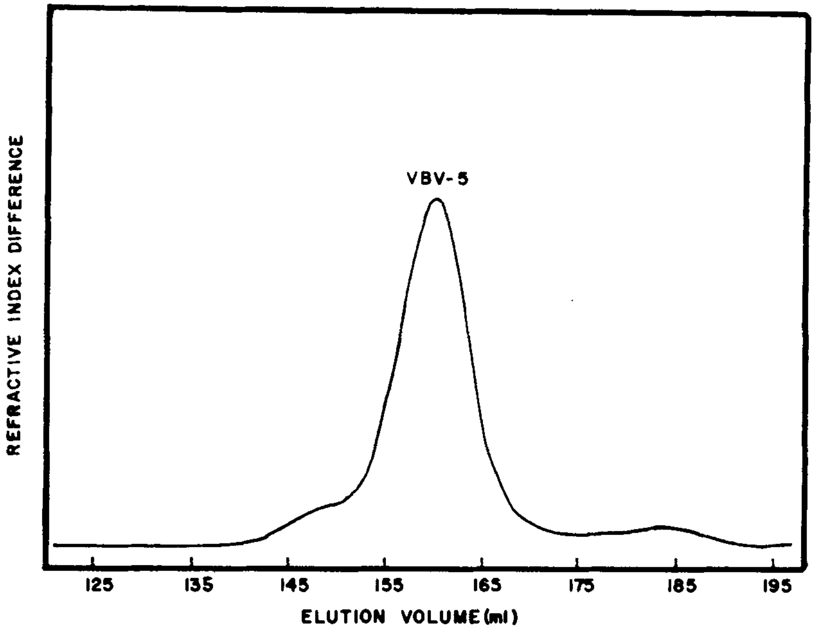

FIG. 5. Gel permeation chromatogram of sample VBV-5 block copolymer.

gram shows three distinct peaks, the polyvinyltoluene peak eluting last was relatively small. This suggested that there was only a small amount of homopolymer present in this sample. The main peak was relatively narrow and generally similar in shape to single peaked SBS curves shown earlier. In contrast to the sharp, well-defined curve for Sample VBV-5, the chromatogram for Sample VBV-6 is shown in Fig. 6. This sample contained 26% vinyltoluene, which is slightly lower than in the previous sample, and was also prepared using a monofunctional organolithium catalyst. These two VBV samples were run consecutively on the same GPC instrument. Although it was intended that the same polymerization technique be used in the preparation of both samples, a comparison of the GPC curves alone suggested that some important differences existed in the preparation of VBV-5 and VBV-6. A review of polymerization data showed that impurities were present in the monomer system for Sample VBV-6 and were slowly terminating the polymerization reaction. Also, the final polymer lacked certain physical properties associated with ABA block copolymers. Hence, in this case, it was known that sample VBV-6 was not a typical ABA block copolymer. The very broad, rolling

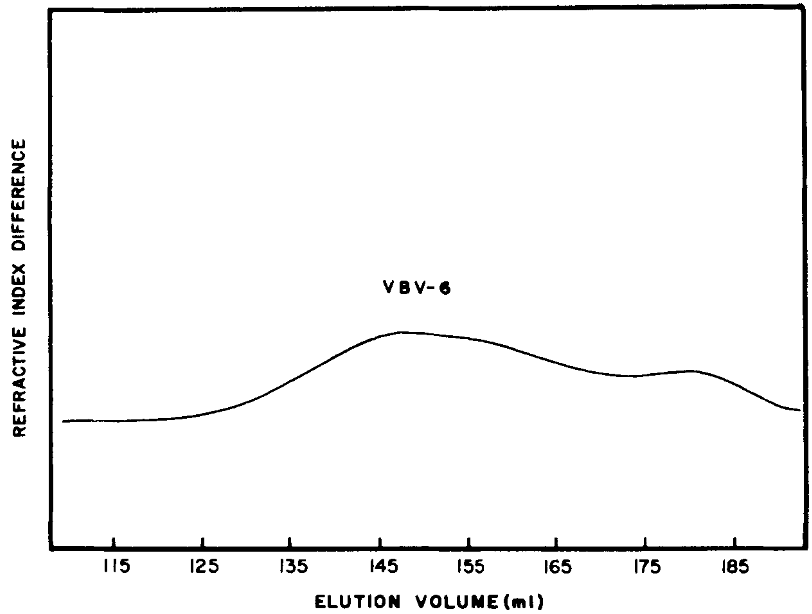

FIG. 6. Gel permeation chromatogram of sample VBV-6 block copolymer.

chromatogram showed a random distribution of high and low molecular-weight species, some of which were probably of the ABA, AB, and A block types. This type of chromatogram is generally observed with random copolymers.

As stated earlier, the preparation of ABA block copolymers can be achieved by several methods. The methods generally use lithium-based initiators in order to attain a high 1,4 chain structure in the diene block, which is important in achieving elastic behavior (7). The use of monofunctional organolithium catalyst, which involves a three-stage sequential polymerization of, for example, styrene, butadiene, and styrene, has already been discussed. Another approach involves the use of dilithium initiators. Here the sequence of monomer addition is reversed. The difunctional catalyst polymerizes the diene monomer in two directions first. The thermoplastic monomer adds last. Figure 7 shows the chromatogram (Model 200 instrument) for Sample SBS-7 which was polymerized using a dilithium catalyst. Sample SBS-7 contained approximately 35% styrene. As is evident from the chromatogram, this sample had only one observable peak and a very sharp distribution curve.

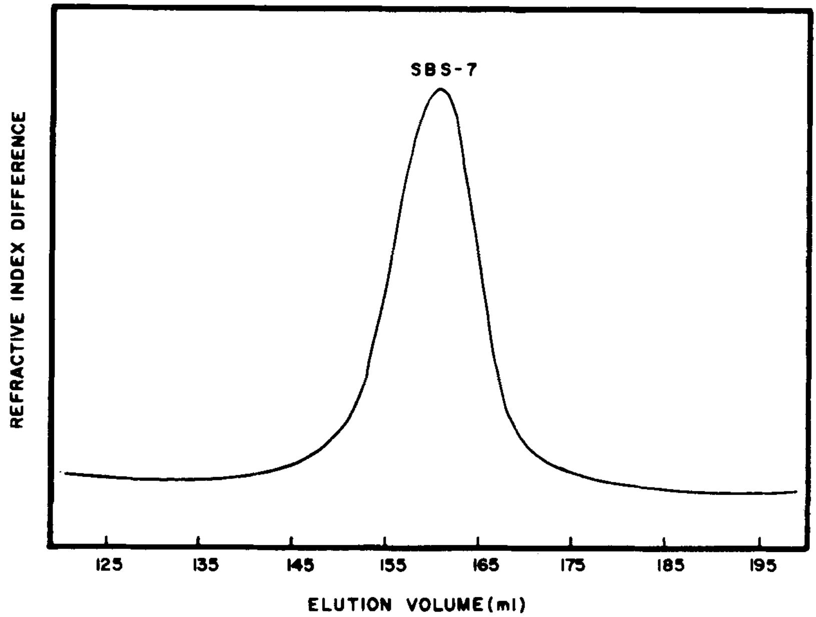

FIG. 7. Gel permeation chromatogram of sample SBS-7 block copolymer.

Figure 8 shows the chromatogram (Model 200 instrument) of sample SBS-8 which was also prepared using a difunctional lithium catalyst. Sample SBS-8 contained 46% styrene, which is slightly higher than Sample SBS-7. The main SBS peak for Sample SBS-8 eluted at about the same elution volume as that for SBS-7, near 160 ml. However, this sample had a pronounced high molecular-weight tail, which is easily seen. The physical properties, that is, the stress-strain data and the physical appearance of this sample, were similar to that expected for an ABA block copolymer. The presence of the high molecular-weight material in the GPC curve was somewhat surprising, and its origin is not completely understood. However, it is believed that an accidental side reaction had occurred late in the polymerization, resulting in incomplete termination of the system. This permitted some of the polymer molecules to continue growing to higher molecular weight.

A third approach in the preparation of ABA block copolymers involves the use of a monofunctional catalyst to prepare the AB anion, which is then linked together using a reactive halogen coupling agent (*10*). The chromatogram for poly(α-methyl styrene–butadiene—

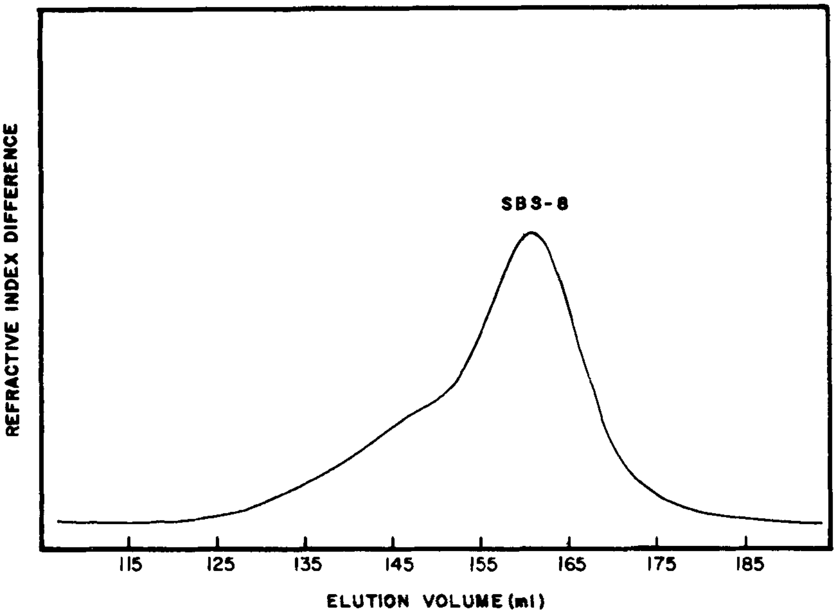

FIG. 8. Gel permeation chromatogram of sample SBS-8 block copolymer.

α-methyl styrene) block copolymer prepared using a coupling technique is shown in Fig. 9. This sample, which contained 40% α-methyl styrene, was also analyzed using the Model 200 instrument. As seen from the chromatogram, this sample had three peaks; the main ABA peak appearing at about 155 ml, the AB peak which appeared at about 165 ml as a shoulder on the tail-end of the main ABA peak, and the A block homopolymer peak appearing at about 185 ml. The presence of the homopolymer peak, as discussed earlier, probably can be attributed to system impurities which terminated the polystyryllithium anion. The presence of the AB copolymer was believed to be due to incomplete coupling of the AB anion with the coupling agent.

Heller and co-workers used GPC to study a poly(vinylbiphenyl–isoprene–vinylbiphenyl) block copolymer prepared by a coupling technique using phosgene as a coupling agent (*10*). Their chromatograms also contained three peaks. A compositional analysis of the block copolymer was made quantitatively by GPC from a knowledge of the refractive index increments of the homopolymer portions A and B and the over-all composition of the final product. A light-scattering study

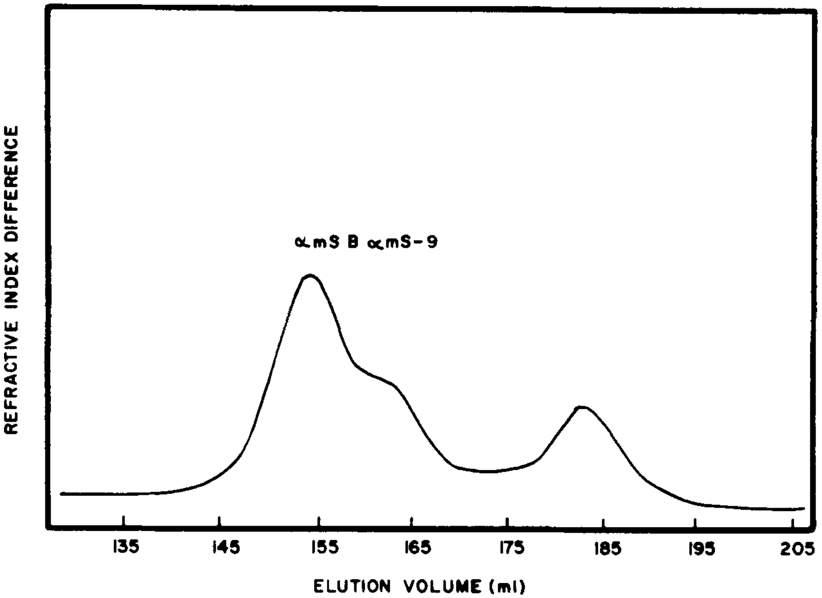

FIG. 9. Gel permeation chromatogram of sample αmSB-αmS-9 block copolymer.

provided data on the differential refractive indices, and osmometry was used to obtain molecular-weight data.

A series of six SBS block copolymers, which exhibited two or three peaks in the chromatograms, were analyzed for the polystyrene content and its molecular weight by GPC. In order to accomplish this, polystyrene standards of known molecular weight and very narrow molecular-weight distributions were injected into the GPC to obtain the peak elution volumes. A plot of the peak elution volumes versus number-average molecular weights was constructed as shown in Fig. 10. Also, various concentrations of a polystyrene standard were prepared and injected into the GPC to determine the peak area versus concentration relationship (Fig. 11). The molecular weight and polystyrene calibration data were then used to determine the number-average molecular weight and concentration of the polystyrene homopolymer in the six SBS block copolymer samples. Table 1 shows the results obtained.

The last column on the right in Table 1 lists the expected SBS composition. The results for per cent polystyrene indicate how much of the styrene content was lost to homopolymer formation. The data

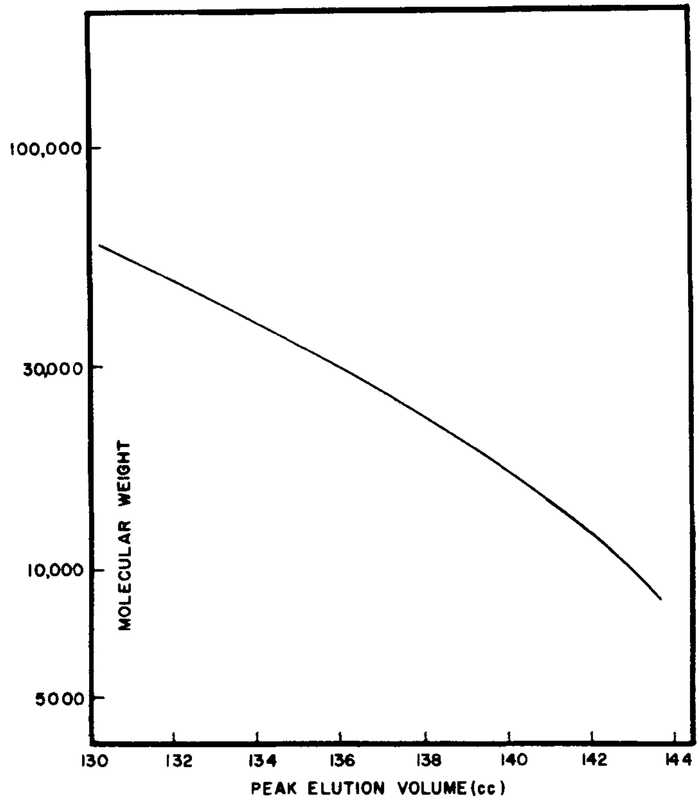

FIG. 10. Plot of peak elution volume vs. $\bar{M}_n$ for polystyrene standards.

suggest that, in general, as the styrene content was increased, the polystyrene level also increased. The high number-average molecular weights for the polystyrene portion suggested that the polystyryllithium anion probably was terminated at about the time the second sequential addition was made.

The same type of information can also be obtained for AB and ABA components providing standards of known molecular weight and composition are available. Although an additional study of this type is not yet complete, work along these lines is progressing.

CONCLUSION

It has been shown that ABA block copolymers prepared using monomers and catalyst systems free of impurities generally yield

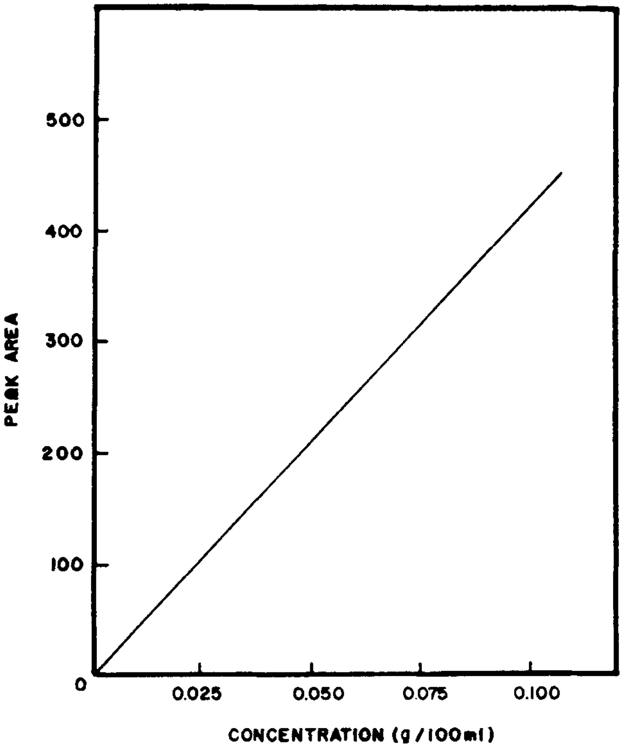

FIG. 11. Plot of peak area vs. polystyrene concentration.

TABLE 1

Analysis of Homopolymer in SBS Block Copolymer

Sample	Peak elution volume (ml)	Peak area	Concn. (g/100 ml)	$\bar{M}_n$[a]	% Polystyrene[b]	SBS composition
A	135.4	91.00	0.0220	33,000	7.33	23-54-23
B	139.1	80.75	0.0195	21,000	6.49	15-70-15
C	132.3	266.28	0.0650	47,000	21.54	26-48-26
D	135.4	115.02	0.0275	33,000	9.17	17-66-17
E	134.7	180.88	0.0440	36,000	14.68	27-46-27
F	136.8	137.97	0.0335	28,000	11.07	21-58-21

[a] From polystyrene calibration curve.

[b] Based on total weight of polymer (SBS + P-S).

single-peaked chromatograms. Hence, GPC could be considered a candidate for a quality control technique to monitor block copolymer polymerizations, as well as for studying coupling efficiency. It is believed that this work leads to the conclusion that a total characterization of thermoplastic elastomers is very important, since performance characteristics of the copolymers are closely related to their structural features.

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