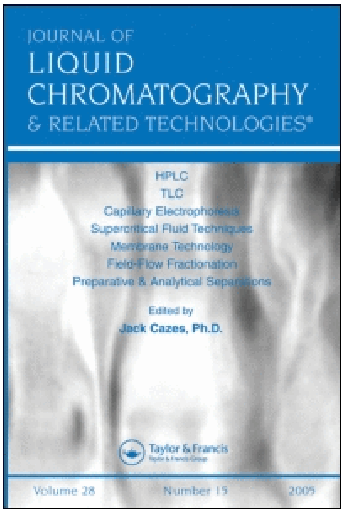

**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Problems in Determining Compositional Heterogeneity of Copolymers by Size-Exclusion Chromatography and UV-RI Detection System

Sadao Mori[a]; Tooru Suzuki[a]
[a] Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie, Japan

**To cite this Article** Mori, Sadao and Suzuki, Tooru(1981) 'Problems in Determining Compositional Heterogeneity of Copolymers by Size-Exclusion Chromatography and UV-RI Detection System', Journal of Liquid Chromatography & Related Technologies, 4: 10, 1685 — 1696

**To link to this Article: DOI:** 10.1080/01483918108064840

**URL:** http://dx.doi.org/10.1080/01483918108064840

JOURNAL OF LIQUID CHROMATOGRAPHY, 4(10), 1685-1696 (1981)

# PROBLEMS IN DETERMINING COMPOSITIONAL HETEROGENEITY OF COPOLYMERS BY SIZE-EXCLUSION CHROMATOGRAPHY AND UV-RI DETECTION SYSTEM

Sadao Mori and Tooru Suzuki
Department of Industrial Chemistry, Faculty of Engineering,
Mie University, Tsu, Mie 514, Japan

## ABSTRACT

The compositional heterogeneity of styrene-methylmethacrylate copolymer has been evaluated by a UV-RI dual-detector method and by a RI detector-pyrolysis-gas chromatographic method and problems associated with the determination of the chemical heterogeneity by a UV-RI method are discussed. The quotient of signals H(UV)/H(RI) of both the detectors (UV and RI) for polystyrene increased at the extreme parts of the molecular weight distribution owing to non-linearity of UV response. The correction of the quotient of signals of both detectors for the copolymer was proposed. The UV and RI response factors for the copolymer were supposed to differ from those for homopolymers. Reproducibility for the detector responses influences the values of chemical heterogeneity much more than expected. To overcome these problems, the detection method to obtain each composition independently using different detectors will be preferable.

## INTRODUCTION

It is well known that copolymer properties are affected by its composition in addition to molecular weight. Most copolymers may have the molecular weight distribution in addition to the composition distribution. In order to obtain precise values of these distributions, one must determine the molecular weight distribution independently of composition, followed by determination of the relation between composition and molecular weight, or inversely, the composition distribution must be determined independently of molecular weight, followed by determination of molecular weight at each composition. Several attempts have been made by size-exclusion chromatography (SEC, or GPC) to obtain the relationship between molecular weight and composition. However, in SEC, elution order is dependent on molecular size rather than molecular weight, and molecules of different compositons might have the identical molecular size. Therefore, one can not obtain the precise molecular weight distribution and composition distribution for copolymers by SEC. The measurement of compositional heterogeneity of copolymers by SEC has nevertheless significance under the careful consideration, because SEC is the simplest technique to separate polymers by their molecular sizes.

The use of dual detectors or spectrophotometric detection with dual wave-lengths for analysis of SEC eluents gives information about compositional heterogeneity. A combination of ultraviolet (UV) and differential refractive index (RI) detectors is frequently used, which is applied to the copolymer one component of which has UV absorption, such as styrene-butadiene copolymer (1-3). A combination of RI and infra-red (IR) detectors, where RI is used as a concentration monitor and one component of the copolymer is determined by IR, is applied to the copolymer both components of which have or do not have UV absorption, such as vinyl chloride-vinyl acetate copolymer (4). Selection of two appropriate wave-lengths in IR enables determination of heterogeneity by an IR detector alone (5). Pyrolysis gas chromatography (PGC) has been applied to determine composition of SEC fractions using RI as a concentration monitor (6).

Both UV and RI detectors are estimated to be stable and reliable instruments. The use of a UV-RI dual-detector system, therefore, has been regarded as a precise technique for the determination of compositional heterogeneity of copolymers. However, inconsistency of the compositional heterogeneity at the extreme parts of the molecular weight distribution has been observed in the results obtained by a UV-RI dual-detector method and by a RI detector-PGC method in our laboratory. In this paper, the compositional heterogeneity of styrene-methylmethacrylate copolymer has been evaluated by a UV-RI dual-detector method and by a RI detector -PGC method, and problems associated with the determination of the chemical heterogeneity by a UV-RI dual-detector method are discussed.

## EXPERIMENTAL

### Apparatus

A Model LC-08 high-speed preparative liquid chromatograph (Japan Analytical Industry Co., Mizuho-cho, Tokyo 190-12, Japan) equipped with UV(254 nm) and RI detectors and two Shodex A80M HP SEC columns (500 x 8 mm i.d.) packed with polystyrene gels used for polymer fractionation was used for SEC. Chloroform was used as solvent (the mobile phase), The same apparatus was used for PGC as reported previously (6).

### Samples

Styrene-methylmethacrylate copolymers (PSM) were prepared in our laboratory by solution polymerization in benzene using $\alpha,\alpha'$-azo-bis-isobutyronitrile as an initiator. The composition of the copolymers was determined using as ultra-violet spectrophotometer. A PSM having styrene content 48.6 wt% was used as a sample for the determination of compositional heterogeneity by SEC. A polystyrene sample prepared in our laboratory was used as a reference material. Several polystyrenes of known molecular weights and of narrow molecular weight distributions were used for calibration of SEC columns.

### Measurement of SEC

Flow rate of the mobile phase was 1.0 ml/min. Concentration of sample solutions was 0.2% for fractionation of PSM and 0.1% for calibration. A 0.5 ml portion of the solutions was injected into the liquid chromatograph. Attenuation of RI was x8 ($8 \times 10^{-5}$ RI unit full scale) and UV x4 (0.04 O.D. full scale). Both chromatograms from UV and RI detectors were used for calculations of compositional heterogeneity and molecular weight distribution.

Twenty-two 0.5-ml fractions were collected over the elution range of the sample PSM.

## Distributions of composition and molecular weight

Step 1. Chromatograms from UV and RI detectors were divided into equal parts every 0.25 ml and height (response) at each point i was measured. As UV and RI detectors were connected in series in this order, the dead volume was measured by the elution difference of the peak maximum of several monodisperse samples and it was estimated to be 0.2 ml: the elution volume of a molecule in a RI detector is the elution volume of the same molecule in a UV detector plus 0.2 ml.

Step 2. The ratio, $R_j$, of responses of UV and RI detectors at elution point j was calculated using

$$R_j = (A_{UV})_j \,/\, (A_{RI})_j \qquad (1)$$

$(A_{UV})_j$ and $(A_{RI})_j$ were calculated using next equation

$$A_j = (H_{i-1} + 2H_i + H_{i+1}) \,/\, 8 \qquad (2)$$

where $H_i$ is the height of the chromatogram (UV or RI) at elution point i. The subscript j corresponds to the elution point i of even number (i.e., j = i (even number)/2). When chart speed of recorder is 1cm/min and the dimension of H is cm, then $A_j$ represents the area (unit:$cm^2$) of the chromatogram surrounded by the points i-1 and i+1.

Step 3. Styrene weight fraction, $W_s$, at elution point j was calculated using

$$(W_s)_j = \frac{K_M R_j}{K_s' - (K_s - K_M)R_j} \qquad (3)$$

where $K_s$, $K_s'$ and $K_M$ are response factors of RI and UV for styrene and RI for methylmethacrylate (MMA) determined from homopolymers or copolymers by using the next equation

$$\Sigma A_j = K \cdot G \qquad (4)$$

where G is weight of polymer injected. Dimension of K is $cm^2/mg$ at attenuations x1 (RI) and x0.01AUFS (UV).

Step 4. The RI response of the SEC chromatogram of the copolymer sample was corrected using

$$(H_{corr.})_j = (H_{uncorr.})_j\ (2.29 - 1.29(W_s)_j) \qquad (5)$$

The RI response of PS is 2.29 times that of PMMA.

Step 5. Molecular weight of the copolymer at the elution point j was calculated using

$$(M_c)_j = 0.806(M_s)_j + 0.194(m_s)_j\ (M_s)_j \qquad (6)$$

where $(M_s)_j$ is the molecular weight of polystyrene obtained from the polystyrene calibration curve at the elution point j and $(m_s)_j$ is the styrene mole fraction at the point j. This equation was obtained as follows. The equation 11 in the literature (4) was converted into the equation

$$M_{copolymer} = m_A M_A + m_B M_B \qquad (7)$$

where subscripts A and B mean components A and B in the copolymer. A ratio of the molecular weight of a PMMA obtained by a classical method to that calculated using the polystyrene calibration curve was 0.806, then

$$(M_{MMA})_j = 0.806\ (M_s)_j \qquad (8)$$

Replacing A and B with MMA and S and substituting eq. (8) into eq. (7), we obtain the equation (6). Average molecular weights of the copolymer were calculated using $(M_c)_j$ in step 5 and $(H_{corr.})_j$ in step 4.

Step 6. The differential molecular weight distribution curve was constructed after converting the values of dW/dV of the normalized SEC chromatogram into those of dW/d log M using the copolymer calibration curve which was constructed using eq. (6).

PGC of the fractions

The stainless-steel column (300 cm x 3 mm i.d.) was packed with Diasolid L coated with 2.5% PEG6000. The procedures for construction of the calibration curve and pyrolysis of the fractions were the same as reported previously (6), except column temperature being 110 °C and pyrolysis temperature 600 °C. About 10 μg of the copolymer from each fraction were pyrolyzed.

## RESULTS AND DISCUSSION

The differential molecular weight distribution curve and the chemical heterogeneity of PSM obtained and calculated from SEC chromatogram through step 1 to step 6 and the chemical heterogeneity of PSM obtained by PGC are shown in Figure 1. Styrene weight fraction obtained by a UV-RI dual-detector method increases at the extreme parts of the molecular weight distribution curve. The situation is quite different for PGC method, where the copolymer seems to have a uniform composition over the whole range of molecular weights.

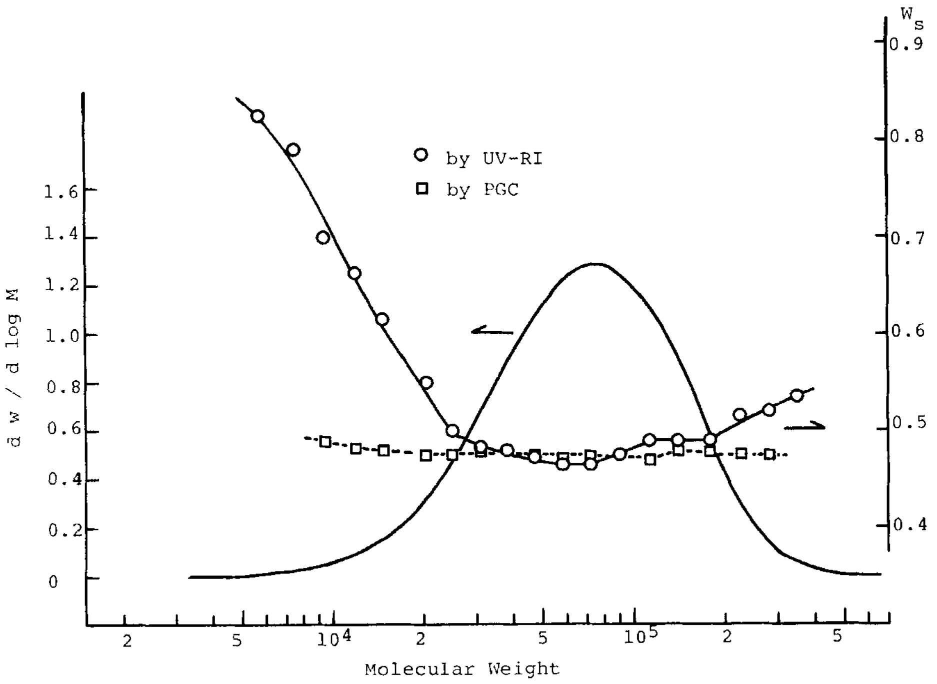

FIGURE 1. The molecular weight distribution and chemical heterogeneity of a styrene-methylmethacrylate copolymer

Response factors $K_S$, $K_M$ and $K_S'$ are assumed to be constant, whereas the value of $R_j$ will vary with the composition: that is, if $R_j$ is constant for all elution volumes, then, the copolymer will have a uniform composition. Since polystyrene is homopolymer with a constant composition, the quotient of signals $A_{UV}/A_{RI}$ (=R) of both the detectors should be constant for all elution volumes. In practice, however, the result is completely different. Figure 2 shows the SEC chromatograms (RI and UV) of a polystyrene sample ($\overline{M}_w$ = 73000, $\overline{M}_n$ = 36000) and a plot of $R_j$ against the elution volume. A dead volume (0.2 ml) was corrected on the chromatogram measured by an RI detector.

The variation of $R_j$ against the elution volume as in Figure 2 suggests that there is no linear relation between the concentration of a solute and a response of both RI and UV detectors or either of the two. In general, responses of RI and UV detectors are to be proportional to the concentration of a solute in a dilute solution. However, in our laboratory, a next equation was obtained for a polystyrene solution in the range of 0.001 to 0.2 mg solute/ml chloroform and of 0.00075 to 0.085 absorbance at 275 nm of a UV detector

$$\log C = 1.116 \log A + 0.483 \qquad (9)$$

where C is the concentration of a polystyrene and A is absorbance. If the response of an RI detector is proportional to the concentration of a solute (this will be checked hereafter), it can be estimated using eq. (9) that the value $R_j$ increases with decreasing the concentration. Therefore, one of the solution to the problem that the value $R_j$ for polystyrene varies with the concentration will be to use the concentration rather than the height in eq. (2).

The other solution to the problem is to correct the value $R_j$ in eq. (1) for a copolymer multipling by a correction factor which was obtained by dividing the average of $R_j$ (= 0.931 in Figure 2) by the value of $R_j$ at each elution volume for a polystyrene sample. This correction factors are shown in Figure 2. Improvement by

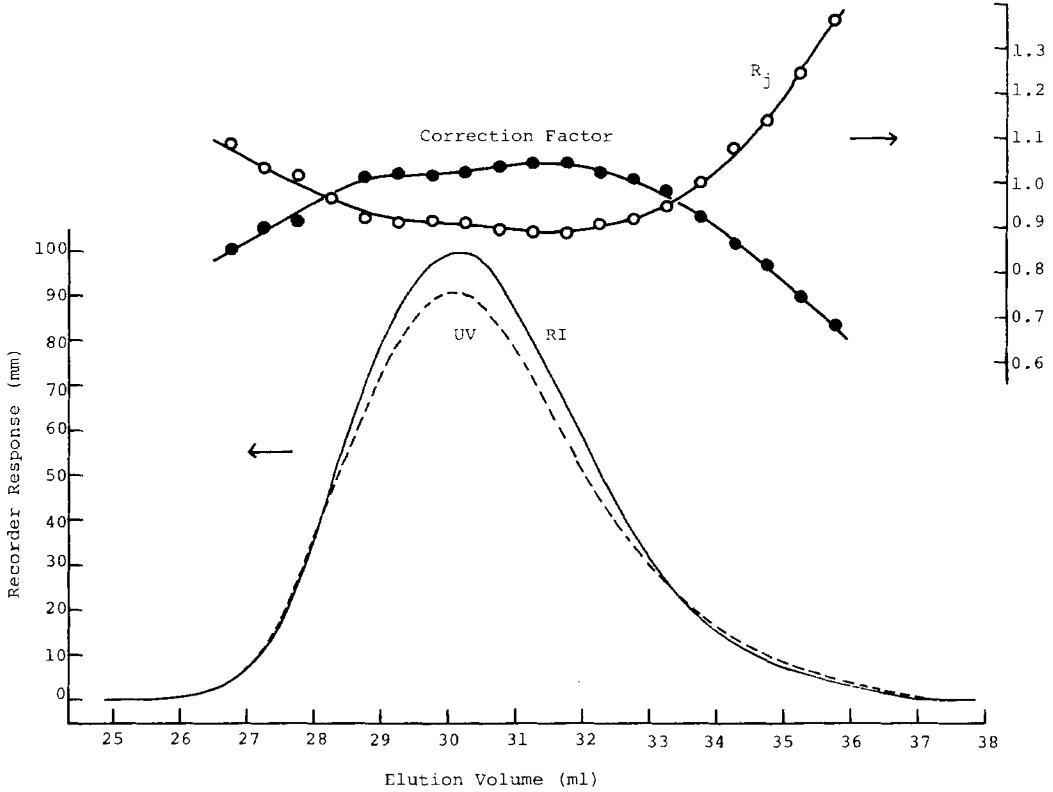

FIGURE 2. SEC chromatograms and plots of $R_j$ and correction factors against the elution volume for a polystyrene sample ($\bar{M}_w$ = 73000, $\bar{M}_n$ = 36000).

correction was observed and the result is shown in Figure 3 with the uncorrected values and the results by PGC for comparison.

One of the reason for the variation of $R_j$ with concentration will be explained by eq. (9). The other reason has been shown by Bressau (7) that the connecting tube disturbs not only by shifting the elution curve, but also by altering its shape, resulting in the deformation of the elution curves and the variation of the quotient curve of signals $H_{RI}/H_{UV}$ of both the detectors. He recommended the use of columns with a large diameter for the multiple detection of narrowly distributed polymer samples. Stojanov and his co-workers (3) have not observed such variation of $R_j$ for polystyrene.

The second problem in the UV-RI method lies down on the determination of response factors in eq. (3). The UV response factor $K_s'$, which is determined using homopolymer, fluctuates slightly with polymers obtained by different synthetic processes and their molecular weights. Table 1 shows UV absorbances of

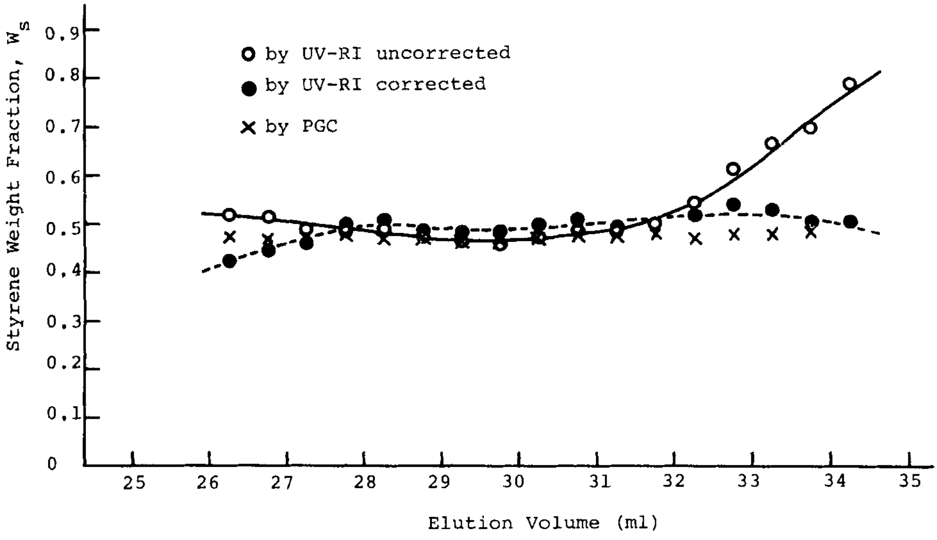

FIGURE 3. Effect of correction of the value $R_j$ to the determination of the chemical heterogeneity

Table 1
Absorbance of Several Polystyrenes in Concentration
1 mg Sample per 10 g Chloroform

| Polystyrene | 253.7 nm | 260 nm |
|---|---|---|
| PS 97200 | 0.260 | 0.327 |
| PS 20400 | 0.260 | 0.326 |
| PS 10000 | 0.259 | 0.324 |
| PS 3600 | 0.259 | 0.324 |
| PS 2100 | 0.255 | 0.319 |
| PS 600 | 0.246 | 0.308 |
| S - 5 | 0.311 | 0.361 |
| PSt - 1 | 0.278 | 0.336 |
| PSt - 2 | 0.282 | 0.336 |

several polystyrenes in solutions in concentration 1 mg polystyrene per 10 g chloroform and in a 1 cm-cell. Polystyrenes from PS97200 to PS600 were synthesized by living polymerization and have narrow molecular weight distributions. Numbers after PS refer to molecular weights. Three polystyrenes from the bottom in Table 1 were synthesized by radical polymerization. Polystyrene S-5 has molecular weight $1\text{x}10^4$ and the other two have $1\text{x}10^5$ to $2\text{x}10^5$. Absorbances in Table 1 correspond to $K_S' = 40$ for PS97200, 42.8 for PS-1, and 47.8 for S-5.

The RI response factor $K_C$ for copolymer can be calculated using eq. (4) and is related to $K_S$ , $K_M$ and $W_S$ as follows

$$K_C = K_M + (K_S - K_M) W_S \qquad (10)$$

Stojanov and his co-workers (8) observed this equation to be valid. However, as shown in Figure 4, some of observed values deviate from the calculated straight line of eq. (10) and the deviation exceeds the standard deviation.

Styrene weight fraction $W_S$ at each elution volume, calculated using eq. (3) and response factors obtained from homopolymers, was about 5% higher than that in Figure 1 and the average styrene weight fraction was 0.540 (the value for unfractionated sample was 0.486). The values in Figure 1 were calculated using response

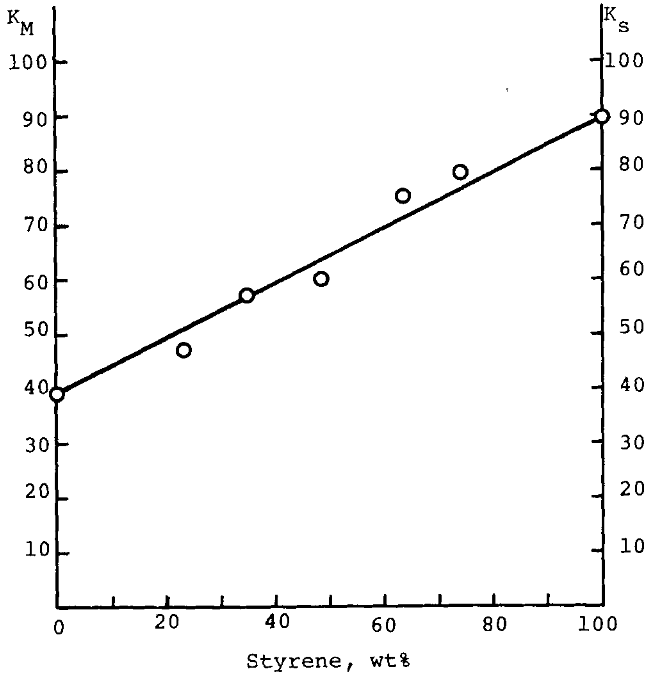

FIGURE 4. Plot of the RI response factor on chemical composition. White circles are observed values.

factors obtained from the copolymer sample by knowing the copolymer composition, the ratio of RI responses for styrene and methyl methacrylate, and UV and RI chromatograms, and the average value of the styrene weight fractions coincideswith the unfractionated value. In case of the sample ($W_s$ = 0.637) in Figure 4, the average value of styrene weight fractions was about 5% lower than that the unfractionated value when response factors from homopolymers were used in eq. (3). Besides these problems, as the equation (3) includes the three response factors and the ration of RI and UV responses, errors from these values are incorporated into the calculated value.

Reproducibility for the detector responses deserves also much attention. Repeatability for the detector responses in the same day was very good and usually less than 1% as the standard deviation, but reproducibility at the different day went sometimes beyond 5%. Application of eq. (3) will make this problem more serious.

## REFERENCES

1. Runyon, J.R., Barnes, D.E., Rudd, J.F., and Tung, L.H., Multiple Detectors for Molecular Weight and Composition Analysis of Copolymers by Gel Permeation Chromatography, J. Appl. Polym. Sci., 13, 2359 (1969).

2. Adams, H.E., Composition of Butadiene-Styrene Copolymers by Gel Permeation Chromatography, Separ. Sci., 6, 259 (1971).

3. Stojanov, Ch., Shirazi, Z.H., and Audu, T.O.K., Determination of Chemical Heterogeneity of Copolymers by Gel-Permeation Chromatography, Chromatographia, 11, 63 (1978).

4. Mori, S., Determination of the Composition and Molecular-Weight Distribution of a Poly(vinyl chloride-vinyl acetate) Copolymer by Gel-Permeation Chromatography and Infrared Spectroscopy, J. Chromatogr., 157, 75 (1978).

5. Mirabella, F.M., Jr., Barrall, E.M., II, and Johnson, J.F., A Rapid Technique for Measuring Copolymer Composition as a Function of Molecular Weight using GPC and IR, J. Appl. Polym. Sci., 19, 2131 (1975).

6. Mori, S., Determination of the Composition of Copolymers as a Function of Molecular Weight by Pyrolysis Gas Chromatography - Size-Exclusion Chromatography, J. Chromatogr., 194, 163 (1980).

7. Bressau, R., Liquid Chromatography of Polymers and Related Materials II, J. Cazes, ed., Marcel Dekker, New York, 1980, P. 73.

8. Stojanov, Ch., Shirazi, Z.H., and Audu, T.O.K., Contribution to the Determination of Chemical Composition of Copolymers by Gel Permeation Chromatography, Chromatographia, 11, 274 (1978).