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Composition of Butadiene–Styrene Copolymers by Gel Permeation Chromatography*

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Summary

An ultraviolet detector was added to the GPC making it possible to determine both molecular weight distribution and composition of butadiene–styrene copolymers as a function of molecular weight. After calibration, several types of commercial and experimental copolymers were analyzed. SBR was found to have a very uniform composition over most of the range of molecular weight. However, the styrene content decreased at the high end of the distribution. Representative samples of anionically polymerized copolymers were also examined. In general, the composition of these polymers varied more than SBR. Usually, the styrene content was high at low molecular weight and decreased as molecular weight increased. Several experimental copolymers that were first metalated and then grafted with styrene were studied. Incomplete grafting as well as the presence of low molecular weight homopolystyrene was readily detected. This appears to be a particularly sensitive method for studying composition of copolymers.

It is quite evident that physical properties of copolymers are dependent on their composition. However, it is not satisfactory to merely control average composition. Minor fluctuations of composition on a molecular level are also important. Thus, actual distribution of the two monomers within polymer chains must be controlled if certain properties are desired. The two extremes are pure block copolymer

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on the one hand and uniform copolymer on the other. Many variations exist between these two.

Considerable information of importance can be obtained by determining the variation in composition as a function of molecular weight. Usually, solution methods (*1*) have been used to obtain this type of information. Fractions of copolymer were separated by addition of nonsolvent and individually analyzed for composition and molecular weight. However, fractionation depends upon solubility parameters which are a function of both composition and size so that clean separations are not obtained. These methods are also time consuming.

Gel permeation chromatography should be useful in this area (*2–4*). Its primary function is to separate polymer molecules of different size and thus determine molecular weight distributions of polymers. Modification of the instrumentation to determine composition of different molecular weight material as it is separated would yield the desired information. This was accomplished by adding an ultraviolet (UV) detector to the gel permeation chromatograph (GPC) in series with the standard differential refractometer normally used. Thus, the refractive index detector (RI) measures total amount of copolymer of a certain molecular weight, while the UV detector establishes its composition.

Since the GPC method of separation depends on the size of the polymer coil in solution, this method is also dependent on composition to the extent that composition influences coil size. Adequate calibration of the GPC in terms of the different compositional variations encountered will permit the results to be expressed as a function of molecular weight (*4*). In this study, no attempt has been made to convert to molecular weight, so the results are shown as a function of GPC counts.

EXPERIMENTAL

The GPC was modified by adding a UV detector, Uviscan III, manufactured by Buchler Instruments. It was placed in line preceding the standard RI detector, and a separate recorder was used for its output. Absorbance at 2600 Å was measured directly.

To minimize solvent effects and obtain maximum transmission by the solvent at 2600 Å, the solvent, tetrahydrofuran (THF), was purified before use in the GPC. It was refluxed over sodium for 4 hr and, after discarding the forerun, was distilled directly into the GPC solvent reservoir. A blanket of nitrogen was maintained during the distillation and use in the GPC. The purity and transmission of the THF was checked periodically with a Beckman DKU Spectrophotometer before use.

Both detectors were calibrated in terms of amount of polybutadiene and polystyrene. It was verified that neither 1,2- or 1,4-polybutadiene absorbed at 2600 Å. Thus, the UV detector is sensitive to only the amount of styrene while the RI detector measures both styrene and butadiene. Consequently,

$$r_{\mathrm{UV}} = K'_s G_s$$
$$r_{\mathrm{RI}} = K_c G_c$$

where r_{UV} and r_{RI} are the outputs of the UV and RI detectors, respectively. K_s and K_c are the proportionality constants, and G_s and G_c are the grams of styrene (s) and copolymer (c). K_c is assumed to be linearly dependent upon composition as follows:

$$K_c = (1 - W_s)K_b + W_s K_s$$

where W_s is weight fraction of styrene and K_b the proportionality constant between the RI detector readings and grams of butadiene. Thus, at each GPC count interval, the fraction of styrene $(W_s)_i$ can be calculated in the following manner:

$$(W_s)_i = R_i \frac{K_b}{K'_s - \Delta K R_i}$$

with

$$R_i = r_{\mathrm{UV}}/r_{\mathrm{RI}}$$

and

$$\Delta K = K_s - K_b$$

The actual calibration was achieved by injecting various amounts of polystyrene, PCC 51,000, obtained from Pressure Chemical Co., and also an anionically polymerized polybutadiene. The results are listed in Table 1. Only one concentration of 1,4-polybutadiene was used to calibrate the RI detector for this polymer. The areas under the curves were determined by graphical integration and used to calculate the proportionality constants listed in Table 1. The output of the UV detector was found to be linear with polymer concentration over the range of interest. Values for the constants inherently depend upon the unit of count interval (0.5 count) used to sample

TABLE 1

Calibration of UV and RI Detectors

Amount (g)	Area[a]	Peak maximum count
	Polystyrene (PCC-51,000)	
RI Detector		
0.000834	208.2	32.11
0.000834	208.3	32.22
0.000417	108.2	32.20
0.000209	52.7	32.16
UV Detector		
0.000834	154.6	31.80
0.000417	79.2	31.78
0.000209	39.1	31.79
	Polybutadiene	
RI Detector		
0.00125	236.9	28.08
	$K_s' = 1.88 \times 10^5$ (UV)[a]	
	$K_s = 2.54 \times 10^5$ (RI)[a]	
	$K_b = 1.90 \times 10^5$ (RI)[a]	
	$\Delta K = 6.45 \times 10^4$ (RI)[a]	

[a] These values are dependent upon the count interval used to sample the curves. The interval is 0.5 count.

the curves. The experimental equation used to calculate the styrene fraction

$$(W_s)_i = \frac{R_i}{0.989 - 0.341R_i}$$

is independent of this count interval because of the use of ratios.

Because the two detectors are in series, their outputs do not coincide on the count axis. The UV curve appears 0.38 counts previous to the RI curve. This was taken into consideration when sampling the two curves. The introduction of the UV detector has added a volume to the system, amounting to 0.265 counts (1.33 ml). The molecular weight calibration has to be modified to account for this if conversion to molecular weight is desired.

DISCUSSION

A number of copolymers of butadiene and styrene were run on the GPC equipped with the two detectors. Several examples are shown graphically in the figures. The normalized GPC curves, showing the molecular weight distribution as a function of counts, are indicated by circles. The ordinate to the left relates to this curve; the units are arbitrary, depending upon the count interval used. The data points represented by squares give the polymer composition (fraction of styrene) as a function of counts (log molecular weight); the scale on the right ordinate is to be used with the square points.

Figure 1 shows the data for a typical SBR. A free radical initiator was used to prepare this polymer, and because the reactivity ratios of the two monomers are different, composition of the copolymer changes with conversion. However, because of relative rates of initiation, propagation, and termination, the molecular weight after very early conversion is practically independent of conversion. Theoretically, this would produce a polymer which would have very little differences in its composition of different molecular-weight species. However, at any one molecular weight, a difference in composition exists depending on whether it was produced early or late in the reaction. In this case, though, only the average value for molecular weight would be measured. Because of the rapidity of the propagation reaction, the composition of any one molecule is very uniform and random. Thus, from the accepted mechanism of free radical polymerization, SBR should have a very uniform composition as a function of molecular weight. Previous work has indicated this (*5*); this study also shows it to be true over the major amount of copolymer. The observed decrease in the amount of styrene at high molecular weight, however, is unexpected and will have to be verified. Although it is true that these data are less precise because the fraction of styrene is calculated from the ratio of outputs of the two detectors and both outputs are small at the extremes of the curves, this decrease appears to be greater than experimental error. It could possibly be related to branching, which would mean that branching would involve material formed at an earlier time in the polymerization and thus contains a lower amount of styrene. More data are needed to clarify this point.

The situation is quite different for an anionic initiator such as butyllithium. In this case, both composition and molecular weight vary with conversion, the former because of the reactivity ratio of the two monomers, and the latter because of the long lifetime of the growing chain. This system produces so-called "live polymers" in the absence of a termination reaction. In the extreme case of a very fast anionic initiation reaction, monodispersed polymer of a

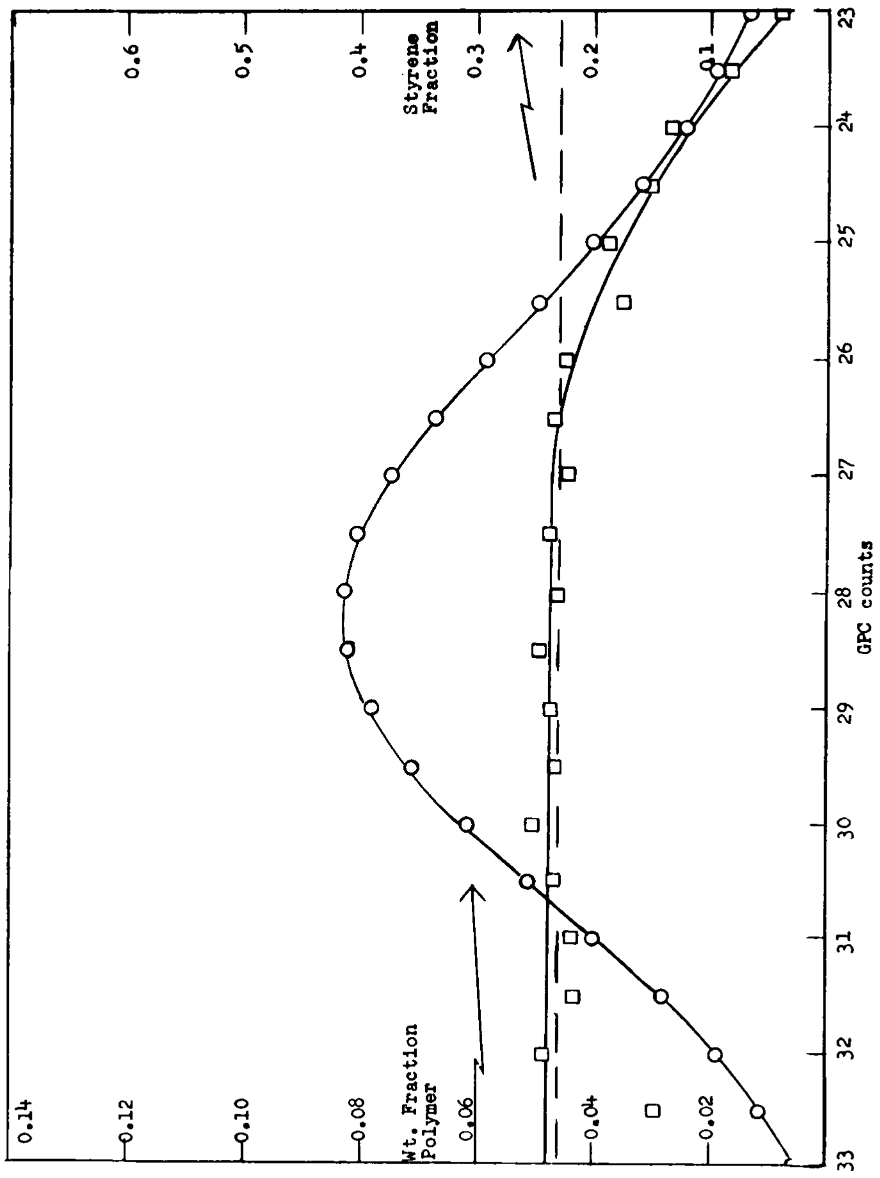

FIG. 1. Composition–molecular weight distribution of SBR, 23.5% styrene.

uniform composition would be produced. In reality, some breadth to the distribution is obtained because initiation and termination reactions do occur. These effects cause a variation in composition as a function of molecular weight. Thus, anionic copolymers of narrow molecular weight would be expected to have a more uniform distribution of styrene as a function of molecular weight than do broad polymers. However, the composition of individual chains varies along their length in contrast to the case of SBR produced by radical initiators.

Figures 2 and 3 are examples of the variation in composition that occurs in uniform copolymers made with anionic initiators. In general, these polymers have a more heterogeneous composition than does SBR which increases with the breadth of the distribution. These polymers were prepared under conditions designed to prevent the formation of blocks of polystyrene. Polymers Nos. 1 and 2 are representative of polymers made under reasonably good control and under "out of control" conditions, respectively. It is obvious that the polymer made under poor control conditions is the more heterogeneous and that the low molecular weight species have higher amounts of styrene. Duplicate runs are shown for Polymer No. 1. The near coincidence of the data indicates the reproducibility of the method.

The effect of adding a randomizing agent, such as an ether or amine, upon compositional heterogeneity is shown in Fig. 4. A uniform composition is obtained even though the molecular weight distribution is rather broad. Again, the amount of styrene decreases rapidly at the high molecular weight end of the distribution, possibly indicating the presence of branching.

Figures 5 and 6 refer to examples of SB (styrene/butadiene) and SBS (styrene/butadiene/styrene) type block copolymers, respectively. The SB polymer (Polymer No. 4) is relatively narrow in distribution and also of very uniform average composition. This indicates that practically all of the initial blocks were active during polymerization of the second monomer to produce essentially SB type polymer. In the case of SBS type (Polymer No. 5), both molecular weight distribution and composition cover a wider range. It appears that the lowest molecular weight material contains a higher percentage of styrene than the bulk of the copolymer. This could be explained by the possible presence of a small amount of low molecular weight homopolystyrene.

Thus, it would appear, experimentally, that the compositional

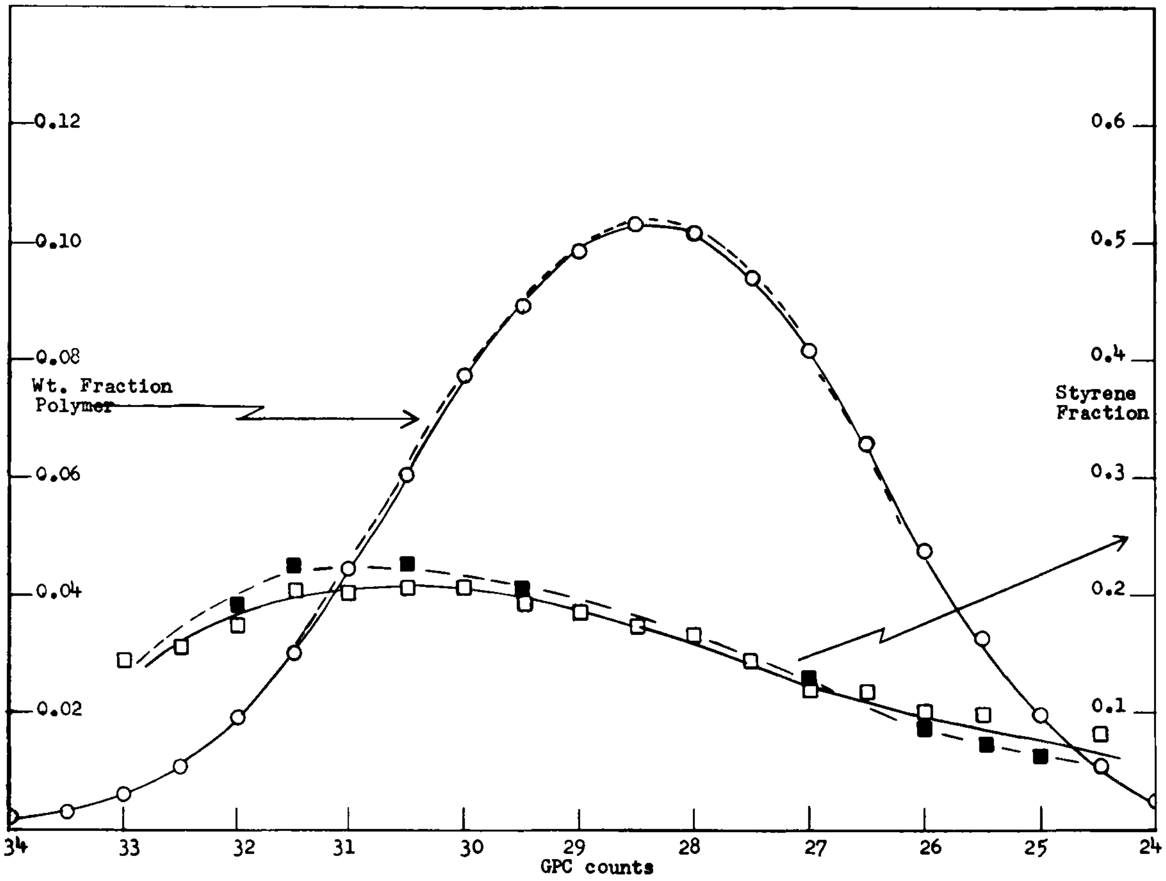

FIG. 2. Composition-molecular weight distribution of uniform butadiene–styrene copolymer. Polymer No. 1: 18% styrene. (—) Run No. 1; (– –) Run No. 2.

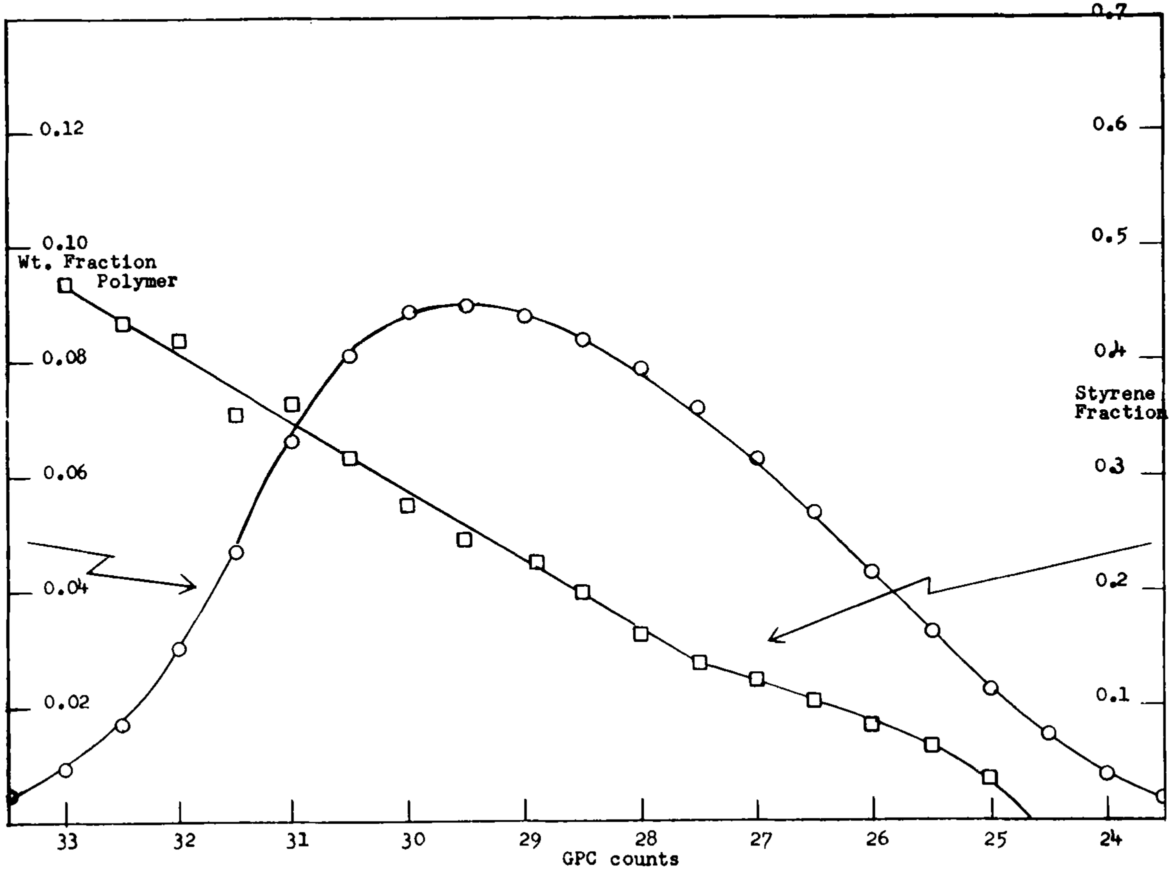

FIG. 3. Composition-molecular weight distribution of uniform butadiene-styrene copolymer. Polymer No. 2: 18% styrene.

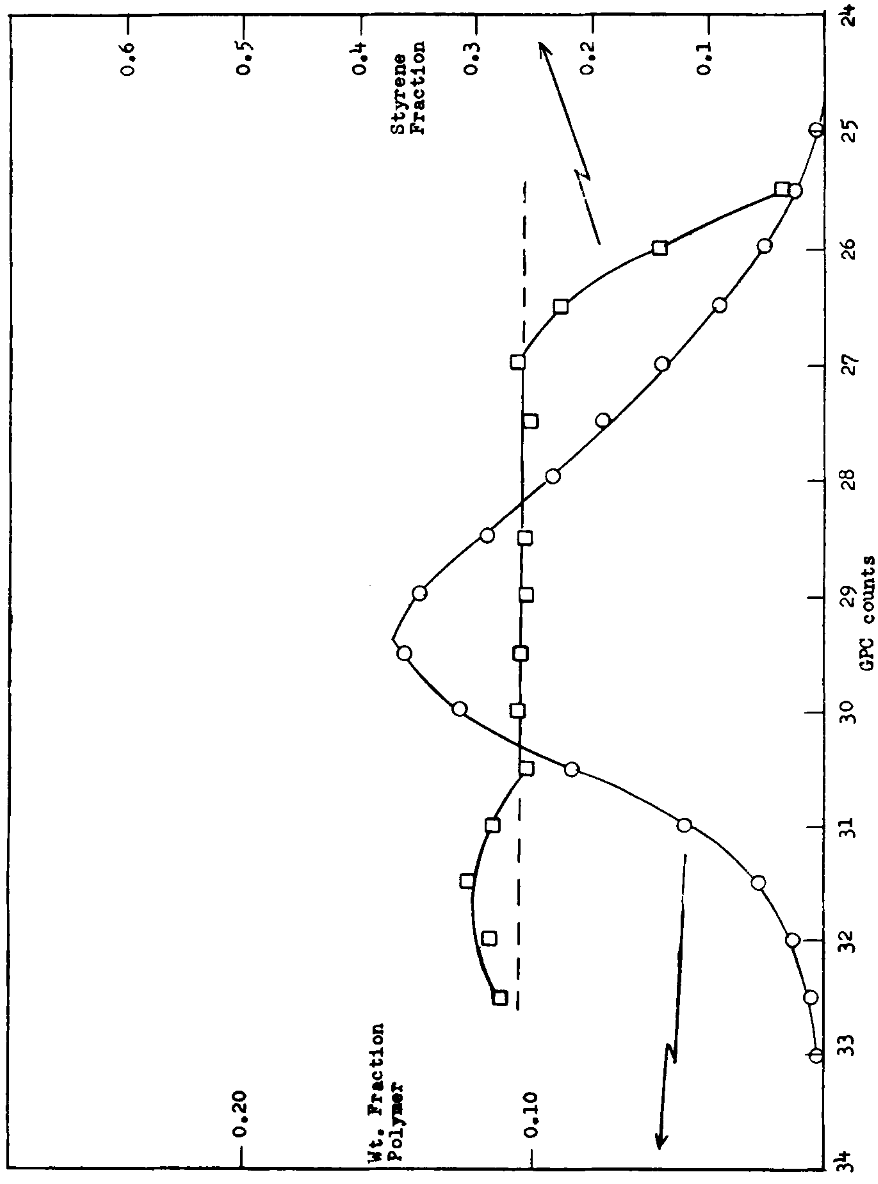

FIG. 4. Effect of randomizing agent upon the composition–molecular weight distribution of butadiene–styrene copolymer. Polymer No. 3: 25% styrene.

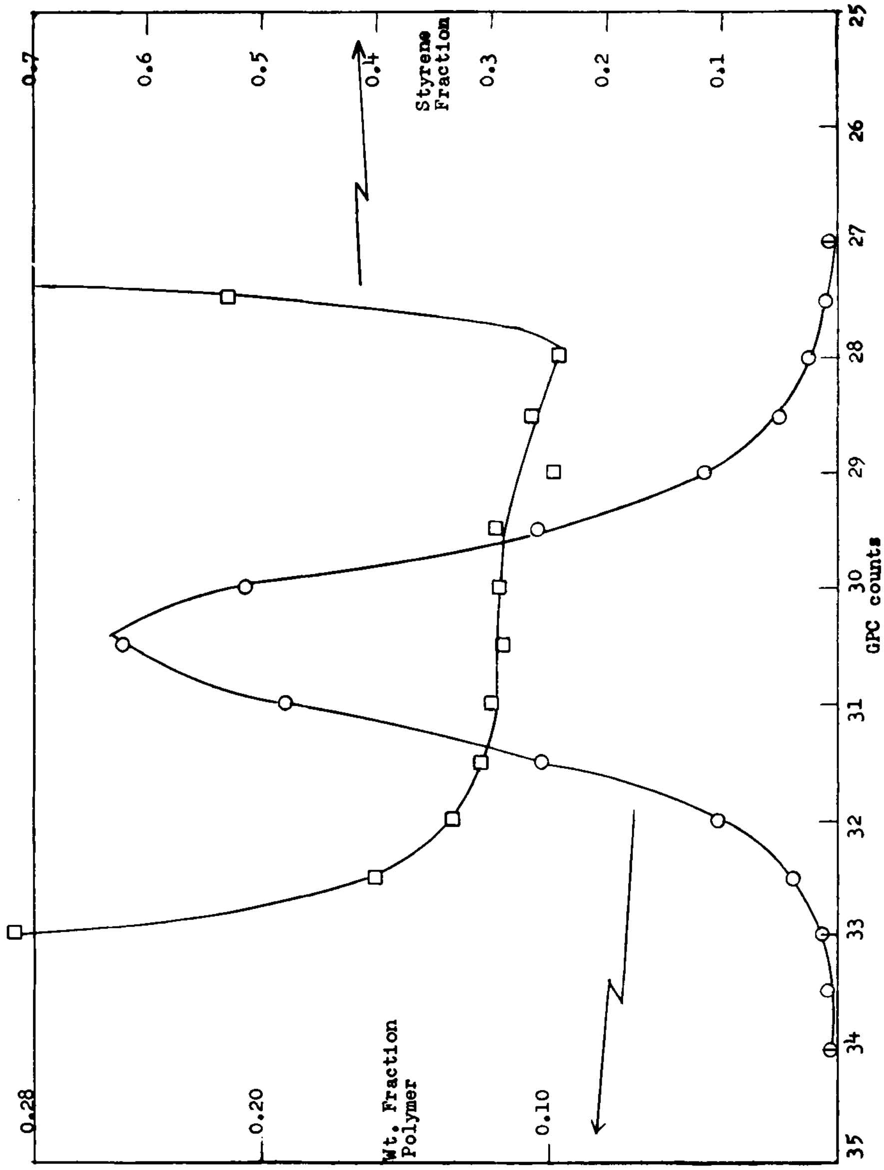

FIG. 5. Composition–molecular weight distribution of SB block copolymer. Polymer No. 4: 25% styrene.

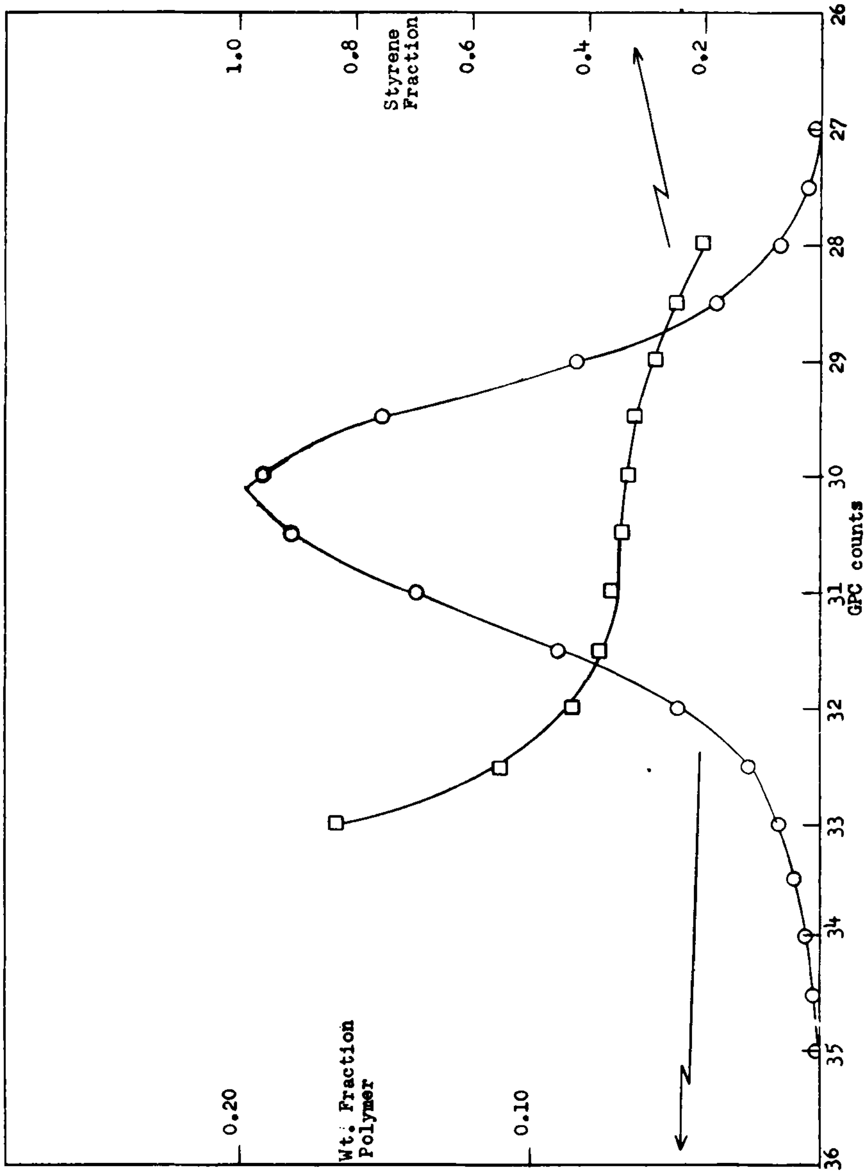

FIG. 6. Composition–molecular weight distribution of SBS block copolymer. Polymer No. 5: 30% styrene.

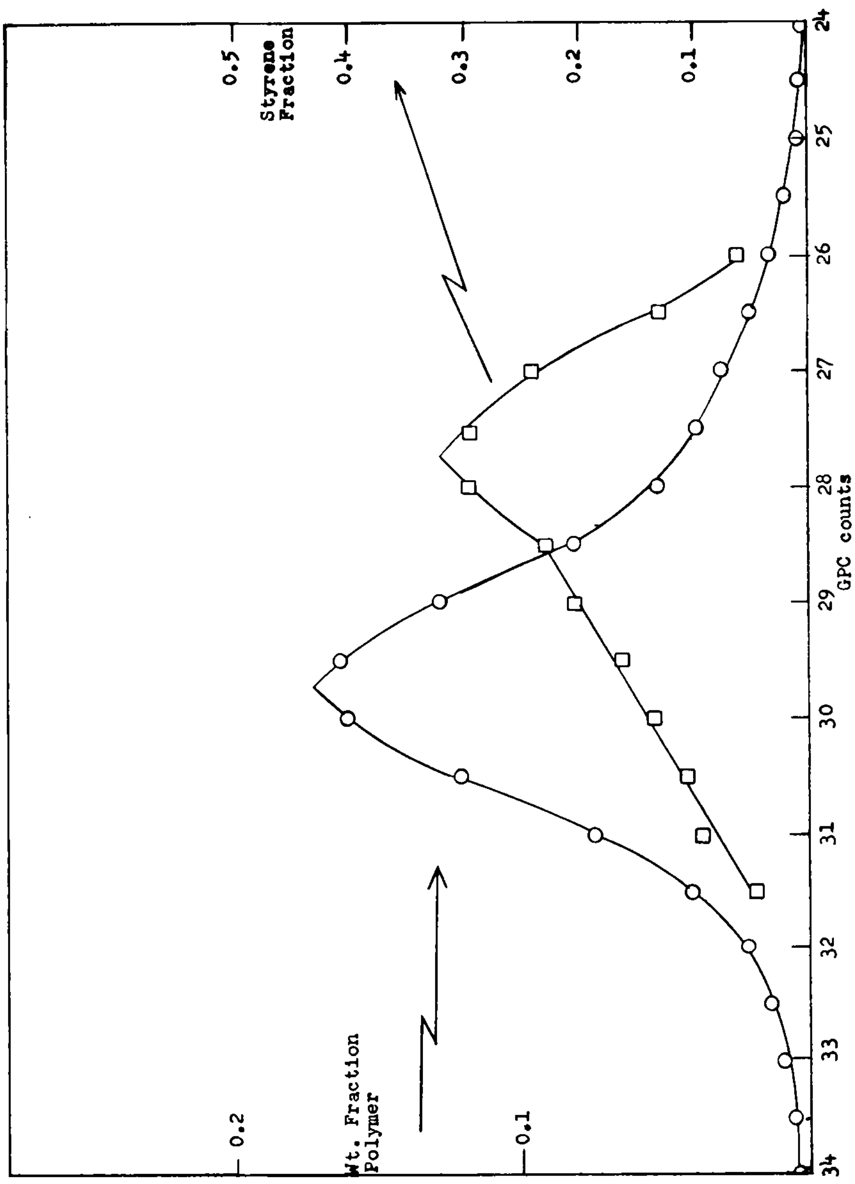

FIG. 7. Composition–molecular weight distribution of grafted copolymer. Polymer No. 6: 20% styrene.

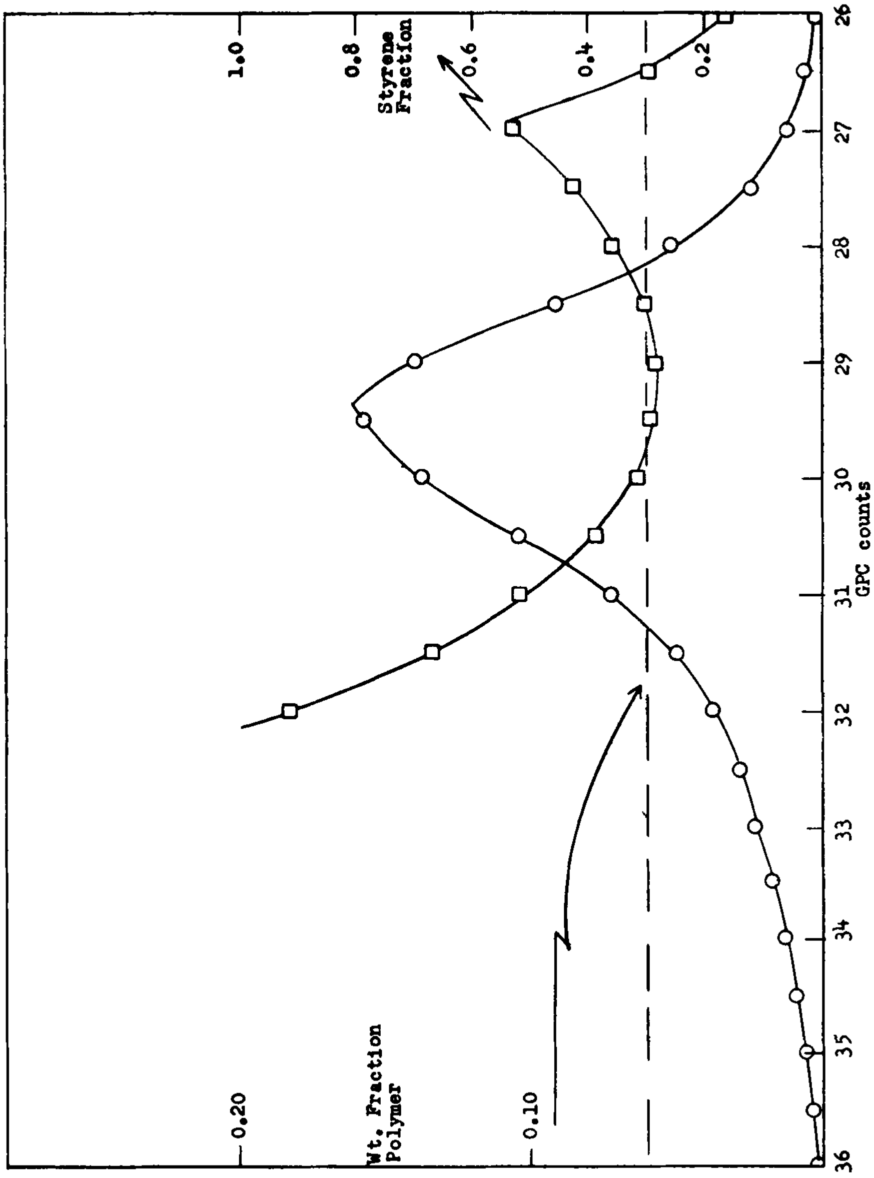

FIG. 8. Composition–molecular weight distribution of grafted copolymer. Polymer No. 7: 30% styrene.

heterogeneity of the anionic polymers roughly parallels the breadth of the molecular weight distribution.

Figures 7 and 8 are indicative of another type of material studied, namely, graft copolymers. These are experimental polymers which have been metalated and then have had styrene grafted on the polybutadiene backbone. The shape of the curves in the two figures depicting the distribution of styrene suggests that metalation and subsequent grafting were incomplete. There must have been considerable homopolybutadiene present that escaped metalation. The grafted polymer would, of course, have a higher average molecular weight than the homopolybutadiene. Polymer No. 7 differs from No. 6 in that, in addition to being a mixture of homopolybutadienes and grafted copolymer, it has some low molecular weight homopolystyrene present.

These examples serve to illustrate the versatility of the method. With a relatively inexpensive modification, the GPC can be used to obtain information concerning the composition of copolymers in addition to the usual molecular weight distribution. Useful information can be gained concerning the application of various polymerization and grafting techniques. The method should also be useful in studying relationships between physical properties and compositional heterogeneity. As usual, the simplicity and rapidity of the GPC method make it attractive.

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