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DETERMINATION OF THE COMPOSITION OF COPOLYMERS AS A FUNCTION OF MOLECULAR WEIGHT BY PYROLYSIS GAS CHROMATO-GRAPHY–SIZE-EXCLUSION CHROMATOGRAPHY

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SUMMARY

A sample of acrylonitrile–styrene copolymer was fractionated into ten portions by using analytical scale size-exclusion chromatography and the composition of the copolymer fractions was determined by using pyrolysis gas chromatography. A 0.12-ml volume of each fraction was collected in a platinum boat and the copolymer on the boat was pyrolyzed at 700°C after the removal of solvent. The amount of co-polymer pyrolyzed at a time ranged from 0.004 mg to 0.022 mg. The copolymer fractions have an average acrylonitrile content of 24%, the composition ranges from 21% to 30%, with the acrylonitrile content decreasing with increasing molecular weight. These data are in fair agreement with those determined by a dual-detector method, using ultra-violet and differential refractive index detectors. This system can be applied to the determination of both distributions, molecular weight and com-position, of copolymers for which a dual-detector method is inadequate.

INTRODUCTION

The physical properties of copolymers are dependent on their composition and molecular weight. Several studies have been made of the determination of the copolymer composition as a function of molecular weight. Size-exclusion chromato-graphy (SEC) (conventionally gel permeation chromatography, GPC) has been used in combination with ultraviolet (UV) and differential refractive index (RI) detectors for molecular weight and composition analysis of copolymers such as styrene–butadiene[1,2] and 4-vinylphenyl–isoprene[3]. The relationship between copolymer com-position and molecular weight for a poly(styrene–vinyl stearate) copolymer has been investigated by preparative SEC and infrared (IR) analysis of the fractions[4], and by the rapid stop-and-go GPC–IR technique[5]. Molecular weight and composition distri-butions of a poly(vinyl chloride–vinyl acetate) copolymer have been determined by SEC and IR analysis[6,7]. An on-line IR spectrophotometric detector has been used to monitor individual functional groups in a poly(styrene–*tert.*-butyl methacrylate) by repeated injections of the solute, and changing the wavelength setting[8].

The use of a UV detector in series with a RI detector for simultaneous determination of the composition and the molecular weight of a binary copolymer requires the restriction that one component should absorb UV radiation and the other should not. This limits the number of copolymers that can be examined by this UV–RI system. Appropriate selection of the wavelength setting in an IR detector may significantly expand its range of applicability to copolymer analysis, but the limited choice of solvent as the mobile phase to match the wavelength setting for functional groups in copolymers restricts the versatility of the detector.

Pyrolysis gas chromatography (PGC) has been widely used for copolymer composition analysis. Conditions essential to quantitative reproducibility in PGC have been studied and reproducibility can be achieved provided parameters such as pyrolysis-temperature rise time, sample size and sample thickness are carefully prescribed[9]. PGC may offer many advantages over other techniques such as the UV–RI system and IR detection in SEC. One of these advantages is the small sample size, and polymer amounts of less than 0.1 mg are occasionally pyrolyzed at a time. Sample size injected in high-performance SEC is usually 0.5 mg or less, and preparative-scale SEC may be required in order to determine the copolymer composition by an off-line IR detector[7]. Therefore, the utilization of PGC on the SEC fractions may permit the compositional analysis of copolymers the components of which do not absorb UV radiations, or of copolymers for which the application of IR detection is difficult. One example is a combination of SEC, thin-layer chromatography and PGC which has been used for the investigation of a polymethyl methacrylate–polystyrene–polymethyl methacrylate block copolymer[10].

In this paper, the evaluation of the precision and applicability of combined PGC–SEC was undertaken and compared with the dual-detector method, a combination of UV and RI detectors in SEC, in the determination of the percent composition of copolymers as a function of molecular weight. Acrylonitrile–styrene copolymers (ASR) were employed, a small amount of ASR being fractionated by SEC followed by determination of the composition of the fractions by PGC.

EXPERIMENTAL

Apparatus

SEC. Two sets of liquid chromatographs were used. One was a JASCO (Japan Spectroscopic Co., Tokyo, Japan) Trirotar high-performance liquid chromatograph equipped with a JASCO Uvidec-100 variable-wavelength UV detector and a Shodex SE-11 RI detector (Showa Denko Co., Ltd., Minato-ku, Tokyo, Japan). The UV detector was operated at 254 nm with a 10-mm path length microcell. Two Shodex A 80M GPC columns (500 × 8 mm I.D.) packed with a mixture of polystyrene gels of nominal porosity 10^3, 10^4, 10^5, and 10^6 Å were used. The other set was a Model LC-08 high-speed preparative liquid chromatograph (Japan Analytical Industry Co., Tokyo, Japan) equipped with UV and RI detectors and two preparative GPC columns (600 × 20 mm I.D.) packed with Jaigel 3H (corresponding to Shodex H203). Chloroform was used as solvent (the mobile phase).

PGC. A Yanaco (Yanagimoto Seisakusho Co., Kyoto, Japan) G-80 gas chromatograph equipped with a flame ionization detector was used. A Shimadzu Model PYR-2A furnace-type pyrolyzer was employed. The stainless-steel column

(150 cm × 3 mm I.D.) was packed with Diasolid L (100–120 mesh) coated with 5% PEG 6000.

Samples

Two grades of acrylonitrile–styrene copolymers (ASR) were used. One was prepared in our laboratory by solution polymerization in benzene using α, α'-azo-bisisobutyronitrile as an initiator. The nitrogen content in the polymers was determined by Dumas' method. The acrylonitrile contents ranged from 22.2 to 46.4 wt. %. The average molecular weight ranged from 5000 to 10,000 as determined by SEC. The acrylonitrile content of the sample (ASR-5) used for SEC fractionation and PGC analysis was 28.6 wt. %. The other grade was obtained from Mitsubishi Monsanto, Tokyo, Japan. The acrylonitrile contents ranged from 20.0 to 29.0 wt. %, and the average molecular weight from 100,000 to 200,000. The acrylonitrile content of the sample (ASR-24) used for SEC fractionation and PGC analysis was 24.0 wt. %.

Procedures

Calibration curve for PGC. About 5 mg copolymer material of known composition were weighed into a 20-ml volumetric flask and dissolved in 20 ml chloroform. A 20-μl volume of this solution was placed in a platinum boat (capacity *ca.* 40 μl) and dried using a 250-W IR lamp. This procedure was repeated twice, *ca.* 10 μg of the copolymer material being collected in the boat. The platinum boat was then inserted into the pyrolyzer. The pyrolysis temperature was 700°C. Operating conditions for GC analysis: nitrogen flow, 15 ml/min; column oven temperature, 140°C; flame ionization detector, range 10^{-1} with 1/256 attenuation. The ratio of peak area of acrylonitrile monomer to that of styrene monomer was plotted against the copolymer composition and a calibration curve was thus constructed. The product of peak height and peak half-width was used as peak area.

Fractionation of copolymer. The sample ASR-5 (*ca.* 25 mg) was weighed and dissolved in 5 ml chloroform. A 1.5-ml volume of this solution was injected into a Model LC-08 liquid chromatograph. Eleven 10-ml fractions were collected over the elution range of the sample.

The sample ASR-24 (*ca.* 10 mg) was weighed and dissolved in 5 ml chloroform. A 0.5-ml portion of this solution was injected into a Trirotar liquid chromatograph, the flow-rate being 1.0 ml/min. Collection of fractions was carried out at intervals of 80 sec (every 1.33 ml) and ten fractions were collected over the elution range of the sample.

PGC of the fractions. For fractions of the sample ASR-5, a 30-μl portion of each fraction, except Nos. 1 and 11, was placed in a platinum boat and allowed to dry. This procedure was repeated six times and a total of 180 μl of the fraction were collected on the boat. Fractions 1 and 11 were concentrated to one-fourth by volume before being placed in a platinum boat, and then a total of 180 μl of the concentrastes were collected on the boat.

For fractions of the sample ASR-24, a total of 120 μl of each fraction, except Nos. 1 and 10, were collected on the boat. For fractions 1 and 10, 360 μl were collected in total. PGC conditions were the same as for the calibration curve.

Distributions of molecular weight and composition

Step 1. A calibration curve of log molecular weight *vs.* elution volume was constructed using polystyrene standards.

Step 2. A copolymer calibration curve of log molecular weight *vs.* elution volume was constructed from the known compositions of the fractions of ASR-5 or ASR-24 copolymers and by using the polystyrene calibration curve. The copolymer molecular weight obtained from the polystyrene calibration curve was converted into the so-called "working" molecular weight[5] using

$$M_c = M_s (1 - 4.9 \times 10^{-3} \text{ AN mol}\%)$$

$$= M_s(1 - \frac{51 \text{ AN wt.}\%}{5300 + 51 \text{ AN wt.}\%} \tag{1}$$

where M_c = "working" molecular weight of the copolymer, M_s = molecular weight from the polystyrene calibration curve and AN mol% and AN wt.% = acrylonitrile content in mol% and wt.%.

First, the value of M_s for each fraction was determined from the average elution volume of the fraction using the polystyrene calibration curve. Then, the value of M_c for the fraction was calculated from eqn. 1, followed by plotting the value and the average elution volume of the fraction.

Step 3. The RI response of the SEC chromatogram of the copolymer sample was corrected using

$$H_{corr.} = H_{uncorr.} (1 + 0.011 \text{ AN wt.}\%) \tag{2}$$

where $H_{corr.}$ and $H_{uncorr.}$ are the corrected and uncorrected heights of each increment of the elution volume.

Step 4. The molecular weight averages of the copolymer sample were calculated from the values of $H_{corr.}$ obtained in Step 3 and using the copolymer calibration curve in Step 2.

Step 5. The differential molecular weight distribution curve was constructed after converting the values of dW/dV of the normalized SEC chromatogram in to those of $dW/d \log M$ using the copolymer calibration curve.

Step 6. By plotting the relation between M_c and acrylonitrile content of each fraction on the same chart obtained in Step 5, both distribution curves, molecular weight and composition, were visualized.

RESULTS AND DISCUSSION

Fundamentals of PGC

Quantitative analysis of pyrolysis products requires much more stringent control than qualitative identification techniques. Differences in, for example, sample size and sample features, can often significantly affect the decomposition pattern[11]. The major product of degradation of polystyrene and polyacrylonitrile is the

respective monomer and the yield is dependent on temperature and sample size. The copolymer concentration of SEC fractions is variable and the content of copolymers subjected to PGC might be very small. For these reasons, preliminary investigations of experimental factors must be performed before analysis of SEC fractions.

A chloroform solution (0.5%, w/v) of ASR-5 was prepared and various volumes of this solution from 10 μl to 100 μl were loaded into a platinum boat, followed by evaporation of the chloroform. Polymer contents loaded were between 0.05 mg and 0.5 mg. PGC was carried out at various pyrolysis temperatures and peak-height ratios of acrylonitrile monomer to styrene monomer were plotted against polymer weight pyrolyzed. The results are shown in Fig. 1. Both the yields and peak-height ratios of the respective monomers increased with rising pyrolysis temperatures except that the maximum yield of styrene monomer was attained at 650°C. This suggests that sensitive analysis may be performed at higher pyrolysis temperatures. Pyrolysis of lower sample weights gave similar results as shown in Fig. 2. A 0.05% (w/v) chloroform solution of ASR-5 was prepared and the polymer contents
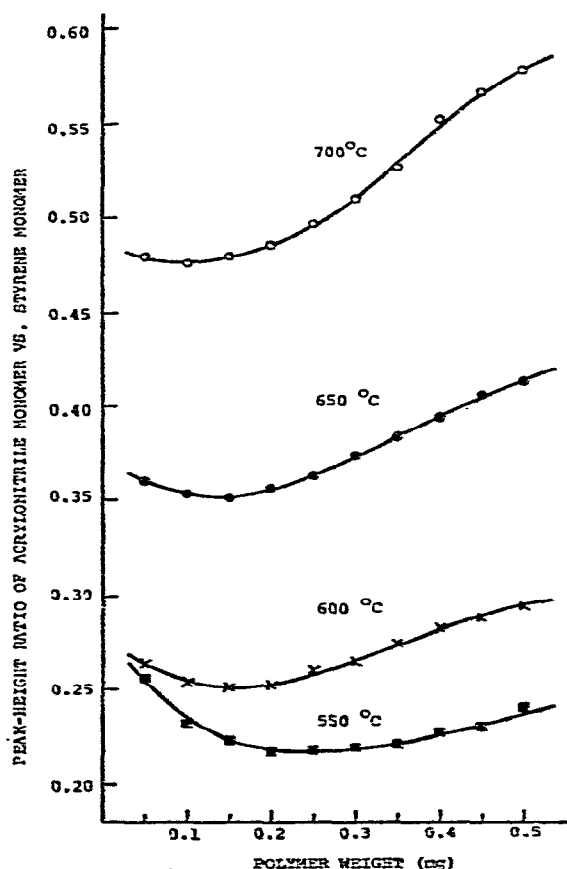

Fig. 1. Variation of ratio of monomer yields with sample weight pyrolyzed. Sample, ASR-5.

loaded into a platinum boat were between 0.005 mg and 0.05 mg. The curves of peak-height ratio against polymer weight exhibit a minimum, which demonstrates that the peak-height ratio is dependent on the weight of the pyrolyzed sample. On the other hand, the peak-area ratio is independent of the sample weight (see Fig. 2).
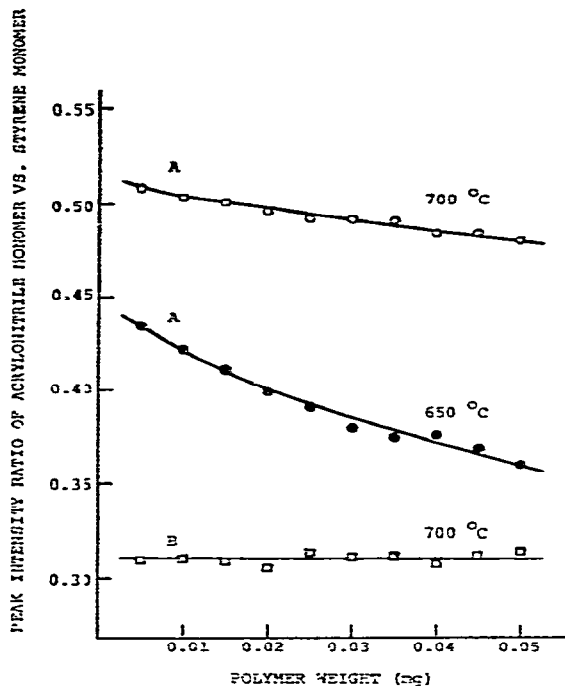

Fig. 2. Variation of ratio of monomer yields with lower sample weight pyrolyzed and comparison of peak height and peak area. A, Peak-height ratio; B, peak-area ratio. Sample, ASR-5.

A PGC calibration curve of the ratio of peak areas of acrylonitrile and styrene monomers *versus* acrylonitrile content obtained from physical mixtures of homopolymers (polystyrene and polyacrylonitrile) differed significantly from that obtained from copolymers of known composition as shown in Fig. 3. This difference may be due to the difference in rates of degradation between copolymers and homopolymers. The yield of acrylonitrile monomer from the physical mixture was 50% less than that from the copolymer of the same composition, and that of styrene monomer 25% more. The peak positions of styrene monomer and other products from polystyrene were delayed by *ca.* 7 sec compared with those from the styrene unit of the copolymer. In this study a PGC calibration curve has been constructed by using copolymers of known composition.

The repeatability of pyrolysis is excellent and the relative standard deviation of the ratio of peak areas ranges from 1.0% to 1.5%. The reproducibility at different sample loads is also good and the relative standard deviation is less than 1.5%. The standard deviation of the acrylonitrile content is 0.15 wt.%. The calibration data were not affected by the molecular weight difference in the range studied.
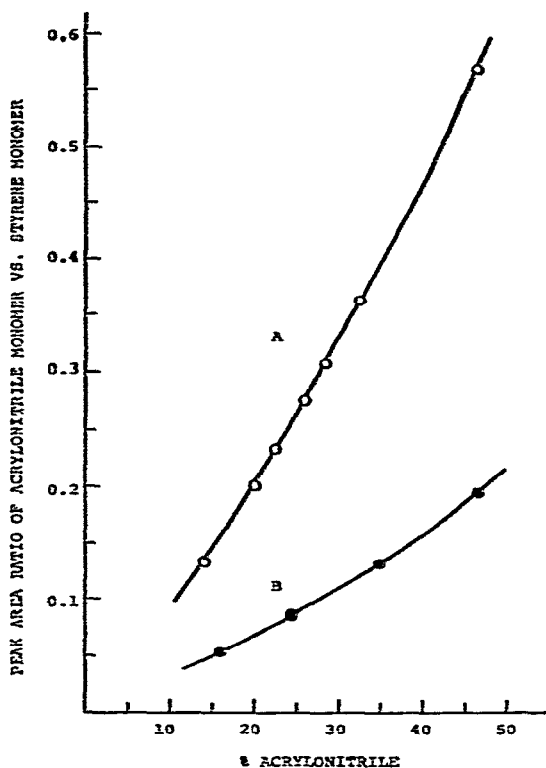
Fig. 3. Comparison of the ratio of respective monomer yields between copolymers (A) and physical mixtures of homopolymers (B). Sample weigth pyrolyzed, 2 mg.

Composition and molecular weight of fractions

ASR-5. The copolymer material (7.5 mg; 1.5 ml of 0.5% solution) was fractionated into eleven portions and the copolymer content in each solution fractionated ranged from 0.045 mg to 1.545 mg. The copolymer amount pyrolyzed at a time ranged from 0.0027 to 0.0278 mg. The variation of the pyrograms with polymer weight pyrolyzed is shown in Fig. 4 for fractions 1 and 2. For fraction 2, the pyrolysis patterns are somewhat different, but the numerical value of the ratios of peak area of acrylonitrile and styrene monomers does not change with sample size except A in Fig. 4 which is about two-thirds that of the others. In addition, hydro-carbons such as methane, ethane and ethylene increased in yield. The minimum sample amount pyrolyzed should by 0.002 mg under the present experimental conditions. Therefore, a volume of 180 μl for fraction 1 is too small to obtain an accurate value for the peak ratio.

For comparison purposes, known weights of the copolymer fraction were collected on the boat. The copolymer content in each solution fractionated was estimated from the area on the SEC chromatogram occupied by each fraction and *ca.* 0.006 mg (from 40 μl to 330 μl for fractions 2–10) of the copolymer were pyrolyzed. The compositions of copolymer fractions as determined by both procedures are summarized in Table I, together with the values calculated by a dual-detector method
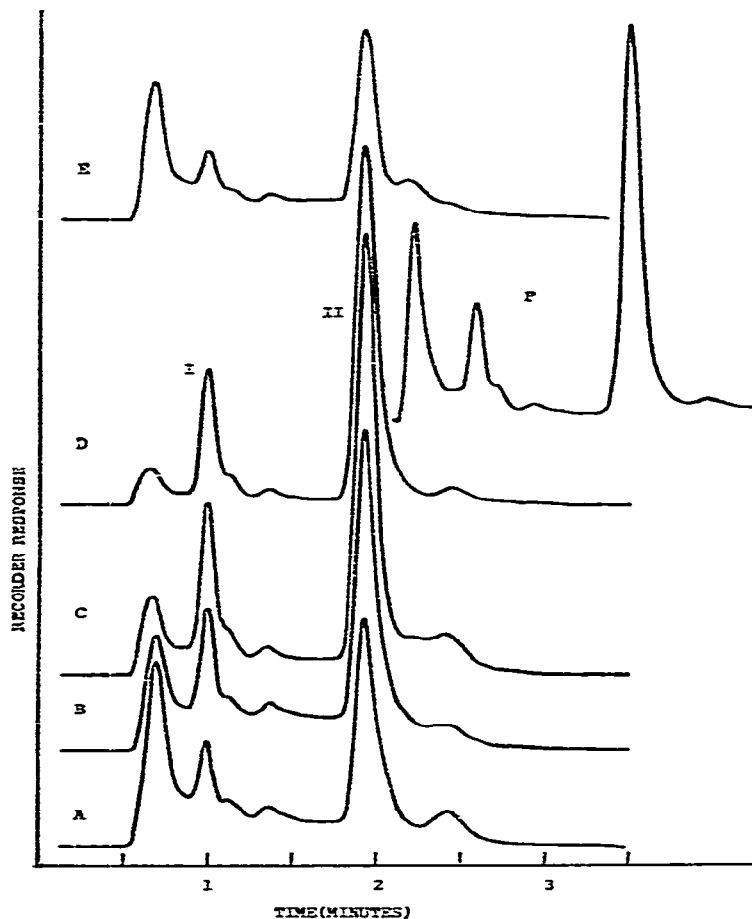
Fig. 4. Pyrolysis gas chromatograms of fractionated copolymer ASR-5 at different pyrolysis amounts. A–D, Fraction 2; E–F, fraction 1. Sample volume, weight and GC sensitivity: A, 40 μl, 1.0 μg, $10^{-1} \times 1/32$; B, 60 μl, 1.5 μg, $10^{-1} \times 1/32$; C, 180 μl, 4.6 μg, $10^{-1} \times 1/64$; D, 300 μl, 7.7 μg, $10^{-1} \times 1/128$; E, 180 μl, 1.2 μg, $10^{-1} \times 1/32$; F, 180 μl (a concentrate), 4.8 μg, $10^{-1} \times 1/64$. Peaks: I = acrylonitrile; II = styrene.

which will be discussed elsewhere. These results are in good agreement with each other. The average acrylonitrile content for the whole copolymer as calculated from the acrylonitrile content and the weight percent of each fraction is listed in the same column. These values are in fair agreement with the analysis of the unfractionated sample (28.6 wt. %).

The weight percent of each fraction was calculated from the area of the SEC chromatogram defined by the dotted line (see Fig. 5). A correction was made for the difference in response factors between polystyrene and polyacrylonitrile using eqn. 2. In the range of chemical compositions studied, the correction does not significantly influence the results of the weight percent for each fraction. The molecular weight of each fraction was calculated from the average elution volume of the fraction using the polystyrene calibration curve and eqn. 1. Molecular weight averages

TABLE I

ACRYLONITRILE CONTENT AND MOLECULAR WEIGHT OF ASR-5 FRACTIONS

Fraction No.	Acrylonitrile content (wt.%)			Weight percent fraction (%)		Molecular weight × 10⁻³
	By definite volume	By definite weight	By D-D method*	Uncorrected	Corrected	
1	24.2	(24.2)	25.6	0.9	0.9	54
2	25.5	26.0	25.9	3.5	3.4	27.5
3	27.2	27.0	27.2	10.0	9.9	16.6
4	27.7	27.7	28.2	17.1	16.9	11.1
5	28.8	28.6	29.1	20.6	20.6	7.5
6	29.3	29.3	28.9	18.1	18.2	5.0
7	30.1	30.3	29.9	13.7	13.8	3.35
8	30.7	30.8	30.5	8.8	8.9	2.25
9	31.3	31.5	31.5	4.7	4.8	1.55
10	31.6	31.9	30.9	2.0	2.0	1.02
11	33.3	(33.3)	33.9	0.6	0.6	0.66
Calculated average composition	28.9	29.0	29.0			

* Dual-detector method.

of the whole copolymer, calculated by using the corrected SEC chromatogram (Step 3) and the copolymer calibration curve (Step 2), are $\overline{M}_w = 8.01 \cdot 10^3$ and $\overline{M}_n = 4.38 \cdot 10^3$.

ASR-24. The copolymer material (1.0 mg; 0.5 ml of 0.2% solution) was fractionated into ten portions and the copolymer amount pyrolyzed at a time ranged from 0.0019 mg to 0.0220 mg. The normalized size exclusion chromatogram, the polystyrene calibration curve (Step 1) and the copolymer calibration curve (Step 2) are shown in Fig. 5. Fractionation of the copolymer was carried out at indicated by the dotted lines on the chromatogram.

The SEC chromatogram of the copolymer must be corrected using eqn. 2 when a differential refractometer is used as a detector. This equation has been derived from the assumption that the response factor of polystyrene is 2.1 times that of polyacrylonitrile.

The molecular weight averages for the copolymer calculated according to Step 4 are $\overline{M}_w = 1.79 \cdot 10^5$, $\overline{M}_n = 6.44 \cdot 10^4$ and $\overline{M}_w/\overline{M}_n = 2.78$. The values calculated assuming a constant composition are slightly higher: $\overline{M}_w = 1.81 \cdot 10^5$, $\overline{M}_n = 6.63 \cdot 10^4$ and $\overline{M}_w/\overline{M}_n = 2.73$. In the range of chemical compositions and molecular weights studied, the chemical composition does not significantly influence the results of SEC analysis.

Fig. 6 shows a normalized differential molecular-weight distribution curve calculated by Step 5, and the acrylonitrile content as a function of molecular weight. The composition distribution curve calculated by a dual-detector mehtod is also shown. The comparison of these methods will be discussed elsewhere. The average acrylonitrile content for the whole copolymer as calculated from the composition and
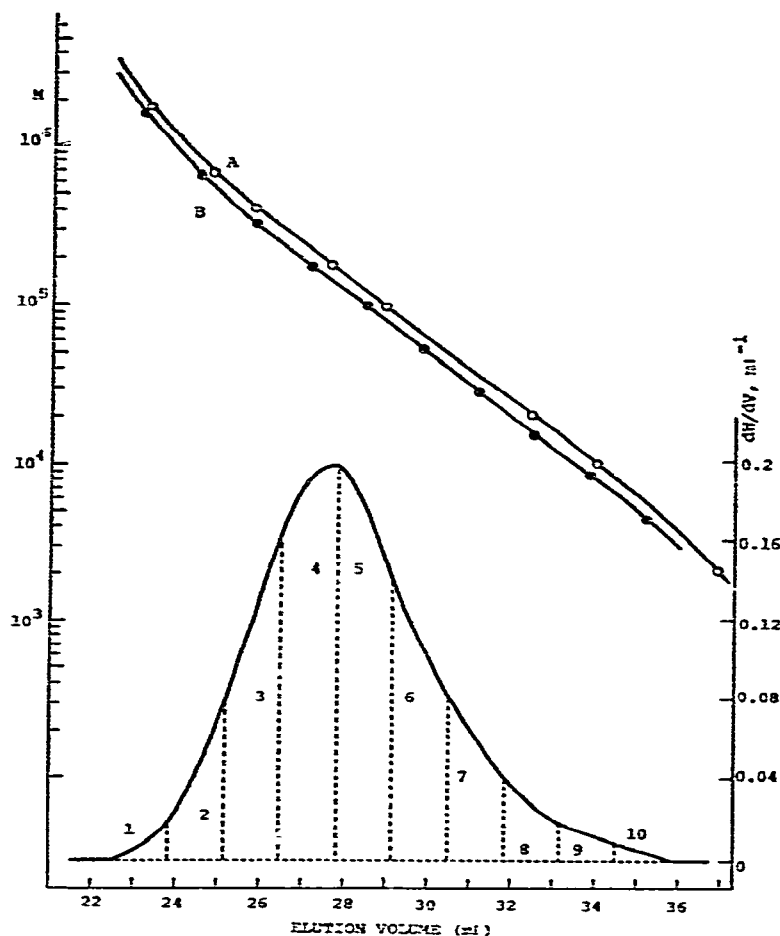
Fig. 5. Normalized size exclusion chromatogram, polystyrene calibration curve (A) and copolymer calibration curve (B) for ASR-24 copolymer.

the weight percent of each fraction was 24.4 wt. %, which is in good agreement with the value for the unfractionated sample (24.0 wt. %).

Eqn. 1 has been derived from

$$M_{\overline{z}} = M_s \times \frac{53 \text{ AN mol\%} + 104 \text{ ST mol\%}}{104 \times 100} \tag{3}$$

where 53 and 104 are the molecular weights of monomer units of acrylonitrile and styrene, respectively. This equation is based on the concept of "working" molecular weight[12], and its validity will be discussed elsewhere.
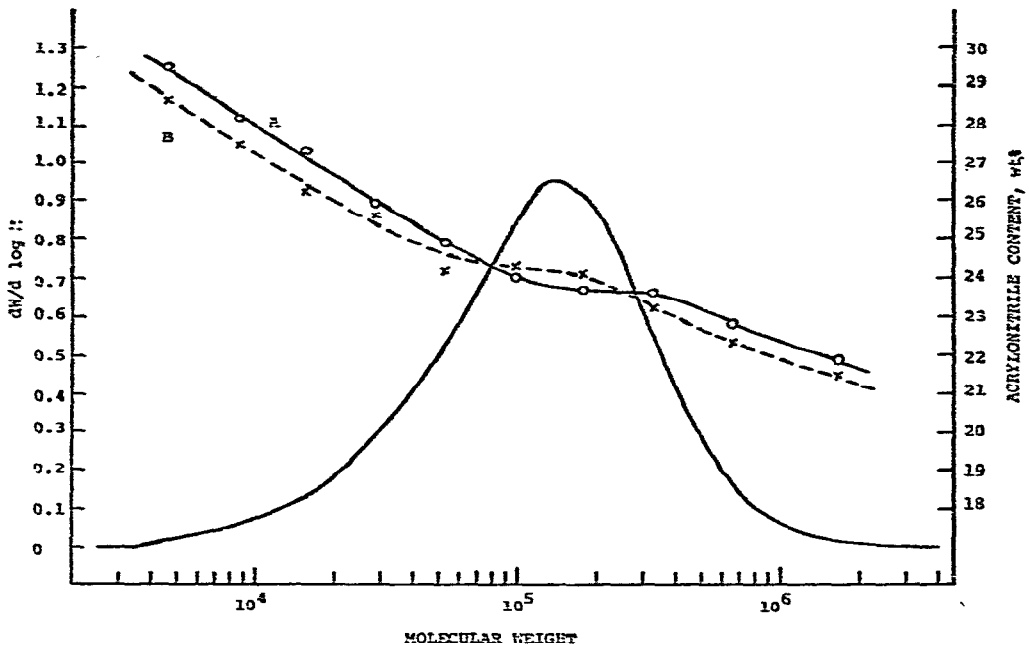
Fig. 6. Normalized molecular weight and composition distribution curves of ASR-24 copolymer, obtained by PGC (A) and by a dual-detector method (B).

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