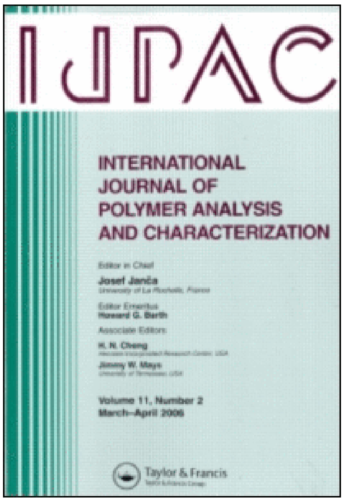

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Eiichi Kawai[a]; Hyun-Suk Shin[a]; Kenji Ogino[a]; Hisaya Sato[a]
[a] Department of Material Systems and Engineering, Tokyo University of Agriculture and Technology, Tokyo, Japan

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Separation of Styrene - Methyl Methacrylate - Acrylonitrile Terpolymers by Composition Using High-Performance Liquid Chromatography

Eiichi Kawai, Hyun-Suk Shin, Kenji Ogino,
and Hisaya Sato
Department of Material Systems and Engineering,
Tokyo University of Agriculture and Technology,
Tokyo, Japan

Separation of styrene - methyl methacrylate - acrylonitrile terpolymers by chemical composition was studied using high-performance liquid chromatography (HPLC). Cross-linked polyacrylamide (PAA) gel or polyacrylonitrile (PAN) gel was used as a stationary phase for normal-phase HPLC and cross-linked polystyrene (PS) gel for reversed-phase HPLC. Each system was based on a solvent gradient, and the separation was governed by an adsorption mechanism. Terpolymers were successfully separated by the cross-fractionation, i.e., the combination of two types of HPLC systems with PAN and PAA columns or PAN and PS columns. The chemical composition distribution (CCD) of a high-conversion terpolymer was analyzed by this cross-fractionation technique with the combination of PAA and PAN columns. The CCD obtained experimentally was reasonably consistent with that of theoretical calculation.

Keywords: Adsorption; Liquid chromatography; Polymer gel; Cross-fractionation; Terpolymer; Chemical composition distribution

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Address correspondence to Hisaya Sato, Department of Material Systems and Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan.

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INTRODUCTION

Most statistical copolymers exhibit chemical composition distribution (CCD). Even in the case of low-conversion polymerization, the copolymers show a statistical composition distribution because of limited molecular weight. When the composition of residual monomers changes with increased conversion, the composition distribution of copolymers becomes broader. Since CCD strongly affects physical properties, it is important to analyze it. Fractional precipitation, thin layer chromatography, and high performance liquid chromatography (HPLC) have been commonly used for CCD analysis because copolymers can be separated by composition utilizing these methods. HPLC has been widely used for analysis of CCD because of the advantages of high resolution, good reproducibility, and simple automated operation. The separation of copolymers is governed mainly by two enthalpic mechanisms: precipitation-redissolution mechanism or adsorption(and/or partition)-desorption mechanism. In both cases, temperature or solvent gradient is applied to the separation of copolymers. Because it is well known that adsorption-desorption mechanism shows little influence of molecular weight, it is a more suitable measurement of CCD.

In 1979, copolymers of styrene and methyl acrylate were separated by Teramachi et al.[1] according to composition using the adsorption-desorption mechanism with solvent-gradient. Since then, the gradient elution method has been applied to separate several types of copolymers by composition[2–8]. We have reported that highly cross-linked polymer gels exhibit less irreversible adsorption, and HPLC using polymer gel as the packing shows better reproducibility than silica gel. This method was applied to several types of copolymers, such as styrene-butadiene and styrene-methyl methacrylate copolymers[9–14].

This report deals with the separation of statistical terpolymers consisting of styrene (S), methyl methacrylate (MMA), and acrylonitrile (AN) based on the chemical composition. Cross-fractionation using two types of HPLC with different elution conditions are needed to separate terpolymers by chemical composition. The CCD of a high-conversion terpolymer was determined. Until now, analysis of CCD was limited to binary copolymers, and there have been no reports on the analysis of terpolymers.

EXPERIMENTAL

Samples

Statistical copolymers and terpolymers were prepared using benzoyl peroxide as an initiator in bulk under nitrogen atmosphere. The conversion of most samples was kept below 10% for obtaining samples with a narrow chemical composition distribution. Alternatively, high-conversion terpolymer with a broad chemical composition was prepared. Effective average molecular weights M_n and M_w were determined by gel permeation chromatography (GPC) using chloroform as an eluent. The calibration curve drawn by polystyrene standards was used. It is confirmed that all the samples we prepared have weight-average molecular weights over 10^5. The compositions of S-MMA copolymers were determined by ^{1}H nuclear magnetic resonance (NMR), and those of other polymers were determined by elemental analysis.

HPLC

Cross-linked poly(acrylonitrile-ethylene dimethacrylate) (PAN) gel[11] and poly(styrene-divinylbenzene) (PS) gel[15] were prepared by suspension polymerization and poly[acrylamide-methylene bis(acrylamide)] (PAA) gel[16] was synthesized by an inverse suspension polymerization. 2,2′-Azobis (2,4-dimethylvaleronitrile) was used as an initiator and poly(vinyl alcohol) as a stabilizer in suspension polymerization. 4,4′-Azobis(4-cyano valeric acid) was used as an initiator and bentonite as a suspension agent in inverse suspension polymerization. The resulting copolymer beads were washed successively with hot water, acetone, and dimethylformamide (or chloroform) for the removal of the suspension stabilizer, unreacted monomers, and noncross-linked polymer. Small beads with a diameter of 5–10 μm were removed by decantation in acetone. Each material was packed into a 4.6 mm i.d. × 25 cm stainless-steel column by a slurry method. Table I lists the characteristics of packing materials used for HPLC.

HPLC was carried out by a gradient elution using two high-pressure pumps, one for the adsorption-promoting solvent for polymers and the other for the desorption-promoting solvent. The proportion of the des-

TABLE I Characteristics of HPLC Columns

Column	M/D[a]	Divinyl monomer	Pressure (kg/cm^2)	Flow rate (mL/min)	Ex. L[b] (×10^3)	NTP[c]
PAA	50/50	BA	350	4.8	300	1400
PAN	67/33	EDMA	400	1.9	300	2800
PS	30/70	DVB	360	2.0	500	4700

a. Volume ratio of monomer and divinylmonomer

b. Molecular weight at exclusion limit

c. Number of theoretical plates/25 cm

Abbreviation: AA—acrylamide; BA—N,N′-methylene-bis(acrylamide); AN—acry-lonitrile, EDMA—ethylene dimethacrylate; S—styrene; DVB—divinylbenzene

TABLE II Experimental Conditions for HPLC

HPLC	Column	DPS[a]	APS[b]	Gradient (DPS/APS) (vol %)
Normal Phase	PAA	$CHCl_3/CH_3CN$ (80/20 vol %)	hexane	40/60 → 100/0
	PAN	$CHCl_3/CH_3CN$ (80/20 vol %)	hexane	20/80 → 80/20
Reversed-Phase	PS	$CHCl_3$	CH_3CN	0/100 → 60/40

a. desorption-promoting solvent, b. adsorption-promoting solvent

orption-promoting solvent in the eluent was linearly increased in 25 min. The solvent compositions at the start and end of the gradient are shown in Table II.

The two solvents were filtered and the flow rate was 0.5 mL/min. A 10-μL portion of the sample (5 mg/ml) was injected through a Rheodyne 7125 injector. The column temperature was maintained at 30°C by a column oven. The column effluent was monitored with an evaporative mass detector (Applied Chromatography System Co., Ltd., Model 750/14) or a UV detector (Jasco UV-254 II) at 254 nm.

Nonpolar eluent was used for a column packed with polar PAA and PAN gel as normal-phase HPLC, and polar eluent was used for a column packed with nonpolar PS gel as reversed-phase HPLC. In the case of the stationary phase PAN and PAA gel, a mixture of chloroform/acetonitrile (80/20) as the desorption-promoting solvent and hexane as the adsorption-promoting solvent were used. In the case of reversed-phase using PS gel, chloroform as desorption-promoting solvent and acetonitrile as the adsorption-promoting solvent were used. The elution time of each copolymer and terpolymer was determined by injecting the mixtures of four or five polymers using the three types of HPLC systems.

RESULTS AND DISCUSSION

Determination of Elution Time of Co- and Terpolymers

The chromatograms in Figure 1 show the separation of S-MMA (a) and S-AN (b) copolymers, and S-MMA-AN (c) terpolymer using the PAN column. Although the number of theoretical plates of the PAN column is not very high, rather good resolution was observed. The resolution depends strongly on the gradient shape or pore size, rather than the inherent efficiency of the column as described elsewhere[13]. Because of the high molecular weight ($>10^5$) of the samples, retention time was almost

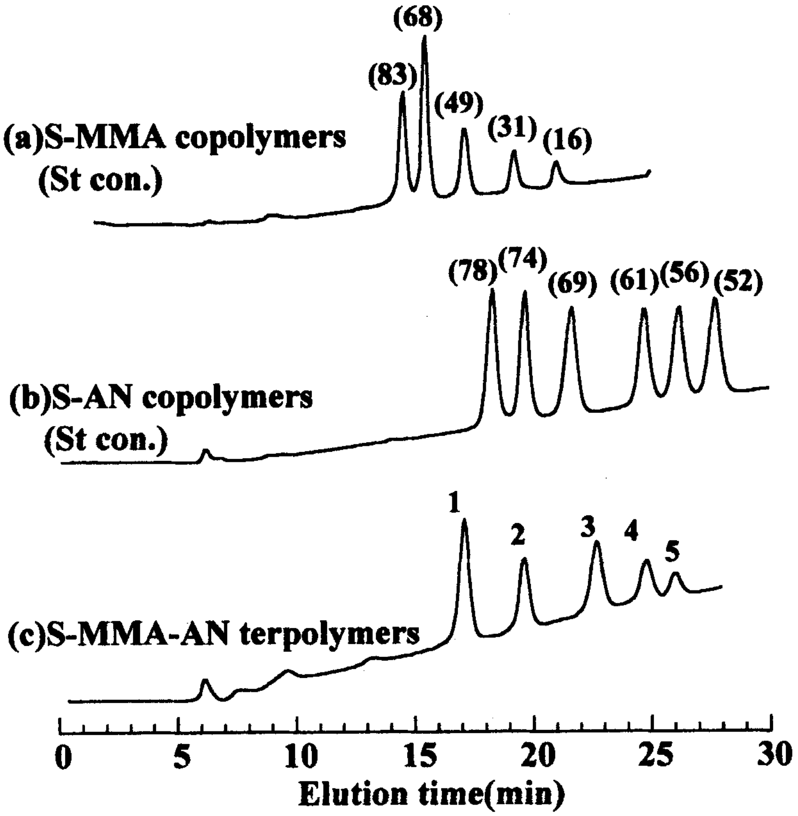


FIGURE 1 Chromatograms of copolymers and terpolymers using PAN column. The values in parentheses are the styrene content of the copolymer: (a) S-MMA copolymers, (b) S-AN copolymers, (c) S-MMA-AN terpolymer (designated in Figure 2 as filled circles) with chemical composition of S/MMA/AN in mol% (1: 63/30/7; 2: 47/40/13; 3: 41/33/26; 4: 26/46/28; 5: 14/57/29). HPLC conditions: see Table II, detector, UV (254 nm).

independent of molar mass even if the polymers were not excluded from the packing pores.[13] The small unknown peak at 6.1 min results from the gradient start. As shown in Figures 1a and 1b, the sample with the higher styrene content eluted earlier for both S-MMA and S-AN copolymers. S-AN copolymers eluted later as compared with S-MMA copolymers with the same styrene content. These elution behaviors are typical for normal-phase HPLC, i.e., the interaction between polar gel and copolymers becomes stronger with increasing polarity of polymer as expected from the fact that polarity of monomeric units follows the order S < MMA < AN.

Figure 1c shows the HPLC chart of a mixture containing five S-MMA-AN terpolymers having different composition. When the PAA column was used, the elution order was the same as with the PAN column for all kinds of copolymers.

Figure 2 represents the relationship between chemical composition of each co- or terpolymer and retention time obtained utilizing the PAN column. In this figure, the content of each monomer unit is proportional to a distance from the point to the opposite side, i.e., the distance from the point to the side AN–S represents the compositional ratio of MMA, and the point to the side MMA–S is the ratio of AN. Therefore, each top of the regular triangle represents the homopolymer, and the polymers on the each side are the binary copolymers. The elution times for all of polymers were determined with PAN column using chromatographic conditions described in the Experimental section. By connecting the point

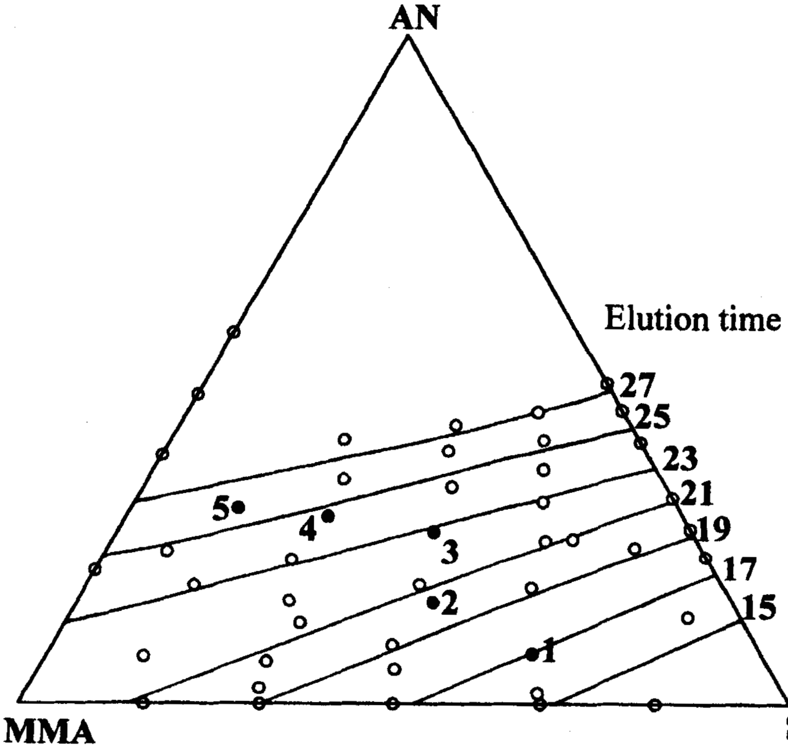


FIGURE 2 Relationship between chemical composition and elution time with the PAN column. The values in the right side represent the elution time (min). Filled circles with numbers belong to terpolymers used in Figure 1.

of samples showing the same elution time, elution lines were obtained. They were practically straight in most polymers. Values on the right side of triangle show the elution time in minutes. This result indicates that the terpolymers on the same elution line elute at the same time although the chemical composition is different, and it is impossible to separate all the terpolymers by one set of HPLC.

The elution lines for PAA and PAN columns as well as for PS and PAN columns are compared in Figures 3 and 4, respectively. In case of reversed phase HPLC, that is, with PS column (a nonpolar stationary phase) and a polar eluent, the elution order is reversed. Although the

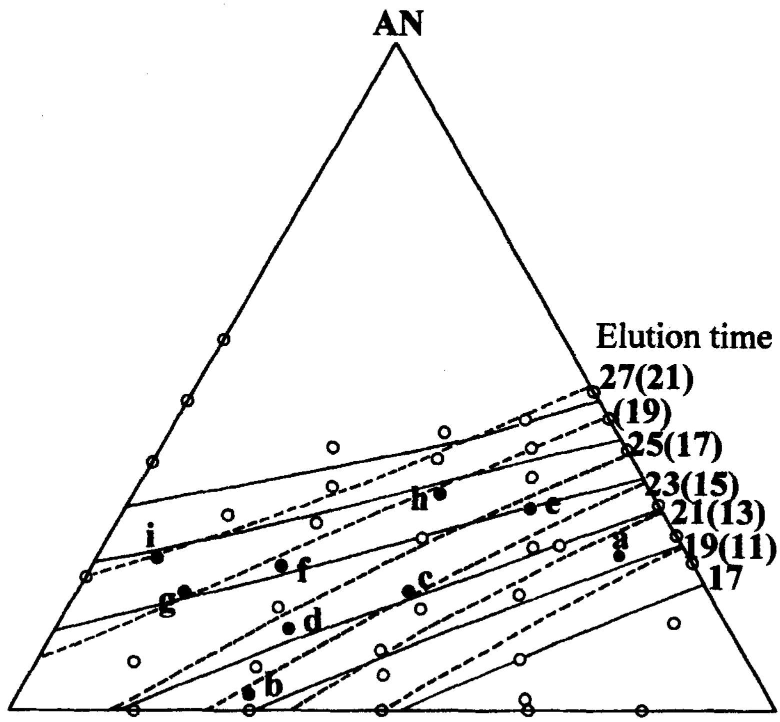


FIGURE 3 Relationship between chemical composition and elution time with the PAN column (solid line) or PAA column (broken line). The values on the right side represent the elution time (min) for the PAN column and those in parentheses for the PAA column. Samples **a–h** were used for the cross-fractionation experiments (see Figure 5). The chemical composition of S/MMA/AN terpolymer in mol%; a: 68/9/23, b: 66/32/2, c: 43/39/18, d: 30/57/13, e: 53/17/30, f: 25/54/21, g: 14/68/18, h: 40/28/32, i: 8/69/23.

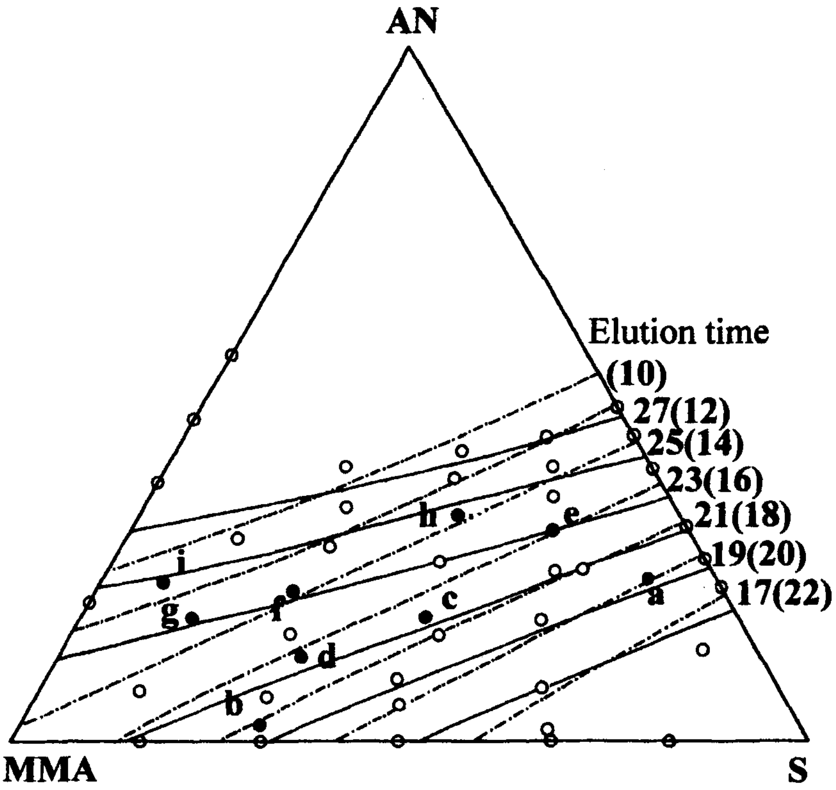
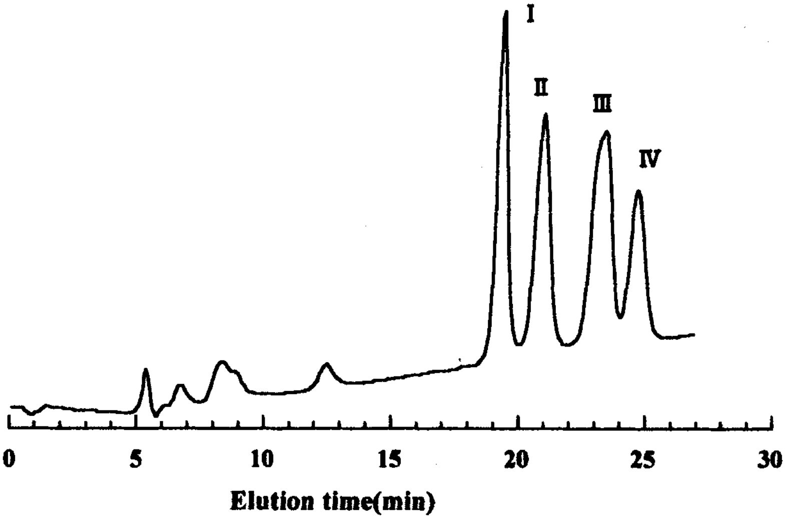


FIGURE 4 Relationship between chemical composition and elution time with the PAN column (solid line) or the PS column (broken line). Samples **a–h** (cf. Figure 3) were used for cross-fractionation experiments.

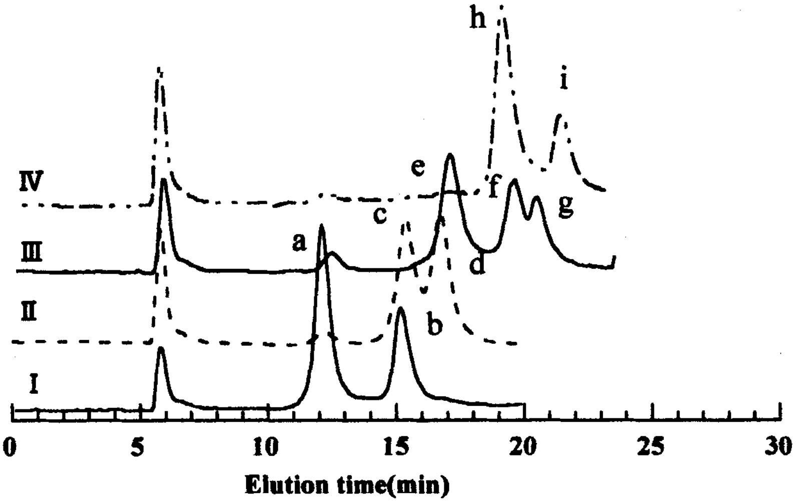
elution order is the opposite, the elution lines obtained with PS column have almost the same slope as those with PAA column. On the other hand PAN column had lower slope than PAA and PS columns. Therefore, it is possible to separate terpolymers by the composition using a combination of PAA and PAN columns or PS and PAN columns.

Cross-Fractionation of Terpolymers

A mixture of nine terpolymers, **a** to **i**, which are shown as filled circles in Figure 3, were separated by the cross-fractionation using two kinds of HPLC. The mixtures were separated with the PAN column into four fractions as shown in Figure 5a. This chromatogram shows



(a) PAN column



(b) PAA column

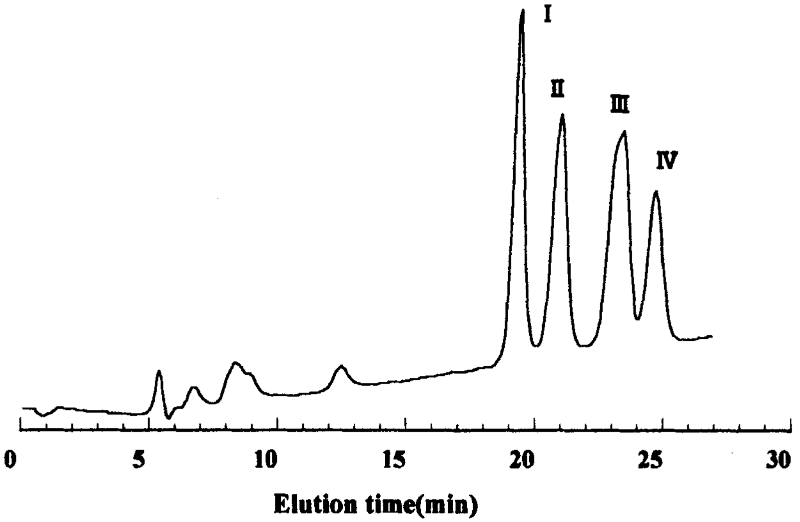
FIGURE 5 Cross-fractionation of terpolymers using PAN and PAA columns. (a) The mixture of samples **a–h** designated in Figure 3 was separated into four fractions (I–IV) using the PAN column. (b) Each fraction was further analyzed with the PAA column. HPLC conditions: see Table II, detector, UV (254 nm).

that it is impossible to separate all the polymers as expected from elution lines (solid lines in Figure 3). For the separation of samples overlapping with each other, a column with different elution behavior from PAN column is needed. Therefore, each fraction was further separated with the PAA column. As shown in Figure 5b, fraction I was separated into **a** and **b**; fraction II into **c** and **d**; fraction III into **e**, **f**, and **g**; and fraction IV into **h** and **i**. Thus, the mixture of nine terpolymers was separated into each component by the cross-fractionation using PAA and PAN columns.

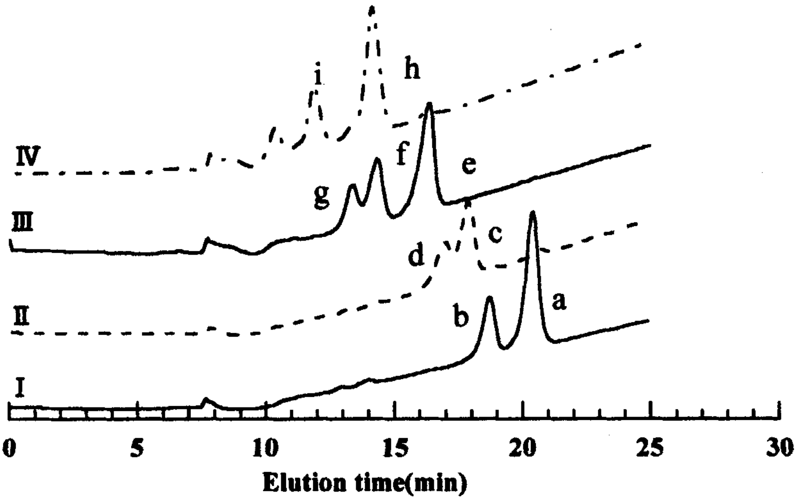
The separation of the same mixture of terpolymers was also examined by cross-fractionation using the PAN and PS columns. Each of the four fractions obtained by the PAN column was further separated by the PS column (Figure 6b) in the same way as previously with PAN and PAA columns. As the result of this separation, two (**a** and **b**), two (**c** and **d**), three (**e**, **f**, and **g**), and two (**h** and **i**) peaks for fraction I, II, III, and IV, respectively, were confirmed. Therefore, the separation of a mixture of terpolymers into each component can successfully be done by the combination of PAN and PAA columns or PAN and PS columns. This cross-fractionation method can be applied to the separation of other terpolymers by chemical composition.

Determination of CCD of Terpolymer

Terpolymer with a broad CCD (average composition: S/MMA/AN = 45.8/27.1/27.1 mol%) was fractionated using the PAA column as shown in Figure 7a. The effluent was collected every 24 s after the sample started to elute and 12 fractions were recovered. Each fraction was further analyzed off-line with the PAN column to obtain 12 chromatograms as shown in Figure 7b. The data processing to convert the chromatogram to CCD is as follows. First, we assumed that each fraction has a single retention time for the PAA column although each sample collection was carried out for 24 s. Next, each chromatogram obtained with the PAN column (Figure 7b) was digitized by drawing vertical lines to the baseline at equally spaced elution time, and normally 16 artificial fractions were characterized by their heights h_i and elution volume $V_{i(\mathrm{PAN})}$ ($i = 1\text{–}16$). The chemical composition of each fraction i was determined from the elution volume observed with the PAA column (all fractions obtained with PAN column were assumed to show the same elution time with PAA column as described above) and the elution volume with PAN column, $V_{i(\mathrm{PAN})}$. Since the effluent was monitored by a UV detector at 254 nm, only the styrene unit was detected, assuming that the absorption by MMA and AN unit was negligible. Thus, the height h_i was divided by the styrene content to convert the chromatogram to the CCD curve.

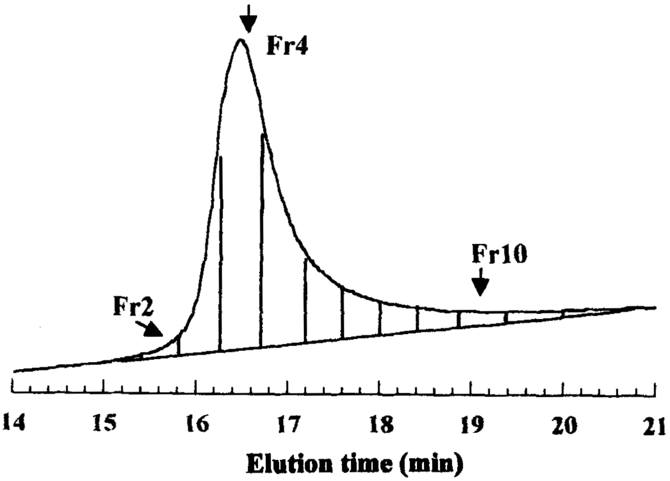


(a) PAN column

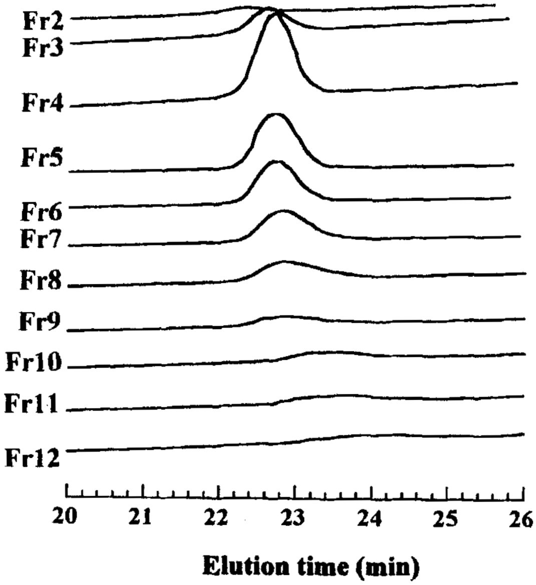


(b) PS column

FIGURE 6 Cross-fractionation of terpolymers using PAN and PS columns. (a) The mixture of samples **a–h** designated in Figure 4 was separated into four fractions (I–IV) using PAN column. (b) Each fraction was further analyzed with the PS column. HPLC conditions: see Table II, detector, UV (254 nm).



(a) PAA column



(b) PAN column

FIGURE 7 Cross-fractionation of a terpolymer with a broad chemical composition distribution. (a) First fractionation with the PAA column. (b) Second fractionation with the PAN column. Sample St/MMA/AN = 45.8/27.1/27.1 mol %. HPLC conditions: see Table II, Detector, UV (254 nm).

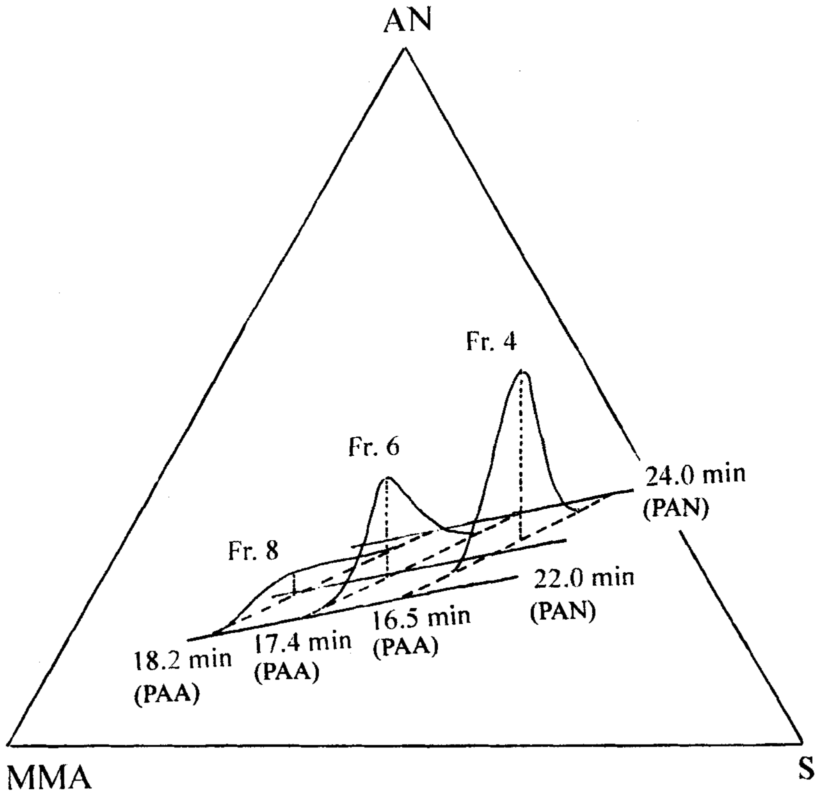


FIGURE 8 Chemical composition distribution of the terpolymer for the 4th, 6th, and 8th fractions.

Consequently 12 CCD curves were obtained and they were drawn into the triangle. The CCD curves for the 4th, 6th, and 8th fractions obtained by the PAA column were plotted into the triangle onto the corresponding elution time lines for the PAA column as shown in Figure 8. Fraction 4 gave the elution time of 16.5 min with the PAA column. With the PAN column, this fraction eluted between 22 and 24 min. By connecting the points having the same height for all the curves, the contour line was obtained. In Figure 9, the contour lines were drawn at every 15% height of the maximum point, i.e., 85, 70, 55, 40, 25, and 10% height of the maximum point.

The composition of the terpolymer can be calculated from the three pairs of monomer reactivity ratios and the molar ratios of monomers present in the reaction mixture utilizing Equation (1). In this equation, M_1, M_2, and M_3 represent S, MMA, and AN, respectively.

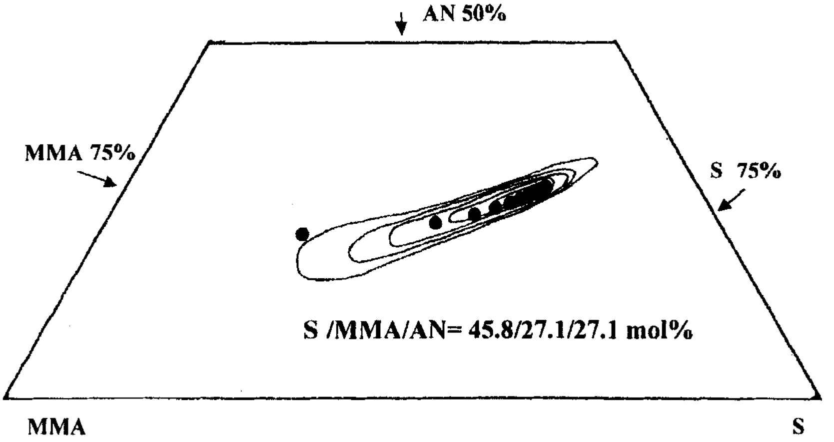


FIGURE 9 Chemical composition distribution of the terpolymer. Contour plot is the experimental results. The filled-in circles are the calculated values.

$$
\begin{aligned}
&d[M_1] : d[M_2] : d[M_3] = \\
&\quad [M_1] * \left(\frac{[M_1]}{r_{31}r_{21}} + \frac{[M_2]}{r_{21}r_{32}} + \frac{[M_3]}{r_{31}r_{23}}\right) * \left([M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}\right) : \\
&\quad [M_2] * \left(\frac{[M_1]}{r_{12}r_{31}} + \frac{[M_2]}{r_{12}r_{32}} + \frac{[M_3]}{r_{32}r_{13}}\right) * \left([M_2] + \frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}}\right) : \qquad (1) \\
&\quad [M_3] * \left(\frac{[M_1]}{r_{13}r_{21}} + \frac{[M_2]}{r_{23}r_{12}} + \frac{[M_3]}{r_{13}r_{23}}\right) * \left([M_3] + \frac{[M_1]}{r_{31}} + \frac{[M_3]}{r_{32}}\right)
\end{aligned}
$$

The three pairs of reactivity ratios were experimentally obtained by binary copolymerization at low conversion: $r_{12} = 0.66$, $r_{21} = 0.57$, $r_{13} = 0.34$, $r_{31} = 0.06$, $r_{23} = 0.94$, and $r_{32} = 0.51$. For the sample with high conversion, the chemical composition was calculated every one percent of conversion, because the terpolymer composition changed by the shift of residual monomer composition. The average composition for each 10% conversion was plotted in Figure 9 as a large dot. The observed CCD agrees well with the theoretical one. This indicates that HPLC is useful for determining the CCD of co- and terpolymers.

CONCLUSIONS

Cross-fractionation using two types of adsorption HPLC systems made it possible to separate terpolymers consisting of styrene, methyl methacrylate, and acrylonitrile by chemical composition, and to analyze the chemical composition distribution (CCD) of the terpolymer. We anticipate that the technique presented here is a powerful method to analyze the CCD of other types of terpolymers, and can provide useful information about the relationship between the physical properties of the terpolymer and its CCD.

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