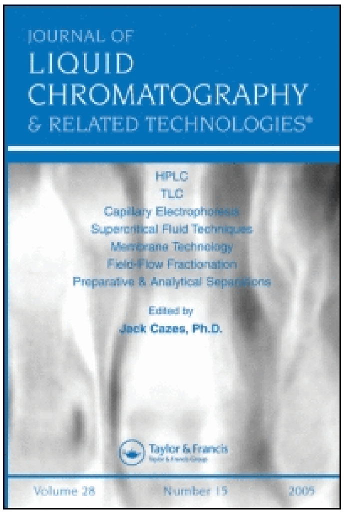

**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Aging of Pressure Sensitive Adhesives. II: Use of Multidetector Sec

Daniel J. P. Harrison[ab]; W. Ross Yates[ac]; Julian F. Johnson[a]
[a] Department of Chemistry, Institute of Materials Science University of Connecticut, Storrs, CT [b] Research Laboratories, Eastman Kodak Co., Rochester, NY [c] Lexington Laboratories, The Kendall Company, Lexington, MA

**To cite this Article** Harrison, Daniel J. P. , Yates, W. Ross and Johnson, Julian F.(1983) 'Aging of Pressure Sensitive Adhesives. II: Use of Multidetector Sec', Journal of Liquid Chromatography & Related Technologies, 6: 14, 2723 — 2737

**To link to this Article: DOI:** 10.1080/01483918308064942

**URL:** http://dx.doi.org/10.1080/01483918308064942

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(14), 2723-2737 (1983)

# AGING OF PRESSURE SENSITIVE ADHESIVES. II: USE OF MULTIDETECTOR SEC

Daniel J. P. Harrison*, W. Ross Yates+
and Julian F. Johnson
Department of Chemistry
and
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

## ABSTRACT

The use of multiple detector size exclusion chromatography is described for the study of aging of pressure sensitive adhesive films based on styrene-isoprene-styrene block copolymers. In this preliminary investigation of thin films, room temperature oxidation resulted in the formation of an easily detected carbonyl chromophore. While the chromophore concentration was monitored with a UV detector on the chromatograph, the molecular weight distribution was measured with a differential refractometer. Several important general implications of this combination of detectors in SEC are described.

## INTRODUCTION

The first paper in this series (1) described initial efforts to elucidate the nature of aging changes in the commercially important styrene-isoprene-styrene (SIS) block copolymers, especi-

---

* Present Address: Research Laboratories, Eastman Kodak Co.,
Bldg. 82, Kodak Park, Rochester, NY 14450

\+ Present Address: The Kendall Company, Lexington Laboratories,
17 Hartwell Avenue, Lexington, MA 02173

0148-3919/83/0614-2723$3.50/0

ally as they are incorporated in pressure sensitive adhesives (PSA). The use of multi-detector size exclusion chromatography (SEC) has proven extremely valuable in this study, and several aspects of its application will be described herein.

The use of SEC for the analysis of polymers has been widely reviewed (2-5). Since SEC is primarily used to determine the molecular weight distribution (MWD) of polymers, it has found extensive use in study of polymer degradation, many such applications of which have been discussed by Abbås (6). Relative changes in MWD are very readily observed, and with extreme care useful information can also be obtained on the kinetics of oxidation chain scission.

The usefulness of SEC for the analysis of random and block copolymers has been increased on occasion by using two or more detectors (7,8,9,10). In these studies, typically one detector (usually ultraviolet or infrared) is used to monitor the concentration of the comonomers, while a second detector (refractive index or light scattering) monitors molecular weight. Harmon and Folt (7) used such a technique to measure the comonomer ratio in SBR. In a similar study, Stojanez et al. (8) investigated both random and block styrene/butadiene copolymers. In the latter, the copolymer composition was determined by SEC, infrared spectroscopy and nuclear magnetic resonance spectroscopy, and although results for the block copolymers were in very good agreement, the random SBR results varied somewhat. This was attributed to a change in the UV extinction coefficient of styrene, depending upon the sequence length in the random copolymers.

Dual detector (UV/RI) SEC has also been used to determine the distribution of olefinic linkages in elastomers (11). In some elastomers, small amounts of unsaturated monomers are incorporated for crosslinking, and to estimate the concentration of these external double bonds, Anderson reacted double bonds in the elastomer with 2,4-dinitro-benzene sulfonyl chloride, thus forming a chromaphore with a high extinction coefficient at 254 nm. While the SEC separated the "stained" elastomer by molecular size, the

RI detector measured the total concentration of polymer and the UV detector provided the concentration of external double bonds. Thus, the distribution of external double bonds as a function of MW was determined.

In the oxidative chain scission of polyisoprene, a similar effect is obtained. According to Shelton et. al. (12), the end group residues after the chain scission of polyisoprene are typically aldehydes and ketones. However, approximately 50% of these residues are α,β-unsaturated carbonyls, which are known to have an extremely high extinction coefficient at about 237 nm (13). It is expected that the polyisoprene mid-block in SIS will behave in an anaglogous manner. It is the use of a combination of UV and RI detectors in SEC for studying aging in SIS formulated PSA's which is investigated in this study.

It should be pointed out that multiple detector SEC has received some criticism by Bressau (14), who contends that the connecting tubing and fittings between detectors not only changes the elution volume but also alters the shape of the chromatogram. In his experiments, 20-50 cm capillary tubing and high dead volume fittings were used. By shortening tubing lengths and using only low dead volume fittings, these problems can be minimized.

## EXPERIMENTAL

The SEC used in these experiments consisted of a Waters 6000A solvent delivery system with a model U-6 sample injector, 4 μ-Styragel columns ($10^5$, $10^4$, $10^3$, and 500Å), a Varian model UV-50 variable wavelength UV detector, and a Waters Model R401 RI detector. These detectors were connected in series, with the RI following the UV detector. Valco low dead volume fittings were used in all connections. The tubing length between the UV and RI detectors was ∿25 cm and the capillary ID was .05 cm. The UV flow through cell was cylindrical (1mm x 6mm) to minimize mixing. The solvent was freshly distilled unstablized THF, and the flow rate was 1.5 $cm^3$/min. The instrument was calibrated with narrow MWD polystyrene standards (Pressure Chemical), but since the Mark-Houwink constants were not known for the SIS block-copolymers used in these experiments, data are reported as a function of elution volume.

Rubber solutions (20% SIS by weight) were mixed for 24 hours in the dark on a gentle wrist action shaker, using nitrogen-degassed toluene (reagent grade) as the solvent. SIS was from a commercial lot of Kraton 1107 (Shell Chemical Company). The resulting solutions were stored in the dark under argon until used.

Solutions were coated with a Gardner Ultra Film Applicator on 25-μm polyethyleneterephthalate films taped to glass plates. The coatings were first dried in the dark at 20-25°C for one hour under a continuous, slow nitrogen purge. They were then heated to 40°C in a 3300-Pa vacuum for 4 hours. During the heating cycle, a small nitrogen leak was provided to the drying system to sweep away any residual toluene or oxygen. It is likely that most of the butylated hydroxytoluene (BHT) incorporated in the rubber manufacturing process will be removed in this vacuum drying step.

UV spectra of polymers in unstabilized THF were recorded with a Beckman Model 25 spectrophotometer.

## RESULTS

In order to determine the optimum wavelength for the UV detector, UV spectra of both polystyrene and polyisoprene in THF were recorded. While the polyisoprene can only be detected below 232 nm, the polystyrene can be detected below 232 nm, and also between 250 and 270 nm. Since it was found that the RI detector responded well to solutions of either polystyrene or polyisoprene, the UV detector was operated at 259 nm, the absorption maximum for polystyrene in that region of its spectrum. It should be noted that UV spectra of the polymer solutions cannot be recorded below ∿224 nm due to a maximum at ∿220 for THF. Further considerations of detector wavelength will be discussed later.

It was found that when solutions taken from thin SIS films were analyzed on this SEC, the UV and RI results were quite

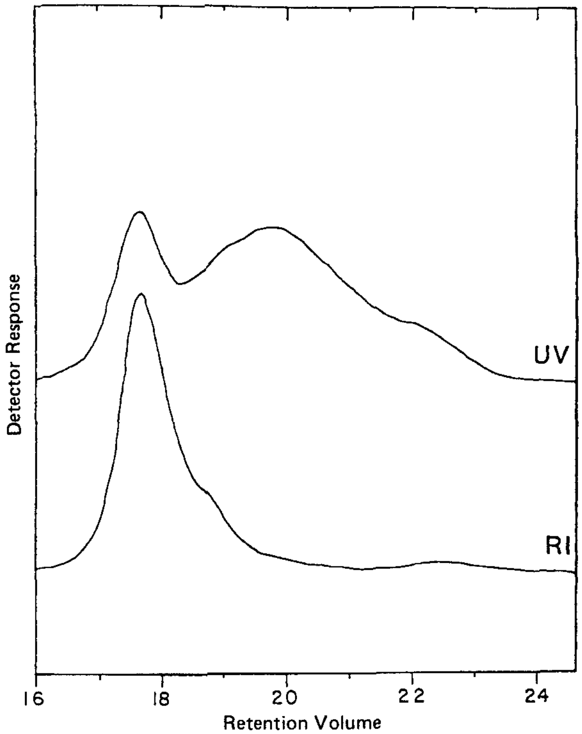

FIGURE 1: SEC chromatograms of unaged 4 μm SIS Films. The UV detector wavelength was fixed at 259 nm and the retention volume was recorded in ml.

different. As seen in Figure 1, the RI detector indicates that very little degradation has occurred to this 0.16 mil unaged SIS film. This molecular weight distribution, is typical of unaged SIS block copolymers. The large peak at 17.8 min ($\sim$2.5 x $10^5$ amu) represents the SIS tri-block molecules, while the shoulder at 18.8 min ($\sim$1.3 x $10^5$ amu) results from SI diblock fragments which did not couple in synthesis. The small peak at 22.5 min ($\sim 10^4$ amu) is polystyrene (PS) homopolymer which terminated prior to anionic polymerization with isoprene. For a general discussion of the synthesis of these block copolymers see Dreyfuss, et al. (15).

On the other hand the UV detector response in Figure 1 appears to indicate that substantial degradation of tri-block SIS

TABLE 1

SEC Fraction Location

| Fraction | Retention Volume (ml) |
|---|---|
| 1 | 16.0 - 17.8 |
| 2 | 17.8 - 18.5 |
| 3 | 18.5 - 19.2 |
| 4 | 19.2 - 20.8 |
| 5 | 20.8 - 21.5 |
| 6 | 21.5 - 24.0 |

molecules to di-block SI fragments has occurred, if one views the response in the usual way as an indication of MWD. Since the RI response is unmistakably MWD, it would appear that very little degradation to the SIS film has actually occurred, and that the small amount of degraded material must contain a chromophore whose molar extinction coefficient (ε) is substantially greater than that of polystyrene at 259 nm, thus yielding a large UV response in this region.

In order to determine the chemical moiety responsible for the very large absorbance at 259 nm, a 3.8μm thick film of SIS was dissolved in THF and fractionated in the SEC. Six fractions were collected, two from the SIS region, one from between the SIS and the SI peaks and three from the SI to the PS region (Table 1). UV spectra (220-290nm) were recorded for each of these fractions and the results are summarized in Figure 2. It was observed that fractions 1 and 2 are composed largely of polystyrene and polyisoprene, as expected. Fraction 3 shows some traces of polystyrene as well as a broad shoulder centered at 240 nm on the large polystyrene/polyisoprene absorption. In fractions 4, 5, and 6, very little polystyrene is observed at 260 nm while the shoulder observed in fraction 3 is now resolved into a peak which has its maximum at approximately 237 nm.

The Woodward-Fieser rules for carbonyl compounds (13), predict that a substituted α,β-unsaturated carbonyl will strongly

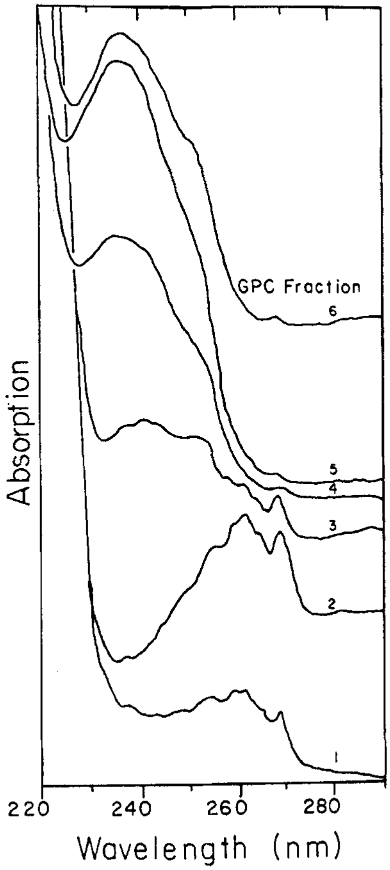

FIGURE 2: Ultraviolet spectra of SEC fractions in THF. The retention volume range of each fraction is shown in Table 1.

absorb between 220 and 250 nm. It has been shown by Shelton et al. (12) that such compounds are formed in the oxidative chain scission of polyisoprene. While low MW compounds like 2-butenone are a volatile product of this oxidative chain scission, other α,β-unsaturated carbonyls may exist as end groups on the isoprene chain after scission.

In addition to this maximum of 237 nm, a strongly absorbing shoulder at ∿250 nm is also observed in fraction 3-6. This is probably a similar residue with a slightly different structure. This shoulder extends well beyond 259 nm and thus is responsible for the interference observed in the UV chromatogram (Figure 1), since its extinction coefficient may be as much as an order of magnitude greater than that of PS at this wavelength. Thus, while the RI detector shows very little material in the SI to polystyrene region of the chromatogram, a small amount of material with a high extinction coefficient produces a large UV detector response at 259 nm.

As a result of this finding, SEC chromatograms of 2.5-μm SIS films were recorded with the variable wavelength UV detector at 237 nm. A comparison of UV chromatograms at 237 nm, 226 nm and 259 nm is shown in Figure 3. At 226 nm both polystyrene and polyisoprene absorb strongly, while the α,β-unsaturated carbonyl residue absorbs only moderately. The SI and SIS peaks thus resemble those found in the RI response, and are strongly related to MWD in the polymer; there is however some interference from the strongly-absorbing carbonyl group, as seen by comparison with the RI chromatogram in Figure 1. The SEC chromatogram run at 237 nm is very sensitive to both polystyrene and PI. The chromatogram recorded at 259 nm is less sensitive to the carbonyl group, and moderately sensitive to the polystyrene, however, the carbonyl group still dominates.

These results point out a potential problem from using a fixed wavelength UV detector alone to study MWD in polymers susceptible to oxidation. If only the UV detector at 254 nm had been used in this study, as an example, the results would have

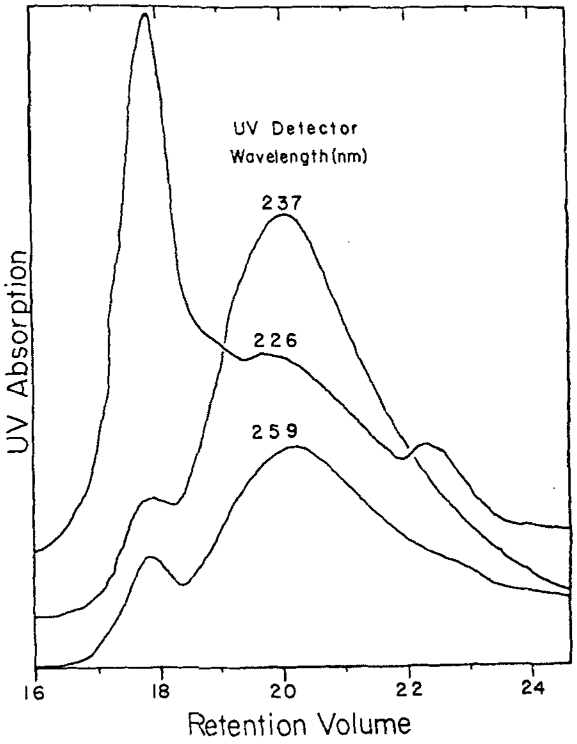

FIGURE 3: SEC chromatograms of 2.5 μm SIS films using a variable wavelength UV detector at 259, 237 and 256 nm.

been very misleading. Data collected at 254 nm would lead one to believe that extensive degradation of SIS tri-block to SI diblock had occurred, while in fact very little occurred, and the small amount of degradation which did occur was accompanied by formation of a product with a very large extinction coefficient. Information obtained simultaneously from UV (226 nm) and RI detectors prevent this misinterpretation. Thus, whenever possible, it is desirable to use both detectors simultaneously when studying unsaturated polymers under conditions of degradation.

From this information it seems that this is a very sensitive method of detecting carbonyl groups that result from the oxidative chain scission of polyisoprene. However, in order for this tech-

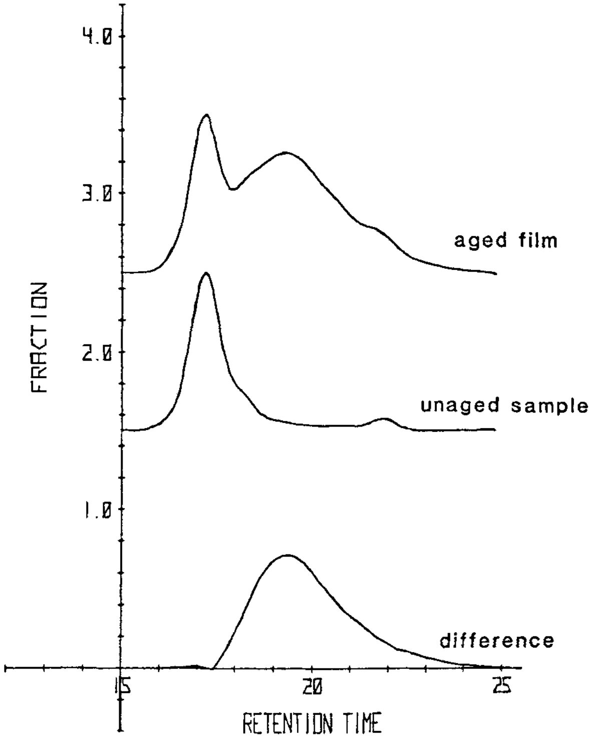

FIGURE 4: SEC difference chromatograms using an UV detector fixed at 237 nm. Normalization of the chromatograms was achieved through dividing the detector response by the response at the SIS peak (16.8 ml). The unaged sample was taken from a bulk SIS lot. The aged film was coated from the same lot and had a dry thickness of 8.6 µm. It was aged in air for seven hours at 80°C.

nique to be at least semi-quantitative, a method of normalization must be designed. Using the information obtained from both RI and UV detectors, we have found that the concentration of SIS molecules in a given sample is essentially constant, for short aging times at temperatures no greater than about 80°C. Also, since this anionically polymerized polymer has a very narrow MWD, one can achieve normalization by dividing each point on the chromatogram by the SIS peak height.

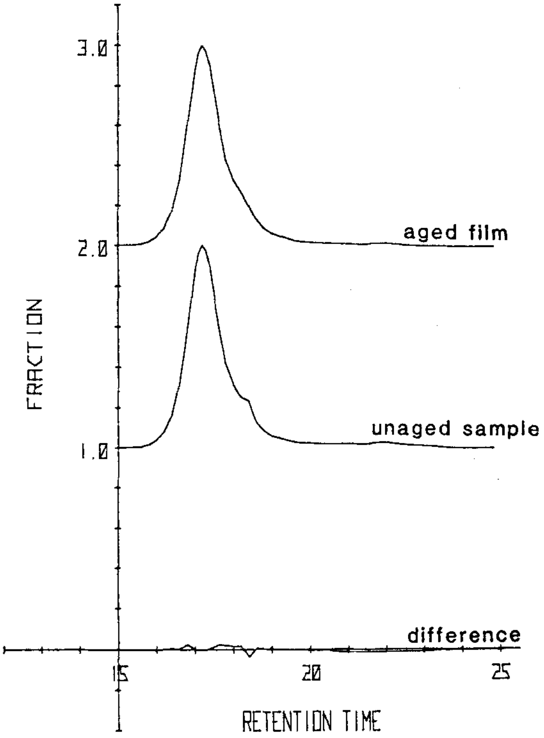

FIGURE 5: SEC difference chromatograms using a RI detector. Normalization of the chromatograms was achieved through dividing the detector response by the response at the SIS peak (16.8 ml). The unaged sample was taken from a bulk SIS lot. The aged film was coated from the same lot and had a dry thickness of 8.6 µm. It was aged in air for seven hr. @ 80°C.

Once the data have been normalized, changes in the carbonyl content can be followed with aging time. In order to facilitate such an experiment, a difference chromatogram is determined by subtracting the chromatogram of an uncoated and unaged sample from one of a coated and/or aged sample, so long as each chromatogram was previously normalized to the SIS peak height. The area under the resulting, difference chromatogram represent the carbonyl content in the sample being investigated. If the film volumes are standardized to 1cm x 1cm x the film thickness, the relative concentration of carbonyl groups in a film can be calculated from the area under the difference chromatogram. Using such a standard sampling volume, the relative concentration of carbonyl groups in films of varying thickness can be compared.

Figure 4 illustrates the subtraction procedure used. In this case, the chromatogram of SIS bulk polymer is subtracted away from one of an aged (7 hr, 80°C, Air) 8.6 µm SIS film. The area under the difference chromatogram is then calculated and used as a measure of the carbonyl content in the specimen. To illustrate the soundness of this technique, figure 5 shows the subtraction of the RI chromatogram of SIS bulk from one of SIS film aged seven hours at 80°C in air. The difference chromatogram shows that the two films are essentially equivalent, with no appreciable mass change of SIS to SI having occurred.

## DISCUSSION

Although SEC is well suited for studies of polymer degradation, detector choice is crucial. In the case of thin SIS block copolymers films a fixed UV detector at 254 nm can give misleading results due to interference from carbonyl bands. By using both a variable wavelength UV detector and an RI detector, the extent of oxidation is easily followed. Further, if the UV detector is set to a wavelength at which the degradation product absorbs, substantial information on the degradation process can be obtained. Such a method has been developed for studying the oxidation of thin SIS block copolymers films used in PSA's. The method measures the formation and/or deterioration of carbonyl groups which absorb at 237 nm. Such groups are typically found as chain end residues after oxidative scission (12).

Further improvement of such experiments could be made by using a UV spectrometer which is capable of quickly scanning (1-2 sec.) the flowing eluent from the SEC (16). This would yield a separate UV spectrum for each segment of the chromatogram. Thus typical components could easily be identified.

In the SIS films examined in this study, the presence of small amounts of oxidative chain scission products had a dramatic effect on the ultraviolet detection of these materials. It is believed that surface oxidation of these films was responsible for this effect. It has been shown by Chang et al. (17) that polybutadiene (PB) films exposed for short periods to room temperature air showed a dramatic increase in adhesive bond strength to other identical films. It was believed that surface oxidation was responsible for this effect. Polyisoprene also undergoes such surface oxidation. However, since chain scission predominates over crosslinking, no covalent bonds are formed across the adhesive interface, as in the case of PB, and no increase in adhesive strength is realized.

The films studied in these experiments were very thin (∿2.5 μm) and the surface to bulk ratio was sufficiently high to allow the detection of these materials. Other methods such as multiple internal reflectance infrared spectroscopy (MIR/IR) proved too insensitive to detect the surface oxidation in these films. However, in SIS films aged for several hours at 95°C MIR/IR was found to be very useful. (1) The results of those experiments were found to be in agreement with the FTIR studies of Shelton (12).

Future studies will further characterize surface oxidation in SIS films. These data will then be used to develop a model of the influence of surface oxidation on the aging of SIS based PSA's.

## ACKNOWLEDGMENTS

One of us, D.H. wishes to acknowledge the support of Avery International Corporation which provided a research fellowship for these investigations.

## REFERENCES

1. Harrison, D.J.P., Johnson, J.F. and Yates, W.R., Aging of Pressure Sensitive Adhesives I: Stability of Styrene-Isoprene-Styrene Block Copolymer Films at 95°C, Polym. Eng. Sci., 22(14), 865, 1982.

2. Cazes, J., XXIX. Gel Permeation Chromatography, J. Chem. Ed., 43(7) and 43(8), 1966.

3. Ouano, A.C., Barrall II, E.M. and Johnson, J. F., Gel Permeation Chromatography, Chapt. 6 in Polymer Molecular Weights, Slade, P.E. and Jenkins, L.T., eds., Marcel Dekker, New York, 1975.

4. Abbott, S.D., Size Exclusion Chromatography in the Characterization of Polymers, Am. Lab., 9(8), 41, 1977.

5. Gaylor, V.F. and James, H.L., Gel Permeation Chromatography (SEC), Anal. Chem., 50(5), 29R, 1978.

6. Abbås, K.B., Molecular Characterization of Degraded Polymers, in Liquid Chromatography of Polymers and Related Materials II, Cazes, J. and Delamare, X., eds., Marcel Dekker, New York, 1980, pp. 123-142.

7. Harmon D.J. and Folt, V.L., Multidetectors for Analysis of the Composition of Copolymers as a Function of Molecular Size Distribution by Steric Exclusion Chromatography, Rub. Chem. Tech., 46(2), 449, 1973.

8. Stojanov, C.H., Shirazi, Z.H., and Audu, T.O.K., Contribution to the Determination of Chemical Composition of Copolymers by Means of GPC, Pak. J. Sci. Ind. Res., 20(3), 161, 1977.

9. Tung, L.H., Block Copolymer Molecular Weight by GPC, J. Appl. Polym. Sci., 24, 953, 1979.

10. Gallot, Z., Utilization of Multidetector Systems for Gel Permeation Chromatography, in Liquid Chromatography of Polymers and Related Materials II, Cazes, J. and Delamare, X., eds. Marcel Dekker, New York, 1980, pp. 113-122.

11. Anderson, J.N., The Distribution of Olefinic Linkages in Elastomers, J. Appl. Polym. Sci., 18, 2819, 1974.

12. Shelton, J.R., Pecsok, R.L. and Koenig, J.L., FTIR Studies of the Uninhibited Oxidation of Elastomers, ACS Symp. Ser., 95, 75, 1979.

13. Silverstein R.M., Bassler, G.C. and Morrill, T.C., Spectroscopic Identification of Organic Compounds, 4th ed., John Wiley and Sons, New York, 1981.

14. Bressau, R., Problems in Multiple Detector of GPC Eluents, in Liquid Chromatography of Polymers and Related Materials II, Cazes, J. and Delamare, X., eds. Marcel Dekker, New York, 1980, pp. 73-93.

15. Dreyfuss, P. and Fetters, L.J., Elastomeric Block Polymers, Rub. Chem. Tech., 53, 729, 1980.

16. Saitoh, K. and Suzuki, Multiwavelength Detection for Liquid Chromatography with a Repeat-Scanning Ultraviolet-Visible Spectrophotometer, Anal. Chem., 51(11), 1683, 1979.

17. Chang, R.J., Gent, A.N., Hsu, C.C. and Sehgal, K.C., Bonding Elastomer Layers Together by a Surface Oxidation Reaction, J. Appl. Polym. Sci., 25, 163, 1980.