

# Aging of Pressure-Sensitive Adhesives III. Studies of Surface Oxidation with Multidetector Size Exclusion Chromatography

DANIEL J. HARRISON,\* W. ROSS YATES,<sup>†</sup> and JULIAN F. JOHNSON, *Institute of Materials Science and Department of Chemistry, University of Connecticut Storrs, Connecticut 06268*

## Synopsis

The use of multidetector size exclusion chromatography is described for studying oxidation in styrene-isoprene-styrene block copolymer films. It is shown that exposure of these films to atmospheric oxygen causes surface oxidation of the isoprene midblocks and that the antioxidant system used is incapable of preventing this. Higher temperature exposure initially merely accelerates the surface reaction but is followed after an induction period by severe bulk-phase degradation. The implications of ambient temperature surface oxidation of SIS-based pressure-sensitive adhesives are discussed.

## INTRODUCTION

The use of size exclusion chromatography (SEC) for the analysis of polymers has been widely reviewed.<sup>1-4</sup> Since SEC is primarily used to determine the molecular weight distribution (MWD) of polymers, it has found extensive use in the study of polymer degradation, many such applications of which have been discussed by Abbås.<sup>5</sup> Pressure-sensitive adhesives (PSA) based on styrene-isoprene-styrene (SIS) block copolymers undergo aging, which is thought to be oxidative in nature.<sup>6</sup> It has been shown in a previous paper<sup>7</sup> that size exclusion chromatography could be used to study the degradation of SIS-based PSAs. The dual detector SEC used in this study revealed the presence of small amounts of  $\alpha$ ,  $\beta$ -unsaturated aldehydes (UA) in thin SIS films. These UAs may be formed in the oxidative chain scission of the polyisoprene midblocks. This would be consistent with the mechanism proposed by Morand<sup>8</sup> for the oxidative chain scission of *cis*-polyisoprene (PI) and experimentally confirmed by Shelton et al.<sup>9</sup> With respect to the polyisoprene midblocks in SIS, the mechanism also appears to apply. Gas chromatographic/mass spectrometric (GC/MS) analysis of the volatile oxidation products of thin SIS films<sup>6</sup> found many of the products predicted for the oxidative degradation of polyisoprene by Morand,<sup>8</sup> including a complex caprolactam.

In the SEC analysis of thin SIS films (5–30  $\mu\text{m}$  thick),<sup>7</sup> the differential refractive index (RI) detector response appeared to indicate no change in

\* Present address: Research Laboratories, Bldg. 82, Kodak Park, Eastman Kodak Co., Rochester, New York 14450.

<sup>†</sup> Present address: Lexington Laboratory, The Kendall Company, 17 Hartwell Avenue, Lexington, Massachusetts 02173.

the MWD upon coating and drying the film. However, the ultraviolet detector (237 nm) responded as if substantial chain scission of the SIS triblock molecules to SI diblock fragments had occurred. A solution of the same SIS film was then fractionated with the SEC. Ultraviolet spectra (220–290 nm) of each fraction were then recorded and revealed the presence of a strong maximum at  $\sim 240$  nm in the diblock fractions. This strong absorption is indicative of the presence of  $\alpha$ ,  $\beta$ -unsaturated aldehydes.<sup>10</sup> These UAs were not detected in the triblock elution segments of the chromatograms, lending further support to Morand's chain scission mechanism predicting the formation of UA end groups. Since these UA chromophores are known to have very high extinction coefficients ( $\epsilon \geq 10,000$ ),<sup>10</sup> very small concentrations can induce a large response from an UV detector operating at a wavelength near their absorbance maximum ( $\lambda_{\text{max}}$ ). As no MW degradation was observed with the RI detector of this SEC, it was proposed that the oxidation products were confined to the surface. In this paper the surface oxidation of these SIS films will be further explored.

From this work it was apparent that the UV/RI-SEC might be used as a very sensitive detector of oxidative degradation in SIS and perhaps also for many other soluble unsaturated polymers. Our interest in developing this technique resulted from a broader study of aging in pressure-sensitive adhesives (PSA) based on SIS block copolymers.<sup>6</sup> These PSA formulations have been known to experience aging problems,<sup>11</sup> but in a preliminary study of the aging of commercially prepared PSAs, it proved difficult to isolate the exact cause of the problem.

Recently, Chang et al.<sup>12</sup> showed that very low amounts of surface oxidation dramatically increase the adhesion between two polybutadiene films and proposed that this effect was caused by an oxidative cross-linking reaction between the films. In the case of polyisoprene films, which undergo chain scission rather than cross-linking, no such effect was observed. In fact, the adhesion between polyisoprene films was shown to decrease upon exposure to air. It is probable that the polyisoprene midblocks in SIS block copolymers undergo a similar chain scission upon oxidation and that PSAs formulated from them should also experience surface oxidation.

In this paper, a study is presented for the use of the UV/RI-SEC technique<sup>7</sup> for the study of surface oxidation of SIS films. First, the effect of film thickness on the UA concentration was investigated, with the expectation of isolating surface from bulk oxidation. Second, the role of film aging was explored, allowing us to establish whether the technique is suitable for following changes in the composition of the films with aging time. The effect of antioxidants on these phenomena was also explored.

## EXPERIMENTAL

The SEC used in these experiments consisted of a Waters 6000A solvent delivery system with a Model U-6 sample injector, four  $\mu$ -Styragel columns ( $10^5$ ,  $10^4$ ,  $10^3$ , and  $500$  Å), 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. The solvent was unstabilized tetrahydrofuran, and the flow rate was 1.5 mL/min. The UV

detector wavelength was fixed at 237 nm with a 16-nm slit width. Other details of the chromatograph are reported in a previous paper of this series.<sup>7</sup>

Rubber solutions (20% by weight) were mixed for 24 h in the dark on a gentle wrist-action shaker, using nitrogen-degassed toluene (reagent grade) as a solvent. The SIS was from a commercial lot of Kraton 1107 (Shell Oil Co.). Both unstabilized and stabilized solutions were used, the latter containing the antioxidant system outlined in Table I. These antioxidants were dissolved in toluene prior to mixing. All solutions were stored in the dark under argon until use.

Solutions were coated with a Gardner Ultra Film Applicator on 24- $\mu\text{m}$  polyethylene terephthalate films taped to glass plates. The coatings were first dried in the dark at 20–25°C for 1 h under a slow nitrogen purge. They were then heated to 40°C in a 3300-Pa vacuum for 4 h. During the heating cycle, a small nitrogen leak was provided to sweep away any residual toluene or oxygen. It is likely that most of the butylated hydroxytoluene (BH) incorporated in the manufacturing process was removed in this vacuum drying step.

Aged and unaged SIS films were analyzed with the SEC. In order to prepare consistent solutions of these films for analysis on the SEC, a technique was devised to measure the film thickness. These measurements of the film thickness were taken from coating weight measurements. The PET backing onto which the films were coated was found to have an extremely uniform thickness. Because of this uniformity, the surface area of the PET film was easily determined by its dry weight. This led to a simple means of estimating the thickness of the SIS film:

1. Weigh a sample of the film coated on the PET backing ( $W_S$ ).
2. Dissolve the film from the PET with THF.
3. Weigh the washed PET backing ( $W_{\text{PET}}$ ), and determine its surface area  $SA$ .

$$SA = W_{\text{PET}}/W \text{ per unit area}$$

4. Determine the coating weight  $W_C$ :

$$W_C = W_S - W_{\text{PET}}$$

5. Divide the coating weight by the surface area of the PET to determine the normalized coating weight  $W_{\text{NC}}$ :

$$W_{\text{NC}} = W_C/SA$$

TABLE I  
Antioxidant System Used with SIS

Antioxidant	Function	Grams per 100 g SIS
Dilaurylthiodipropionate (LTDP)	Peroxide decomposer	1
1,3,5-Trimethyl-2,4,6-tris(3,5-ditert-butyl-4-hydroxybenzene) benzene	Free radical scavenger	1

6. Divide the normalized coating weight by the density of the polymer to determine the normalized sample volume  $V_{NS}$ :

$$V_{NS} = W_{NC}/D$$

7. Since the normalized sample volume corresponds to  $1 \text{ cm}^2$  of coating, the sample thickness  $S_t$  will be equal to the normalized sample volume:

$$S_t = V_{NS}/1 \text{ cm}^2$$

The density measurements were made by Shell Chemical Co.<sup>12</sup> on SIS films and found to be  $0.90 \text{ g/cm}^3$ . With this information on film thickness, a sufficient area of film was dissolved that a 0.01% solution of the polymer in THF was formed. This solution was then filtered through a  $0.5\text{-}\mu\text{m}$  filter into the  $25\text{-}\mu\text{l}$  injection loop of the SEC. The time between film dissolution and injection onto the SEC was kept as short as possible.

It should be noted that this technique yields only an approximate concentration of 0.01 g/ml of polymer. A normalization procedure must therefore be used to compare different runs; this normalization procedure is described in the Results and Discussion section of this paper.

## RESULTS AND DISCUSSION

In an effort to determine whether the UAs were concentrated near the surface of the SIS films, a series of unstabilized films was prepared ranging in thickness from 2.5 to  $33 \mu\text{m}$ . These films were analyzed in the SEC, and the resulting chromatograms are shown in Figures 1 and 2. The RI chromatograms (Fig. 1) showed typical MWDs for SIS block copolymers,<sup>15</sup> with no obvious differences due to film thickness. The UV chromatograms (Fig. 2), however, were very highly dependent on film thickness. Although the UV chromatogram of the  $33 \mu\text{m}$  film most resembled the RI chromatograms,

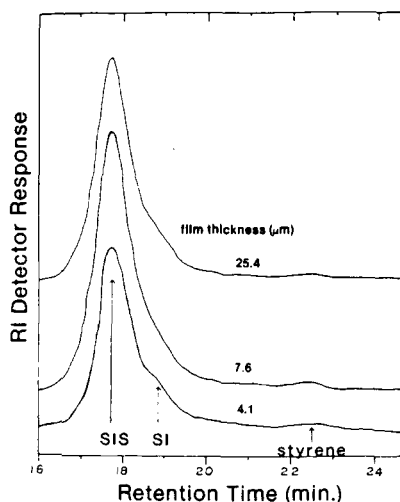


Fig. 1. SEC chromatograms (RI detector) of 25.4, 7.6, and  $4.1 \mu\text{m}$  unaged SIS films.

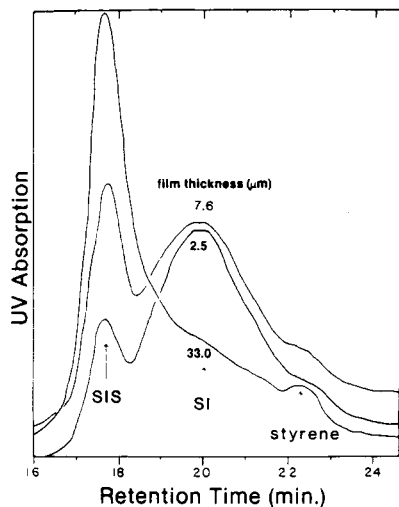


Fig. 2. SEC chromatograms (UV detector, 259 nm) of 33, 7.6, and 2.5  $\mu\text{m}$  unaged SIS films.

the two thinner films showed large responses that are probably due to UA end groups on scissioned SI chains.

The same series of SIS films were aged for 8 h at 75°C, after which they were analyzed with the dual detector SEC and the UA concentrations again estimated. In the previous paper,<sup>7</sup> a method was described that allowed an estimate of the concentration of UA in a SIS film. Since no significant change in the MWD was observed at short aging times, normalization of chromatograms was possible by dividing each point by the SIS peak height. Thus, the normalized chromatogram of an unaged sample could be subtracted from that of an aged sample. The area under the resulting difference chromatogram could then be taken as an estimate of the UA concentration. Figure 3 shows UA concentrations estimated in this way as a function of film thickness for both aged and unaged SIS films. The unaged films show an increase in UA concentration with decreasing film thickness, suggesting that the aldehydes are concentrated at the surface of the film. After aging,

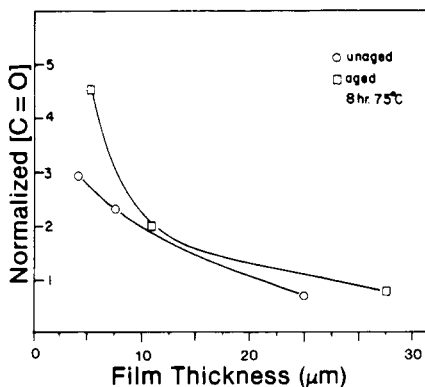


Fig. 3. The effect of film thickness on the unsaturated aldehyde concentration (UV/RI-SEC) of aged (8h, 75°C) and unaged SIS films.

the concentration is increased, but this increase is more dramatic in the thinnest sample. As thin films have a high surface-to-bulk ratio, these data suggest that a thin layer at or near the surface has been degraded. The bulk phase seems to be relatively unoxidized, as evidenced by the fact that there were no apparent changes in the RI chromatograms.

In order to see if antioxidants can prevent this surface oxidation, we prepared a similar series of SIS solutions containing the antioxidant system of Table I. After aging these films up to 305 h in air at 75°C, severe changes in MWD (Fig. 4) were observed. Since the SIS peak height was no longer constant, a new method of data normalization was needed. An alternative method would be to use the area under the RI chromatogram. This method should be satisfactory, since any moderate changes in concentration or injected volume would easily be within the linear range of the detector. However, there is some question of whether the RI response changes as the SIS polymer is degraded. To determine if this change in response might be significant over the extremes of our experiments, three samples were analyzed. Figure 5 shows RI chromatograms of samples aged 0, 2, and 5 h in air at 90°C. The sample aged 5 h has been drastically degraded, and chain scission has broken down most of the triblock copolymer to diblock and smaller fragments.

Two SEC experiments were made on the unaged and 5-h aged samples, and the concentrations of each solution and the injected volumes were all carefully measured. The area under each RI chromatogram was determined by a cut-and-weigh technique. By dividing the RI chromatogram area by the sample concentration, a measure of RI response is achieved; the results are shown in Table II.

As can be seen, the average response of the RI detector for these two samples is within 2%, and we are therefore justified in using the area under

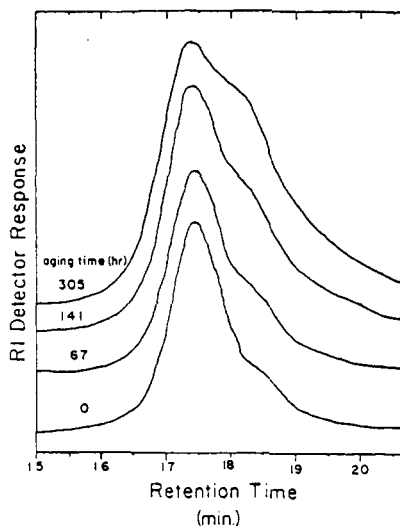


Fig. 4. The effect of aging time (75°C) on the molecular weight distribution (RI-SEC) of antioxidant stabilized SIS films.

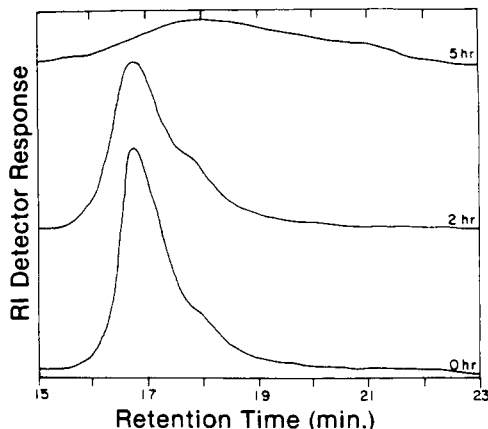


Fig. 5. RI-SEC chromatograms of SIS films aged in air at 90°C for 0, 2, and 5 h.

the RI chromatogram as an accurate internal standard of sample concentration.

The area under the UV chromatogram may now be normalized by dividing by the area under the RI chromatogram. The resulting area will reflect the relative number of UA groups for a normalized sample. This technique appears well suited to studying changes in the carbonyl content of a sample, but considerable additional work would have to be done to put the technique on a quantitative basis.

Using this method, the UA concentration was analyzed for an antioxidant-stabilized 6.4- $\mu\text{m}$  SIS film as a function of aging time. These data are shown in Figure 6 and are compared with the ratio of SIS to SI peak heights from the RI chromatograms. This ratio is a good estimation of the extent of chain scission in these films, particularly since the SIS molecules are nearly monodisperse. These results reveal changes in the SIS film during an induction period. Although the SIS-SI ratio remained constant for nearly 90 min, the UA concentration has increased from its initially low level. This low level is typical for unaged films as well as the bulk polymer. After the induction period, a steady rate of chain scission was observed, accompanied by stabilization in the UA concentration.

It is probable that although the antioxidant system is capable of protecting the bulk molecules, some surface oxidation takes place during the induction period. Initially this surface oxidation seems to result in the formation of some UA end groups,<sup>14</sup> as seen in Figure 6. However, as the degradation continues and the effective antioxidant concentration at the

TABLE II

	Unaged sample	5-h Aged sample
	RI response = RI area/sample conc.	RI area/sample conc.
1	0.03928	0.04058
2	0.03818	0.03826
Average	0.0387	0.0395

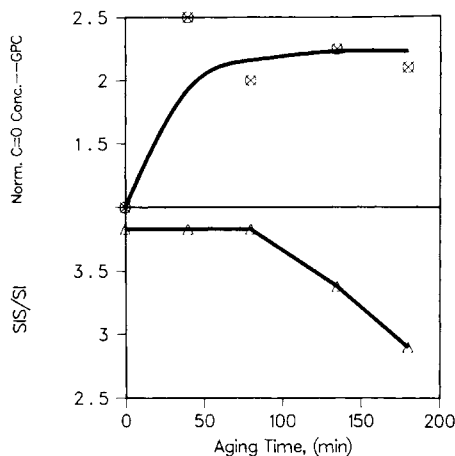


Fig. 6. The effect of aging antioxidant-stabilized SIS films in air at 75°C on both the unsaturated aldehyde concentration and the ratio of SIS to SI peak heights.

surface is depleted, the oxidation conditions at the surface become more severe. This possibly has the effect of further oxidizing the UA end groups to unsaturated carboxylic acids,<sup>16</sup> thus shifting the  $\lambda_{\max}$  of these end groups downward to about 200 nm, well below the UV detector wave-length. It is proposed that a steady state may exist between UA formation and UA oxidation to unsaturated carboxylic acids.

After 90 min aging, conditions are such that the antioxidant system can no longer prevent extensive chain scission from occurring in the bulk. A significant drop in the SIS-SI ratio is observed, indicative of main chain scission. It is also observed that the physical properties of the film change after this induction period from an elastomer to a viscous fluid.

## CONCLUSION

It has been demonstrated that UV/RI-SEC can be a very useful technique for the analysis of SIS films. In fact, the technique is probably useful for studying oxidation of many soluble unsaturated polymers. It may be particularly useful when thin, unsaturated films or coatings are studied, since small amounts of surface oxidation can have large effects on UV absorbance.

By using UV/RI-SEC in a semiquantitative way, the distribution of oxidized material in a film can be estimated. In the case of SIS films, it was shown that the surface was easily oxidized while the bulk remained unchanged. This method is also useful in following changes in a material with aging. Not only are changes in the MWD observed (RI), but also changes in functional group concentration. In this example we found the technique to be particularly suitable for studying the oxidative degradation of SIS films.

The observation that pressure-sensitive adhesives based on SIS block copolymers showed decreases in performance with ambient aging<sup>10</sup> could be a result of the surface oxidation of isoprene midblocks. Even in films protected with antioxidants, surface oxidation occurs. Further studies in this series of papers will explore the effect of this process on the performance of adhesives.



One of us (Harrison) expresses appreciation to Avery International Corporation for providing a research fellowship in polymer science to support this work.

### References

1. J. Cazes, *J. Chem. Ed.*, **43**(7), **43**(8), (1966).
2. A. C. Ouano, E. M. Barrall, II, and J. F. Johnson, Gel permeation chromatography, Chap. 6 in *Polymer Molecular Weights*, P. E. Slade, and L. T. Jenkins, Eds., Marcel Dekker, New York, 1975.
3. S. D. Abbott, Size exclusion chromatography in the characterization of polymers, *Am. Lab.*, **9**(8), 41 (1977).
4. V. F. Gaylor and H. L. James, Gel permeation chromatography (SEC), *Anal. Chem.*, **50**(5), 29R (1978).
5. K. B. Abbās, Molecular characterization of degraded polymers, in *Liquid Chromatography of Polymers and Related Material, Vol. II*, J. Cazes and X. Delamare, Eds., Marcel Dekker, New York, 1980, pp. 123-142.
6. D. J. P. Harrison, Investigations of Aging of Pressure Sensitive Adhesives Based on Styrene-Isoprene-Styrene Block Copolymers, Ph.D. thesis, University of Connecticut, Storrs, CT (1982).
7. D. J. P. Harrison, W. R. Yates, and J. F. Johnson, *J. Liquid Chromatogr.*, **6**, 2723 (1983).
8. J. L. Morand, *Rubber Chem. Technol.*, **50**, 373 (1977).
9. J. R. Shelton, R. L. Pecsok, and J. L. Koenig, in *Durability of Macromolecular Materials*, R. K. Eby, Ed., ACS Symp. Ser., **95**, 75 (1979).
10. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectroscopic Identification of Organic Compounds*, 3rd Ed., John Wiley, New York, 1974.
11. Private communication, Avery International Corp.
12. R. J. Chang, A. N. Gent, C. C. Hsu, and K. C. Sehgal, *J. Appl. Polym. Sci.*, **25**, 163 (1980).
13. J. T. Harlan and L. A. Petershagan, Thermoplastic rubber ABA block copolymers in adhesives, Chap. 19 in *Handbook Adhes.*, I. Skeist, Ed., 2nd Ed., Van Nostrand Reinhold, New York, 1977.
14. A. V. Tobolsky and A. Mercurio, *J. Amer. Chem. Soc.*, **81**, 5535 (1959).
15. P. Dreyfuss and L. J. Fetters, *Rubber Chem. Technol.*, **53**, 729 (1980).
16. E. M. Bevilacqua, *Science*, **126**, 396 (1957).

Received August 17, 1985

Accepted October 17, 1985