

Thermal Degradation of Butadiene–Styrene-Based Rubber

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Synopsis

Thermal degradation of some commercially available rubber based on butadiene–styrene copolymers are studied as a function of composition, temperature, and heating periods using photoacoustic spectroscopy (PAS) technique. It was found that random copolymers are more degradable than block copolymers and that the latter is more degradable than alternate copolymers. Mechanistic schemes leading to the thermal degradation of these synthetic rubbers are given together with a qualitative explanation of the relation between their composition and their thermal stabilities.

INTRODUCTION

In 1863 a French chemist¹ succeeded in preparing butadiene by pyrolysis of amyl alcohol. Lebedev,² a Russian scientist, was the first to polymerize butadiene in 1910. Since then, scientists everywhere have worked hard to prepare useful products from butadiene with an aim to duplicate natural rubber. In 1933 Bock and Tschunker³ reported the first successful attempt for the preparation of butadiene–styrene copolymer from an emulsion polymerization. The synthetic rubber they obtained was of poor quality compared with that of natural rubber. Improvement and development of the technology of synthetic rubber continued on a large scale after the original discovery of Bock and Tschunker. The milestone in the history of synthetic rubber came when Ziegler and co-workers⁴ discovered that ethylene could be polymerized to a high molecular weight at low pressures in air and moisture-free solutions with a triethylaluminum–titanium tetrachloride catalyst. Two different polybutadienes of commercial interest were prepared through the use of coordinate catalysts derived from Ziegler's original catalyst, as well as a third one based on lithium catalysis which was discovered simultaneously by Firestone Tire and Rubber Co. in the United States and by researchers in USSR.⁵ This was the beginning of the true revolution in the polymer field. For example, in 1963, more than 2 billion lb of butadiene were prepared in the United States alone. Almost all of it was consumed in making elastomers and plastics of different varieties.

The most important synthetic rubber and the most widely used rubber in the whole world is the butadiene–styrene copolymer. Therefore, study of the stability of this copolymer became of major concern. In particular, the effect of heat and UV on butadiene–styrene copolymer stability must be carefully investigated. Several scientists studied the oxidative degradation of polystyrene^{6–8} and polybutadiene^{9–11} separately. Others studied

the effect of heat on styrene-butadiene copolymer.¹² All of these scientists used conventional techniques in their studies. Although these techniques have revealed useful information, yet in almost all cases they resorted to a modified form of their samples in order to obtain the information. This may result in data perturbations. In this article, we used a relatively new technique for the study of thermal degradation of polystyrene, polybutadiene, and styrene-butadiene copolymers. This technique is photoacoustic spectroscopy. It was found to be the most useful technique in the study of polymer degradation.¹³⁻¹⁷ Using this technique, solid polymer samples can be studied with ease as they are delivered by the manufacturer. No sample preparations are required. As a result, our data are more reliable and are a true representation of the actual thermal degradation in nature.

EXPERIMENTAL

Photoacoustic Spectrometer. The photoacoustic spectrometer used in this work was described in earlier publications.¹⁸⁻²⁰ A 1000-W xenon lamp was used as a source of excitation. 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. The equipment is completely controlled and operated by a microprocessor.²¹

Samples and Sample Preparation. The commercial synthetic rubber used in this study are: Diene 35 NFA/AC, FR-S 211, Stereon 702A and Kraton 1101. We also studied polystyrene as a reference since the above synthetic rubber are based on butadiene-styrene copolymer. These samples were obtained from Firestone Co., and they were studied as they were delivered by the manufacturer. Cleaning these commercial samples by dissolving them in toluene and then precipitating them by alcohol results in almost the same PAS signal as the noncleaned samples. The PAS spectrum of a fresh (unheated) sample was first recorded and stored as a blank (B) in the microprocessor memory. (B) was then subtracted from the spectrum of each heat-treated sample (S) to yield the net changes (S-B) in the heat-treated sample that might take place as a result of degradation. The microprocessor was then automatically normalized (S-B) against the carbon black reference spectrum (R) to give (S-B)/R signal.

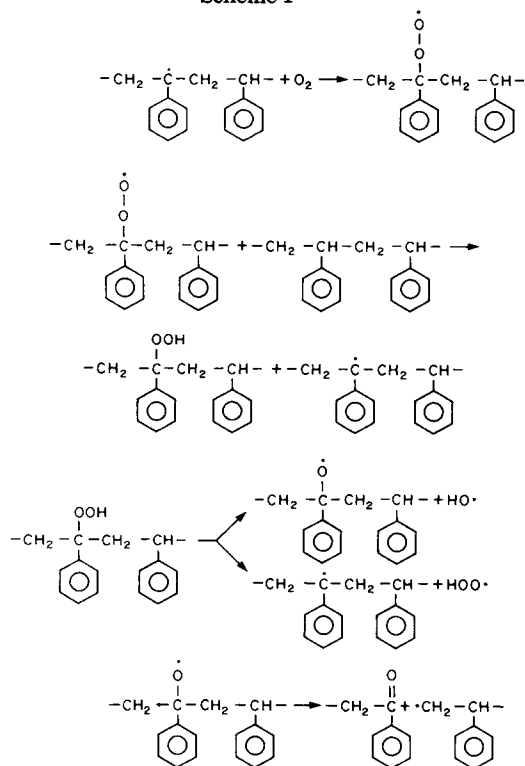
RESULTS AND DISCUSSION

During the exposure of polystyrene to heat at different temperatures in air, degraded polystyrene shows absorption in the UV range between 270 and 280 nm and between 350 and 400 nm. These two peaks are attributed to the formation of C=C in the polymeric chain and chain end carbonyl groups according to Scheme I²²:

However, exposing polystyrene to heat in inert atmosphere will lead to the formation C=C in the main polymeric chain. This effect will give rise to the UV absorption spectra in the range between 250 and 280 nm according to Scheme II:

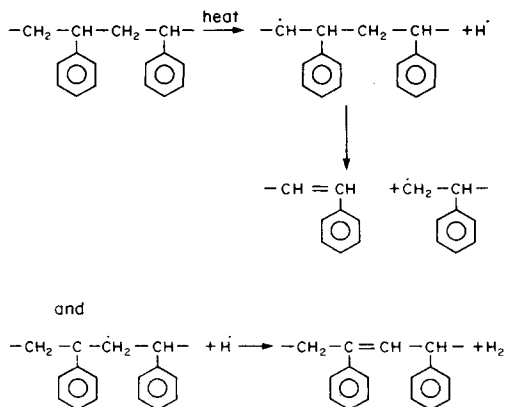
On the other hand, Diene 35 NFA/AC shows intense absorption spectra

Scheme 1



only in the far UV towards 200 nm. For unexposed samples, however, the UV spectra extend beyond 240–290 nm and are due to several different chromophoric groups along the polymeric chain. It is fairly well known that polybutadiene is susceptible to O₂ attack even at room temperature. This reaction is accelerated by heat and UV radiation. During the exposure of

Scheme 2



Scheme 3

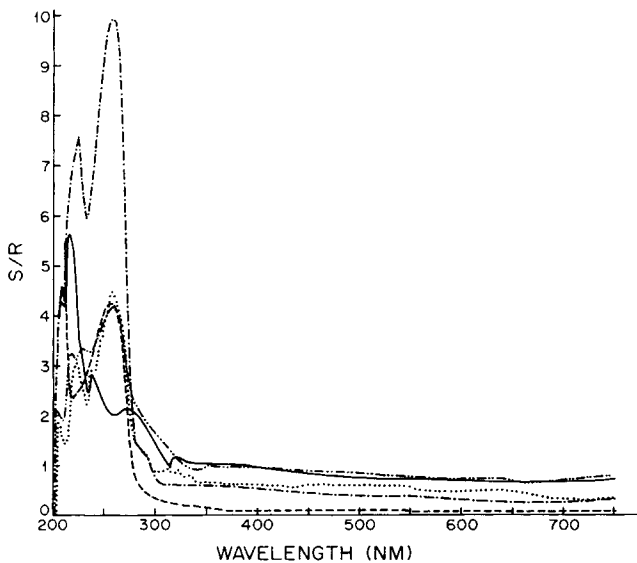
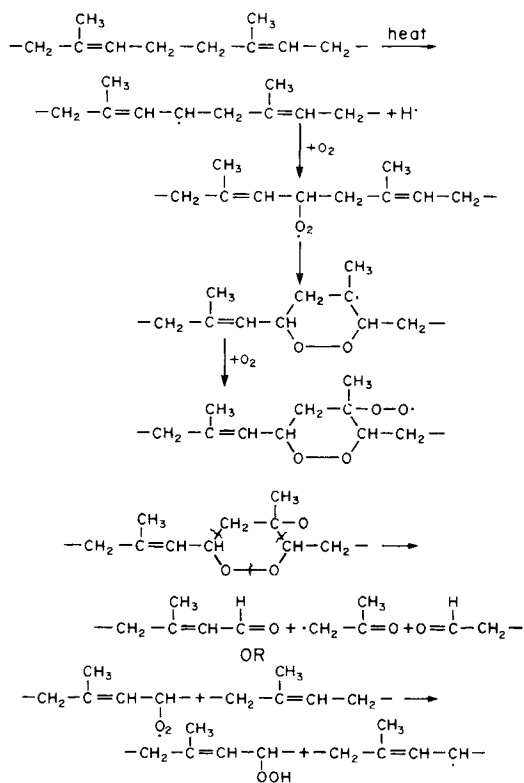


Fig. 1. PAS spectra of: (---) polystyrene; (—) diene; (— · — · —) FR-S; (· · ·) Stereon; (— · — · —) Kraton.

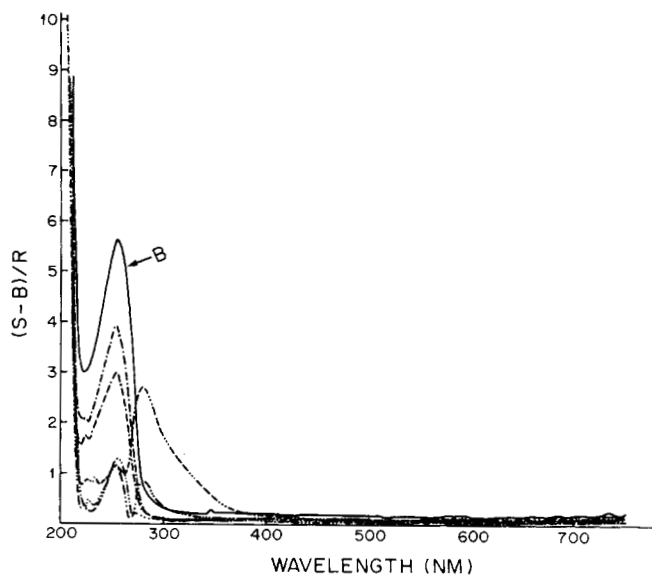


Fig. 2. PAS spectra of polystyrene heated at 170°C for the periods: (— · — · —) 5 min; (— · —) 15 min; (— · — · —) 30 min; (— · — · —) 1 h; (— · — · — · —) 3 h. The solid line curve B is PAS spectrum of the blank sample.

Diene to heat at different temperatures in air, hydroperoxides are generated. This leads to the formation of carbonyl groups with absorption band at about 290 nm. Furthermore, More²³ found two intensive absorption bands at 240 and 280 nm which were attributed to the formation of conjugated carbonyl groups. The mechanism of the reaction steps during thermal oxidation of polybutadiene is illustrated in Scheme III²⁴:

Figure 1 shows PAS spectra of polystyrene, Diene 35 NFA/AC, FR-S, 211,

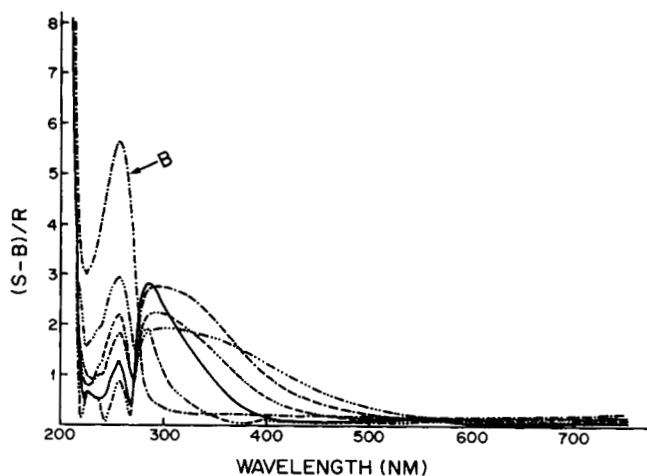


Fig. 3. PAS spectra of polystyrene heated at 200°C for the periods: (— · — · —) 5 min; (—) 15 min; (— · — · — · —) 30 min; (— · — · —) 60 min. The curve (— · —) B is the PAS spectrum of the blank sample.

Stereon, and Kraton 1101 as delivered by the manufacturer. From this figure, one can see that the PAS spectra of FRS-211, Stereon 702 A and Kraton 1101 are a combination of the two basic components: polybutadiene and polystyrene PAS bands.

Exposure of polystyrene to heat at 170°C for periods ranging from 5 min up to 3 h results in its degradation as shown in Figure 2. The PAS band at 260 nm, due to unexposed polystyrene, decreases dramatically, and a new PAS band at ≈ 280 nm with extended tail to 350 nm starts to develop with the exposure time. As explained before, the newly developed band is due to the formation of conjugated carbonyl structure within the polymer chain. Heating polystyrene at temperatures below 170°C for the same exposure periods give undetectable PAS signal due to degradation. However, exposing polystyrene to temperatures above 170°C shows a drastic increase of the PAS band at 280 nm as shown in Figure 3.

Since Diene rubber is susceptible to O_2 attack even at room temperature, as mentioned before, therefore exposure of Diene to almost any temperature results in its degradation. Figure 4 shows the PAS spectra of Diene rubber heated at 170°C for the exposure periods indicated on the figure. It is clear from Figures 2 and 4 that the rate of thermal degradation of Diene rubber is much faster than that of polystyrene under the same exposure conditions. In Figure 4 the PAS band at 290 nm, claimed by Moré²³ appeared after 5 min of heating at 170°C. However, for exposure periods above 5 min, a much broader PAS band appeared at ≈ 350 nm with shoulder at ≈ 400 nm and extended tail to ≈ 550 nm. This might be due to formation of crosslinked diene chains containing conjugated carbonyl structure which is responsible for the observed discoloration of the sample.

Although FR-S 211, Kraton 1101, and Stereon 702 are all synthetic rubbers based on butadiene-styrene copolymer, yet they differ in their com-

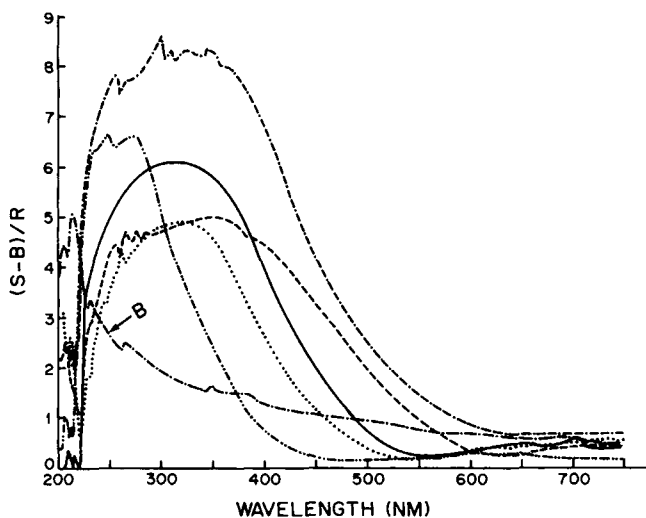


Fig. 4. PAS spectra of diene heated at 170°C for the periods: (—) 3 min; (· · ·) 5 min; (—) 15 min; (- - -) 30 min; (- · -) 2 h. The curve (---) B is the PAS spectrum of the blank sample.

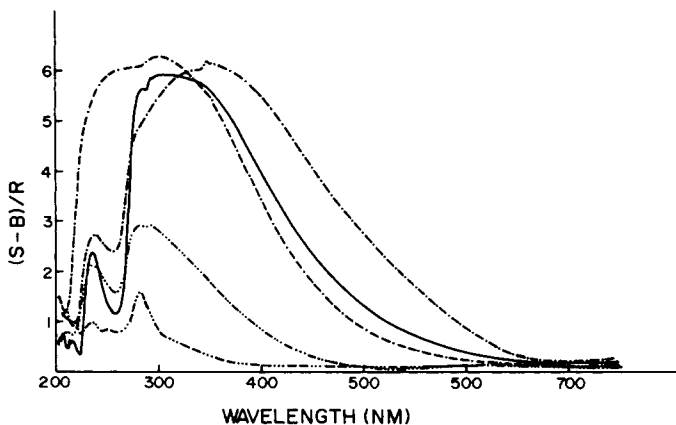


Fig. 5. PAS spectra of the following samples heated at 170°C for 30 min: (— · — · —) polystyrene; (— — — — —) diene; (— — —) FR-S; (— — —) Stereon; (—) Kraton.

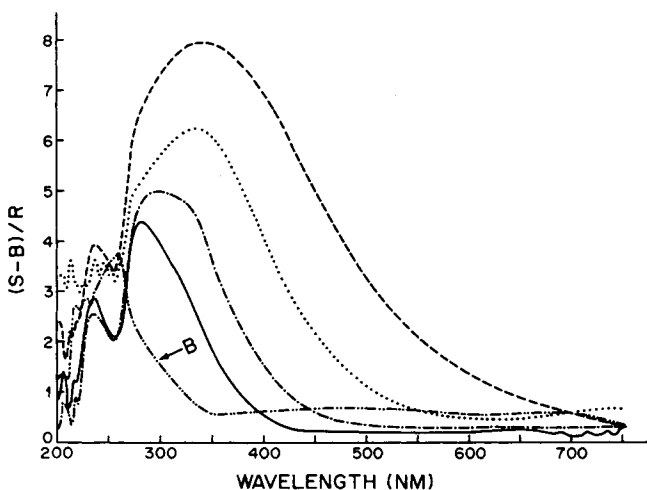


Fig. 6. PAS spectra of FR-S heated at 170°C for the periods: (—) 3 min; (— · —) 4 min; (· · ·) 5 min; (— — —) 15 min. The curve (— · · —) B is the PAS spectrum of the blank sample.

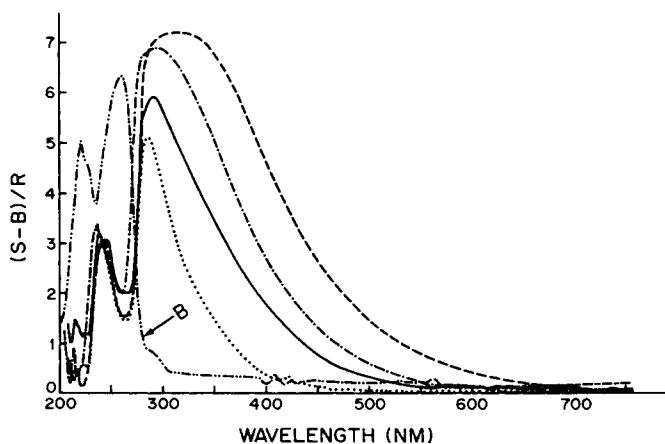


Fig. 7. PAS spectra of Kraton heated at 170°C for the periods: (· · ·) 2 min; (—) 5 min; (— · —) 15 min; (— — —) 30 min. The curve (— · · —) B is the PAS spectra of the blank sample.

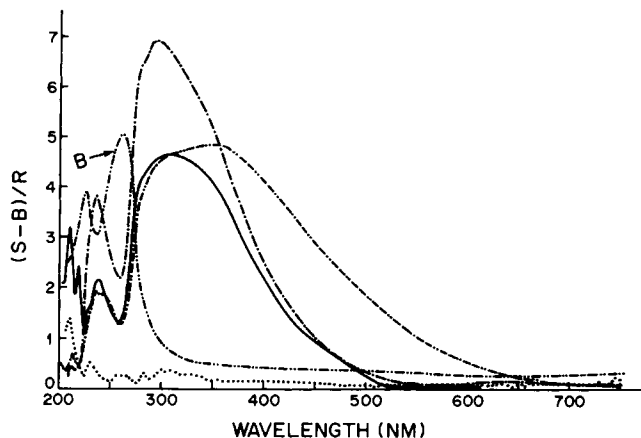


Fig. 8. PAS spectra of Stereon heated at 170°C for the periods (. . .) 5 min; (—) 10 min; (— · —) 15 min; (— · —) 30 min.

positions. For instance, FR-S is a random copolymer, Kraton is a block copolymer, and Stereon is an alternate copolymer. Therefore, their degradation rates are expected to be different. Figure 5 shows the PAS spectra of the above copolymers exposed to heat for 30 min at 170°C. It is clear from this figure that FR-S is more degradable than Kraton, and the latter is more degradable than Stereon. Since the ratio of butadiene to styrene in these copolymers is unknown, one cannot predict exactly the effect of heat on the composition. However, it might be that in the case of Stereon the diene unit of the polymer chain is protected by at least two styrene units from each side. Contrary to that in the case of FR-S and Kraton, there is a higher possibility of the butadiene unit in the main polymer chain being affected by heat with less chance of protection from styrene units as in the case of Stereon. These phenomena were noticed at a wide range of temperatures as evidenced from Figures 6–8.

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