

# Accelerated Weathering of Butadiene–Styrene-Based Rubber

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## Synopsis

Photoacoustic spectroscopy (PAS) was used for the study of accelerated weathering of some selective samples of butadiene–styrene rubber. It was found that, although their accelerated degradation is mainly due to the combined effects of UV and heat, the rate of their degradation solely depends on their compositions.

## INTRODUCTION

The first successful attempt for the preparation of styrene–butadiene-based rubber was in 1929. During that time, scientists were hoping that this new product could overcome the deficiencies of polybutadiene polymer. Between 1942 and 1944 the quality of these synthetic rubbers was drastically improved, and the demand for using them in several products was sharply increased. For example, during this period alone the annual production of styrene–butadiene copolymer reached more than a million tons.

In 1950, cold rubber was successfully polymerized and yielded better quality than the earlier hot polymerized rubber. In 1960, a new type of synthetic rubber was prepared using anionic catalysts such as butyl lithium. This type of rubber is known as solution polymer to differentiate it from the earlier emulsion polymers. Although commercial emulsion rubber is still the most used one, solution rubber is of increasing importance, and as a result its production is increasing yearly. It is also of interest to mention here that both styrene and diene monomers are, at present, prepared mainly from petroleum products, although they could be alternatively prepared through a number of synthetic routes.

When styrene–butadiene copolymer is prepared from its monomers in a random fashion, the resulting polymer is known as random copolymer. Block copolymers, however, were prepared in 1963. The introduction of a short polystyrene block at one end of the styrene–butadiene copolymer chain reduces its cold flow.<sup>1</sup> This cold flow can be further reduced by introducing styrene blocks at both ends of the copolymer chain.<sup>2</sup> This was found to immobilize the chain. Other styrene–butadiene copolymers such as alternate copolymers were also prepared during the course of synthetic rubber development.

All these types of synthetic rubbers are being used in a wide range of important applications. To give an idea of the importance of these polymers, it is expected that Western Europe will produce more than 100,000 tons from the block copolymer alone in the year 1986.

Styrene-butadiene copolymer is an unsaturated hydrocarbon polymer. As a result it can be photooxidized, thermally degraded, attacked by ozone, halogenated, etc. It was found that these factors reduce its useful lifetime. Therefore, studies are needed to assess the effect of these factors on the stability of these synthetic rubbers. In a previous article<sup>3</sup> we initiated this study. The effect of heat on the stability of some styrene-butadiene-based rubber was carried out. In this article, accelerated weathering of the same compounds is investigated.

## EXPERIMENTAL

**Photoacoustic Spectrometer.** The photoacoustic spectrometer used in this work was discussed in earlier publications.<sup>3-11</sup> A 1000 W Xenon lamp was used as a source of excitation. The lamp modulation frequency was 40 Hz. The exit slit of the light scanning monochromator was 2 mm at which the resolution of the spectrometer is 8 nm. Air was used as a coupling medium between the sample and the microphone. Carbon black was used as a reference against which all spectra were normalized. The equipment is completely controlled and run by a Model U62-TMS 9900 Microprocessor and utilizes the capabilities of a PAR Floppy Disk Model 6001/97.

**Samples and Sample Preparations.** All the samples used in this work are the same samples reported in a previous article.<sup>3</sup> They are mainly Diene 35 NFA/AC, FR-S 211, Stereon 702A, and Kraton 1101. We also studied polystyrene since the above synthetic rubbers are all based on butadiene-styrene copolymer. All the samples, with the exception of polystyrene, were obtained from the Firestone Co. Polystyrene was obtained from local dealers. All samples were used as delivered by the manufacturer except polystyrene, which was used in a form of thin films. Accelerated weathering was accomplished by subjecting each sample simultaneously to heat (at 60°C), UV irradiation, and humidity for 8 h followed by 16 h of heat at (35°C) and humidity alone. This accelerated weathering of the samples was accomplished at the Kuwait Institute for Scientific Research.

The PAS spectrum of a fresh (nonirradiated) sample was first recorded as a blank (*B*) and stored on floppy disk. (*B*) was then subtracted from the spectrum of each irradiated sample (*S*) to yield the net changes (*S-B*) that might take place as a result of any degradation. The microprocessor was then automatically normalized (*S-B*) against the carbon black reference spectrum (*R*) to give (*S-B*)/*R* signal. The same reference carbon black (*R*) and the same blank sample (*B*) were used for all irradiated samples of the same kind. This is to insure that all spectra are taken under the same conditions and that any possibility of spectrum variation, from one sample after certain irradiation time to the same kind of sample after a different irradiation time, is eliminated. This was accomplished by first storing (*R*) and (*B*) for a certain kind of sample. Then every time we turned the spectrometer on, we checked to be sure that the spectrometer was working well by using carbon black as both blank and sample. In this way, if we recorded *S/R*, a straight line would be obtained with a PAS signal equal to unity. Once this was accomplished, we called from the memory of the computer the old (*R*) and (*B*) and used them with our sample.

## RESULTS AND DISCUSSION

In a previous article by Abu-Zeid et al.<sup>3</sup> thermal degradation of polystyrene, polybutadiene, and butadiene-styrene-based rubber was discussed in detail. It was found that the PAS spectra of undegraded polystyrene film has two characteristic bands. One band is around 200 nm and the other one is around 260 nm. These two bands have been investigated intensively by several authors.<sup>12</sup> It was found that they are due to the  $^1S \leftarrow S_0$  and  $^2S \leftarrow S_0$  transitions of the benzene ring, where  $S_0$  is ground electronic singlet state,  $^1S$  is the first electronic excited singlet state, and  $^2S$  is the second electronic excited singlet state.<sup>13</sup> This conclusion was based on an experimental observation that benzene itself has two absorption bands around 200 and 260 nm. It is also supported by the fact that the other parts of the polystyrene molecule, such as CH and CH<sub>2</sub>, do not absorb light of wavelengths > 200 nm. The carbonyl groups present in styrene monomer and polymer are responsible for its photoluminescence.<sup>14</sup>

Exposing polystyrene films to heat at different temperatures<sup>3</sup> in air give rise to a new PAS bands, mainly between 270 and 280 nm and between 350 and 400 nm. These two bands are attributed<sup>3</sup> to the formation of C=C in the polymeric chain and chain end carbonyl group. Heating polystyrene at 170°C results in a decrease in the PAS signal of the band at  $\approx$  260 nm and a new band at  $\approx$  280 nm due to development of conjugated carbonyl structure with exposure time. For temperatures < 170°C, however, almost no polystyrene degradation took place, and for temperatures > 170°C drastic increase of the intensity of the PAS band at 280 nm took place.

Rånby and Rabek<sup>15</sup> showed that during the exposure of polystyrene films to UV irradiation, the band between 270 and 280 nm increased with the exposure time. Another band between 350 and 500 nm started to develop and it also increased with the exposure time. This last band appeared only at elevated temperatures in the PAS spectra of thermally degraded polystyrene films.<sup>3</sup> At any temperature < 200°C and for any heating periods, no trace of such a band is observed in the PAS spectra. Even at 200°C this band is only observed for heating periods > 30 min.

It seems (based on the above discussion) that accelerated weathering of polystyrene film results in a combined effect of heat and UV degradation only, and humidity has no effect on its degradation, as evidenced from the PAS spectra of Figure 1. In this figure we show the PAS spectrum of unexposed polystyrene film together with its PAS spectra representing the net changes that took place as a result of accelerated weathering. The unexposed polystyrene film displays its two characteristic PAS bands at  $\approx$  200 and  $\approx$  260 nm. The band at 260 nm decreases with the exposure periods as expected. Simultaneously, two PAS bands, one between 270 and 280 nm and the other between 350 and 500 nm, appear and increase with the exposure time. These two bands are due to the formation of C=C in the polymeric chain and chain end carbonyl group as explained before. A broad band between 400 and 500 nm appeared in the sample exposed for 45 days. This band is due to the increase of conjugated double bond sequence in the polymer chain.

On the other hand, Abu-Zeid et al.<sup>3</sup> showed that polybutadiene is sus-

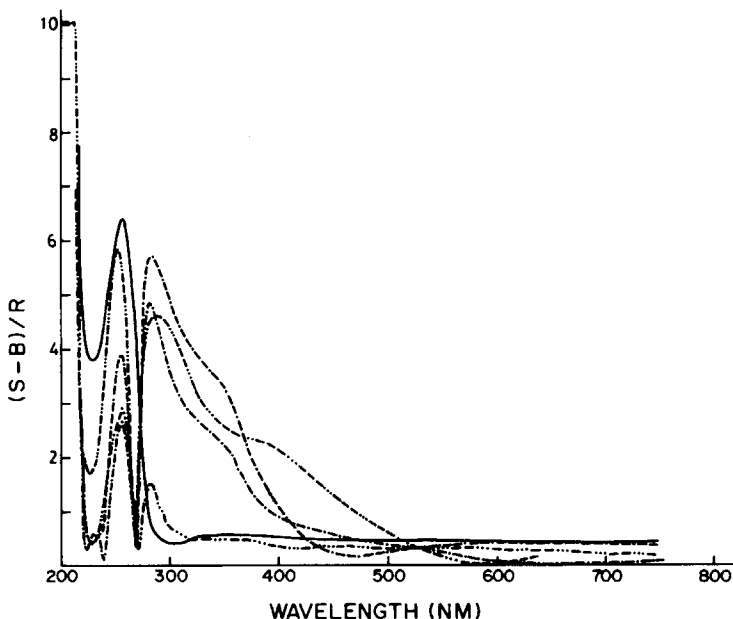


Fig. 1. PAS spectra of polystyrene exposed for 5 days (.....), 13 days (---), 28 days (-.-.-), and 45 days (- - - - -) ( $\times 0.5$ ). The solid line curve is the PAS spectrum of the blank sample.

ceptible to  $O_2$  attack even at room temperature. This  $O_2$  attack is further accelerated by heat and UV irradiation. They also indicated that the rate of degradation of polybutadiene is much faster than that of polystyrene. Unexposed diene 35 NFA/AC PAS spectrum shows an intense band around 200 nm which extends beyond 240–290 nm. The tail of the 200 nm is due to several different chromophor groups along the polymeric chain. Thermally degraded diene, however, develops new bands. One band appears at  $\approx 290$  nm due to the formation of conjugated carbonyl groups. Another band appears at  $\approx 350$  nm with a shoulder at  $\approx 400$  nm that extends to 550 nm. This band is attributed to the formation of crosslinked diene chains containing conjugated carbonyl structure, which is responsible for the observed discoloration of the sample.

During the photooxidation process of polybutadiene, both hydroperoxides and carbonyl groups are formed. Hydroperoxides are generated at the beginning of UV irradiation with a strong absorption in the near ultraviolet, much greater than that of polyolefins.<sup>16</sup> The carbonyl groups appear after intensive induction period during UV irradiation.

Again, accelerated weathering of diene 35 NFA/AC shows a combined degradation effect of heat and UV irradiation only as shown in Figure 2. Humidity, however, plays no significant role in its degradation. In Figure 2, the unexposed diene sample displays the characteristic PAS spectra discussed before. The degraded sample, however, shows a PAS band around 240 nm which is due to the formation of conjugated carbonyl group.<sup>17</sup> For exposure periods  $> 28$  days, a broad band that peaks around 290 nm appears. This band is due to the formation of crosslinked diene chains containing conjugated carbonyl structure as mentioned above.

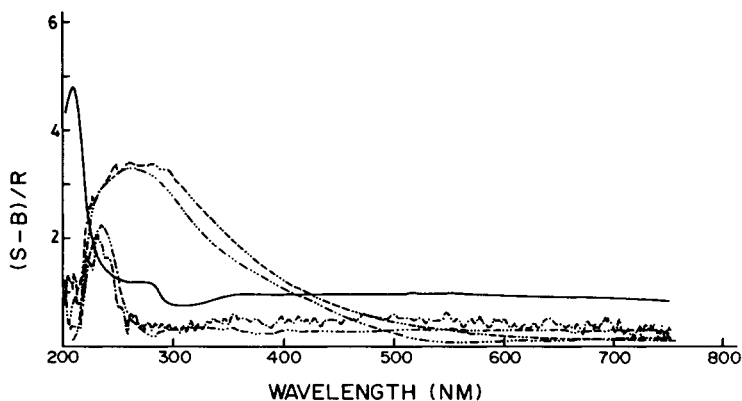


Fig. 2. PAS spectra of Diene exposed for 10 days (-----) ( $\times 2$ ), 20 days (---) ( $\times 2$ ), 37 days (----) ( $\times 0.7$ ) and 60 days (-----) ( $\times 0.7$ ). The solid line curve is the PAS spectrum of the blank sample.

Since FR-S 211, Stereon 702A, and Kraton 1101 are all butadiene-styrene-based rubbers, one would expect that their degradation is a combined effect of the degradation that might take place in their constituents: polybutadiene and polystyrene. The presence of butadiene in these synthetic rubbers make them vulnerable to both heat and UV degradation. Figures 3-5 show the PAS spectra of FR-S, Stereon, and Kraton exposed for periods ranging from 0 to 60 days. It is clear from these figures that the mechanism of the degradation of those synthetic rubbers is indeed a combination of the mechanisms of the degradation of polystyrene and polybutadiene considered separately.

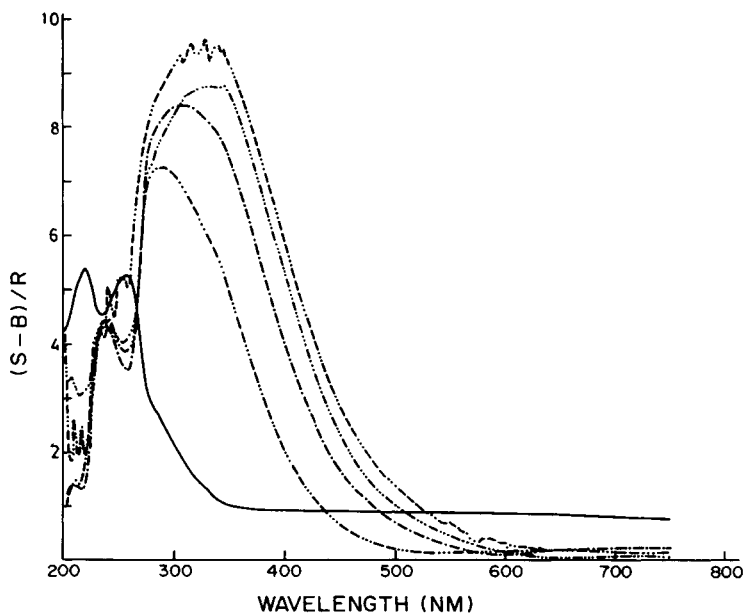


Fig. 3. PAS spectra of FR-S exposed for 10 days (-----), 20 days (---), 37 days (----) ( $\times 0.7$ ) and 60 days (-----) ( $\times 0.7$ ). The solid line curve is the PAS spectrum of the blank sample.

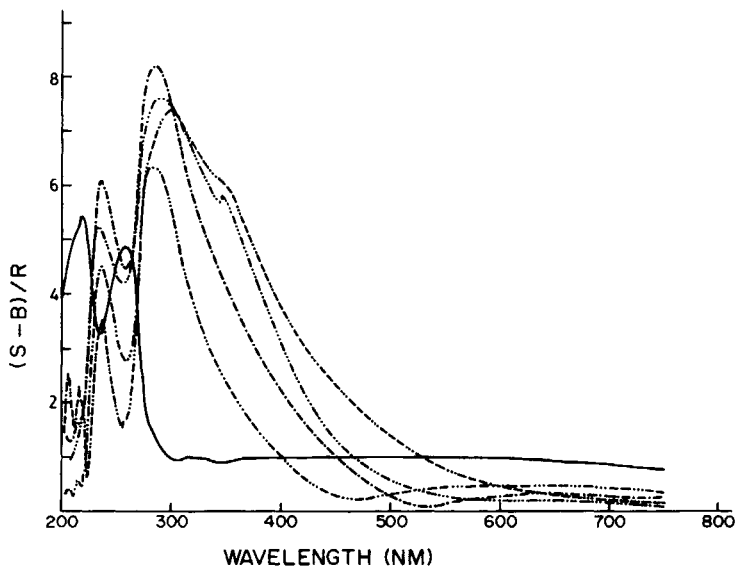


Fig. 4. PAS spectra of Stereon exposed for 10 days (-----) ( $\times 1.5$ ), 20 days (---) ( $\times 1.5$ ), 37 days (-----) ( $\times 1.5$ ), 60 days (-----) ( $\times 1.8$ ). The solid line curve is the PAS spectrum of the blank sample ( $\times 1.5$ ).

In our previous article<sup>3</sup> we indicated that although FR-S, Stereon, and Kraton are all synthetic rubbers based on butadiene-styrene copolymer, they differ in their compositions. We came to the conclusion that thermally FR-S is more degradable than Kraton and the latter is more degradable than Stereon. A quantitative explanation for their degree of degradation was given based on their compositions. For instance, in the case of FR-S, which is a random copolymer, the diene unit is less protected by the styrene unit than in the case of Stereon (alternate copolymer) and Kraton (block copolymer). The data obtained in this article has confirmed our previous finding. It was found that FR-S is still the most degradable polymer, followed by Kraton and Stereon in that order, as evidenced from Figures 3-5.

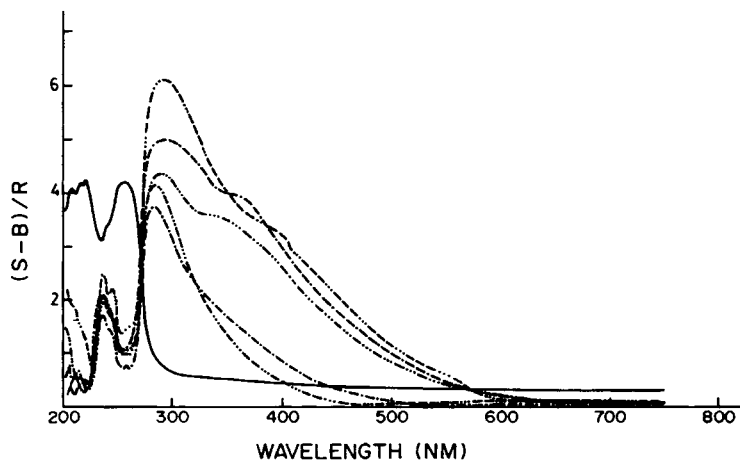


Fig. 5. PAS spectra of Kraton exposed for 10 days (-----), 20 days (---), 37 days (-----), 42 days (-----), and 60 days (-----). The solid line curve is the PAS spectrum of the blank sample.

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