# Evidence of Pyrene Formation in Butadiene–Styrene-Based Rubber Subjected to UV Irradiation

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## Synopsis

A strong pyrene emission was observed when certain block, alternate, and random butadiene–styrene-based rubber films were subjected to intense UV irradiation in vacuum. Weak or no pyrene emission was obtained from the same films when they are irradiated in the presence of $O_2$. A mechanistic scheme leading to pyrene formation in these samples is given together with qualitative explanation of the dependence of pyrene formation on sample composition.

## INTRODUCTION

Recently and in a series of articles Abu-Zeid et al.[1-6] investigated degradation of varieties of polymers using photoacoustic spectroscopy (PAS) technique. Among those polymers investigated were butadiene–styrene-based rubber.[7,8] Thermal degradation of those copolymers was studied as a function of composition, temperature, and heating periods. 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 thermal degradation of those synthetic rubbers were given together with a qualitative explanation of the relation between their composition and their thermal stabilities.

Accelerated weathering[7] of butadiene–styrene-based rubber, however, showed that this degradation is mainly due to the combined effects of UV and heat. Again, in this case, it was also found that the rate of their degradation to be solely dependent on their compositions.

The PAS spectra of all these synthetic polymers, at room temperature, show two strong bands. One band is between 200 and 235 nm and the other band is between 235 and 280 nm, the PAS bands of polystyrene and polybutadiene, respectively. The relative intensities of those two bands were found to be dependent on the relative composition of each sample. PAS spectra of those synthetic rubbers show no absorption bands in the range 300–350 nm, at room temperature, with the exception of FR-S 211 which shows a negligible absorption band in that range. As a result of that, one would expect to see no emission if these synthetic rubbers were excited with 337.1 nm wavelength. The 337.1 nm is a narrow line of the main $N_2$-laser beam and the possibility of the sample being excited in its 280 nm absorption band is remote. In this article we report pyrene formation when certain synthetic rubbers based on

CCC 0021-8995/87/020489-12$04.00

butadiene–styrene copolymers were excited with the main $N_2$-laser beam as evidenced from the observed emission spectra of those samples.

## EXPERIMENTAL

**Photoacoustic Spectrometer.** The photoacoustic spectrometer used in this experiment was discussed in earlier publications.[9-13] A 1000 W xenon lamp was used as a source of excitation. The lamp modulation frequency was 40 Hz. The exit slit of the monochromator was 2 mm at which the resolution of the spectrometer is 8 mm. 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 by Model U62-TMS 9900 Microprocessor and utilizes the capabilities of PAR Floppy Disk Model 6001/97.

**Emission Experiment.** A schematic diagram of the emission experiment used in this work is shown in Figure 1. Two excitation light sources were used. These two sources are: a 1-MW $N_2$-laser Model UV 24 with its tunable Dye Laser Model DL-II, from Molectron, and PRA Model ALH 220 xenon lamp. The setup is arranged in such a way that either light source could be used. For example, when using the main $N_2$-laser beam, the beam splitter is removed from the dye laser unit and the three mirrors $M_1$, $M_2$, and $M_3$ and the collimating lens are used. When using the dye laser beam, the $M_2$ mirror is removed and the collimating lens and the $M_3$ mirror are used. Finally when xenon lamp is used, $M_3$ mirror is removed, and the set of collimating and focusing lenses and mirrors shown in Figure 1 are used. A selecting wavelength monochromator, Kratos Model GM 252, must also be used with the xenon lamp.

Samples front surface excitation was used in this experiment in order to avoid reabsorption. Samples (which are in a form of thin films) were placed in a crystal holder obtained from Air Products and Chemicals Co. to ensure good thermal contact between them and the cooling finger of the closed-cycle helium refrigerator Model CSA-202 B (also from Air Products and Chemicals). Sample temperatures can be varied between 300 and 10 K. The temperature controllers and indicators used in this experiment are Air Products and Chemicals Models APD-G and APD-E.

The detection system is PAR optical multichannel analyzer (OMA 2) which consists of PAR Model: 1257 double intensified detector, 1216 detector controller, 1215 consol, and 1217 flexible disk drive. The monochromator used with OMA2 is McPherson 218 with interchangeable gratings. A collimating lens and an appropriate filler are placed in front of the entrance slit of the monochromator. The 1257 detector is placed on the exit slit of the monochromators as shown in Figure 1. The $N_2$-laser pulse repetition rate and the duration between pulses are controlled via Model 1216 detector controller. Finally we want to mention here that all the emission spectra shown in this article are not corrected for the response function of the instrument.

**Samples and Sample Preparation.** The commercial synthetic rubbers used in this study are FR-S 211, Stereon 702A, and Kraton 1101. These samples were obtained from Firestone Co., and all of them are based on
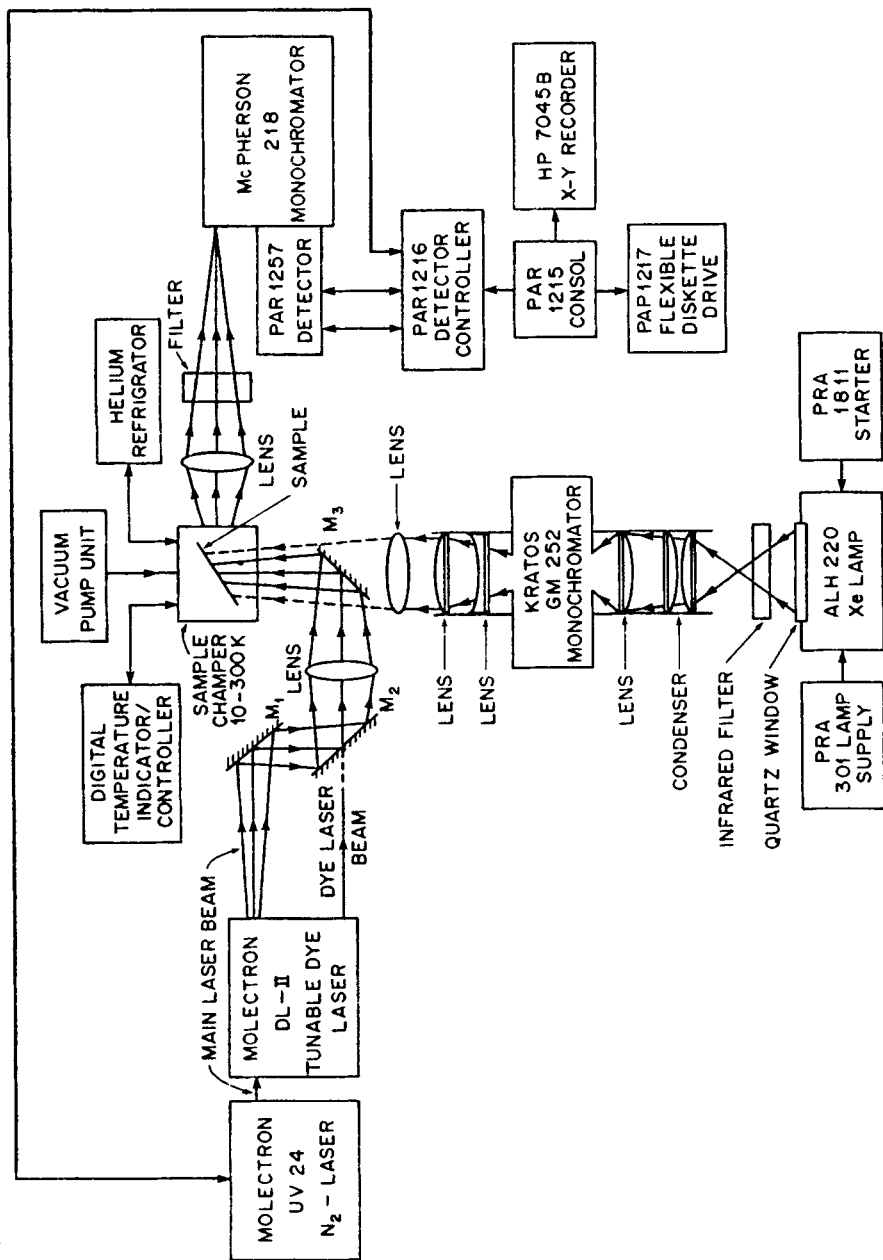
Fig. 1. Schematic diagram of the emission experiment.

butadiene–styrene copolymers. They differ only in their compositions. For instance, FR–S is a random copolymer, Kraton is a block copolymer, and Stereon is an alternate copolymer. Thin films of different thicknesses were made from the solution of these sample in toluene for use in this study.

## RESULTS AND DISCUSSION

Since Stereon, Kraton, and FR–S are all based on butadiene–styrene rubber, as mentioned before, any changes in their composition were found to be due to changes that take place within their constituents: polystyrene and polybutadiene. This fact is supported by our previous results which show that the mechanisms of the degradation of these synthetic rubbers are indeed a combination of the mechanisms of the degradation of polybutadiene and polystyrene considered separately.[7,8] For example, the PAS bands around 200 and 260 nm were found to be due to transitions in the benzene ring in the main chain of polystyrene part of the copolymers.[7] Exposing polystyrene films to different temperatures in air results in the formation of C=C in the polymeric chain and chain end carbonyl groups as evidenced from the developments of the two PAS bands between 270 and 280 nm and between 350 and 400 nm. Ranby and Rabek[14] showed that when polystyrene films are exposed to UV, the band between 270 and 280 nm increases with the exposure time and another band between 350 and 500 nm is developed.

Diene on the other hand can be easily attacked by $O_2$ especially at elevated temperature or when exposed to UV. Photooxidation of polybutadiene results in the formation of hydroperoxides and carbonyl groups with the strong PAS band in the near UV part of the spectrum.

No PAS bands other than those bands indicated above appeared in the spectrum of butadiene–styrene rubber. However, when those samples were excited with 337.1 nm wavelength from the main $N_2$-laser beam, peculiar emission was observed, especially when samples were excited under vacuum.

Figure 2 shows the uncorrected emission spectra of 0.33 mm thick film of Stereon at room temperature in air after being excited with the 337.1 nm wavelength. When the same film was excited with the same wavelength at room temperature while being under vacuum, the distinct emission spectrum of Figure 2 was obtained. This emission spectrum displays all the characteristic emission peaks of pyrene as evidenced from the emission spectrum of 0.01 g/L of pyrene in heptane shown also in Figure 2. For further confirmation of the formation of pyrene in the Stereon thin film as a result of its exposure to UV in vacuum, we introduced pyrene in a Stereon film by dissolving both pyrene and Stereon in toluene and then we made a thin film of the combined solution. The emission spectrum of this film (of thickness = 0.6 mm) is shown in Figure 3 at room temperature and in air. On the same figure, we showed also the emission spectrum of this film under vacuum at 300 and 10 K. It is clear from the spectra of Figure 3 that pyrene peaks become narrower and well resolved at low temperature* with the development of a broader band at the long wavelength portion of the spectrum which could be due to the formation of complexes.[15–17] For that reason we recorded in Figure 2 the

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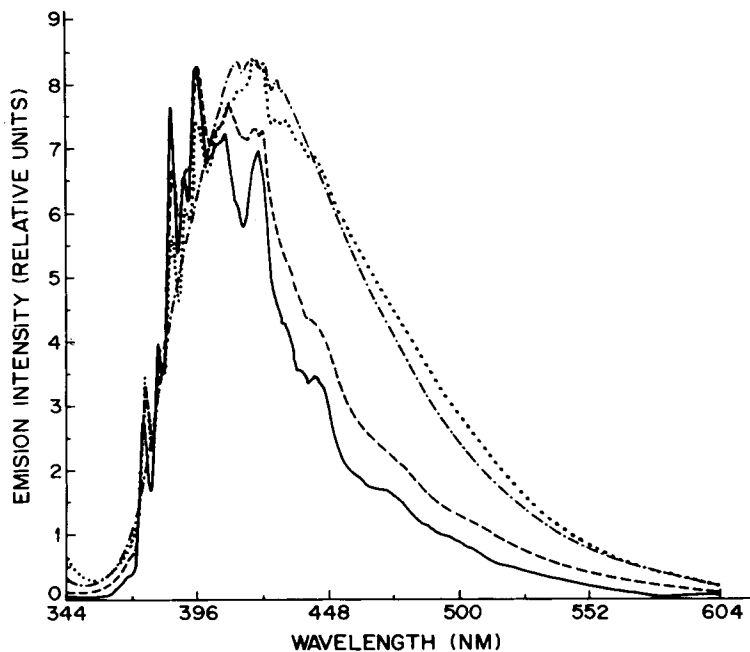*This effect is being confirmed through an experiment in our laboratory on laser line narrowing.

Fig. 2. Uncorrected emission spectra of 0.33 mm thick Stereon film excited with 337.1 nm wavelength: (– · –) at room temperature and in air; (– – –) at room temperature and in vacuum; ( · · · ) at 10 K; (———) the emission spectrum of 0.01 g/L of pyrene in heptane at room temperature.
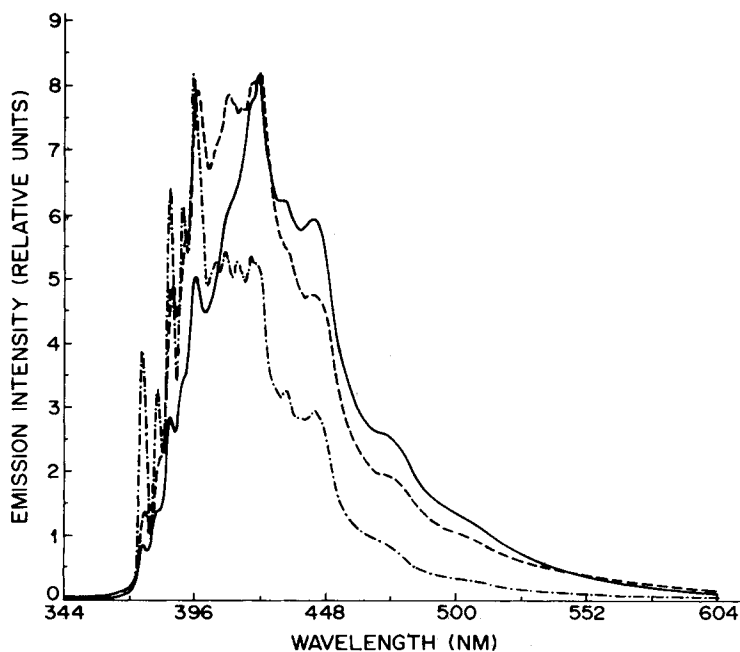


Fig. 3. Uncorrected emission spectra of 0.06 mm thick Stereon film containing pyrene after being excited with 337.1 nm wavelength; (———) at room temperature and in air; (– – –) at room temperature and in vacuum; (– · –) at 10 K.
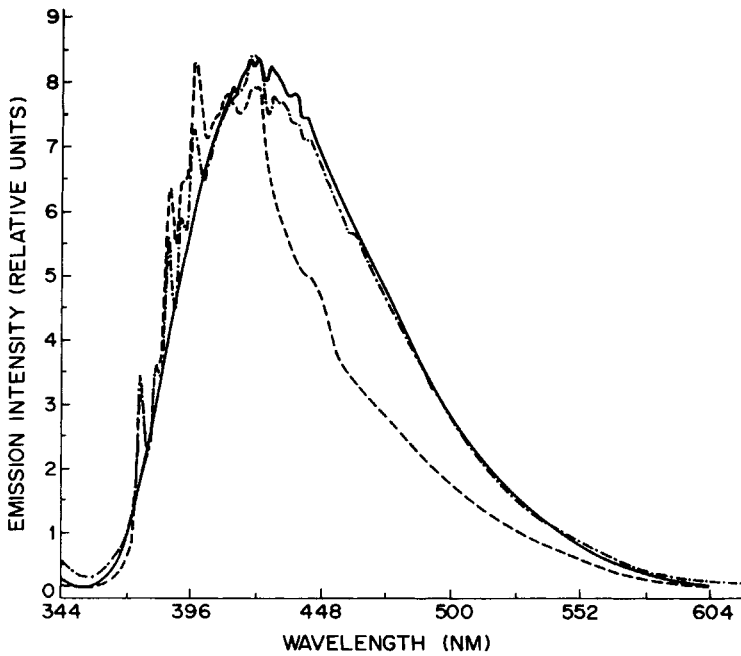
Fig. 4.  Uncorrected emission spectra of 0.16 mm thick Stereon film excited with 337.1 nm wavelength; (——) at room temperature and in air; (---) at room temperature and in vacuum; (-·-) at 10 K.
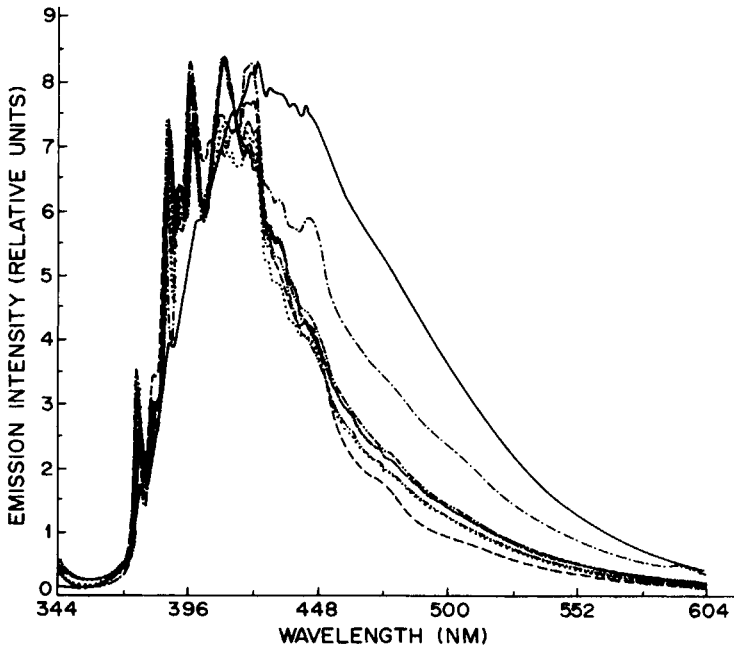


Fig. 5.  Uncorrected emission spectra of 0.06 mm thick Stereon film excited with 337.1 nm wavelength: (——) at room temperature and in air; (---) at room temperature and in vacuum; (-·-) at 10 K; (···) at 100 K; (---·---) at 150 K; (-----) at 200 K; (-····-) at 250 K; (--····--) at 285 K. All spectra were taken during the warmup of the sample from its lowest temperature (10 K).
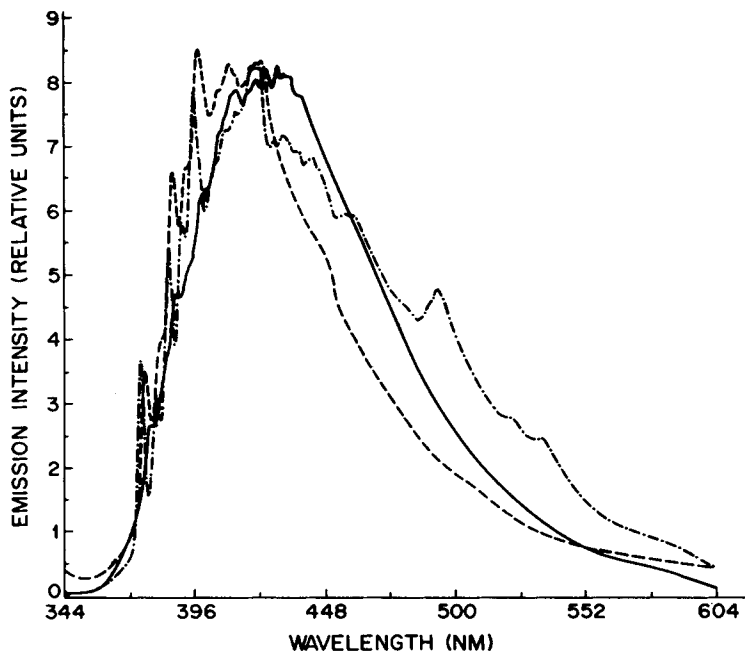
Fig. 6. Uncorrected emission spectra of 0.67 mm thick Kraton film excited with 337.1 nm wavelength: (——) at room temperature and in air; (---) at room temperature and in vacuum; (−·−) at 10 K.

emission spectrum of the 0.33 mm thick Stereon film at 10 K, and indeed the pyrene peaks become much better resolved than the same spectrum obtained under vacuum at room temperature.

We also investigated pyrene emission as a function of the thickness of the thin films. Figure 4 shows the emission from Stereon film of thickness 0.16 mm; in air at 300 K and in vacuum; at 300 K and 10 K. Comparing these spectra with the corresponding spectra of Figure 2, one notices that, although the general trend is the same, (i.e., one can observe only very weak pyrene emission at room temperature when Stereon is excited under atmospheric pressure, and pyrene peaks are much sharper and well resolved at 10 K than at 300 K in vacuum), the pyrene peaks in Figure 4 are relatively sharper and more intense than that of Figure 2. The emission spectrum of 0.06 mm thick film of Stereon is also shown in Figure 5. This is a relatively thin film, and one can easily recognize the peaks of pyrene emission spectrum, even at room temperature and under atmospheric pressure. The striking observation here is that the spectrum of this film under vacuum at 300 and 10 K are almost identical with the spectrum of low concentration of pyrene in heptane (see Fig. 2). Thus it seems that the thinner the film the better and neater the pyrene emission are.

Pyrene emission spectrum has also been observed when Kraton was excited with the main $N_2$ laser beam ($\lambda = 337.1$ nm) with almost the same trend observed in the case of stereon as demonstrated in Figures 6, 7, and 8, although in this case one can recognize the positions of the pyrene spectra at room temperature in the presence of air even in the case of 0.67 mm thick film.
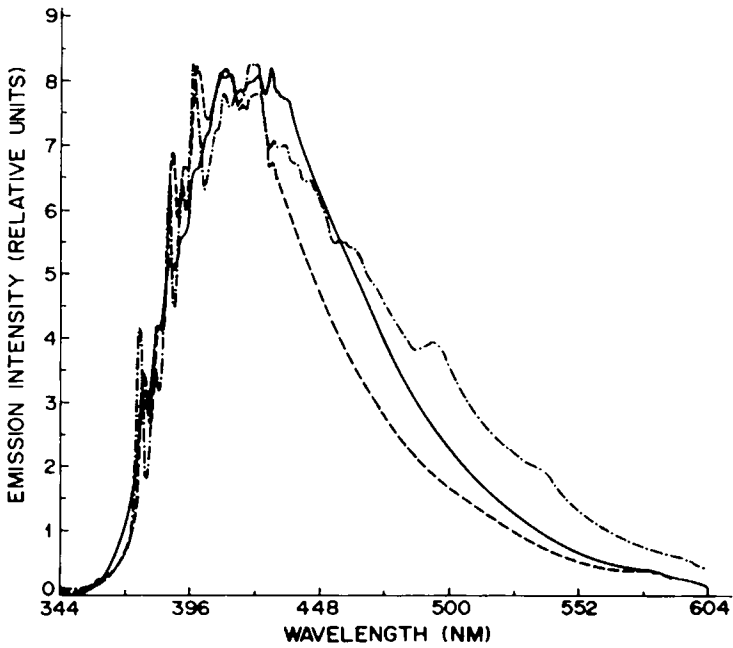
Fig. 7. Uncorrected emission spectra of 0.33 mm thick Kraton film excited with 337.1 nm wavelength: (——) at room temperature and in air; (– – –) at room temperature and in vacuum; (– · –) at 10 K.
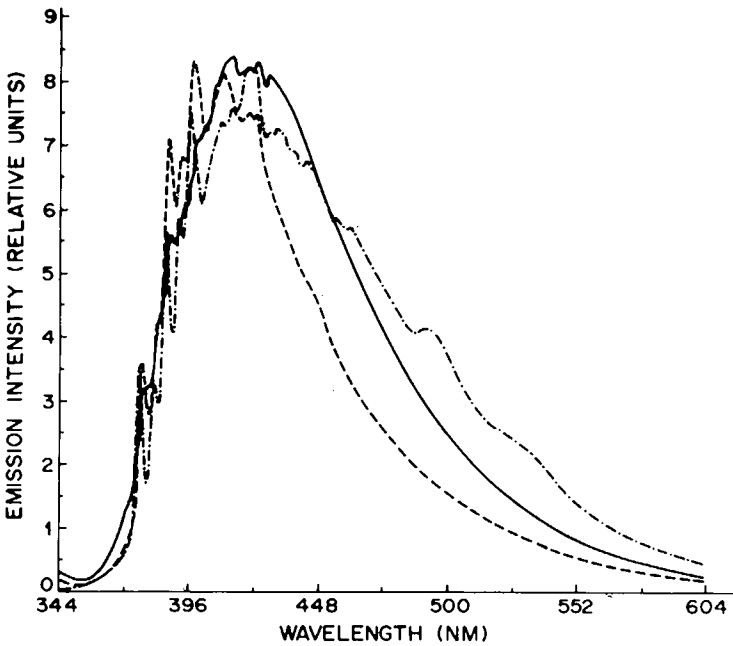


Fig. 8. Uncorrected emission spectra of 0.21 mm thick Kraton film excited with 337.1 nm wavelength: (——) at room temperature and in air; (– – –) at room temperature and in vacuum; (– · –) at 10 K.
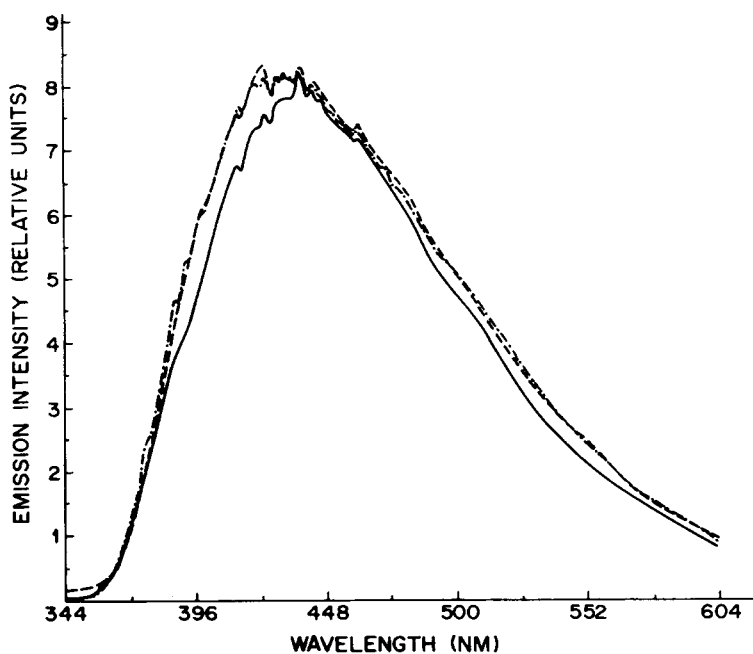
Fig. 9. Uncorrected emission spectra of 0.37 mm thick FR–S film excited with 337.1 nm wavelength: (——) at room temperature and in air; (---) at room temperature and in vacuum; (– · –) at 10 K.
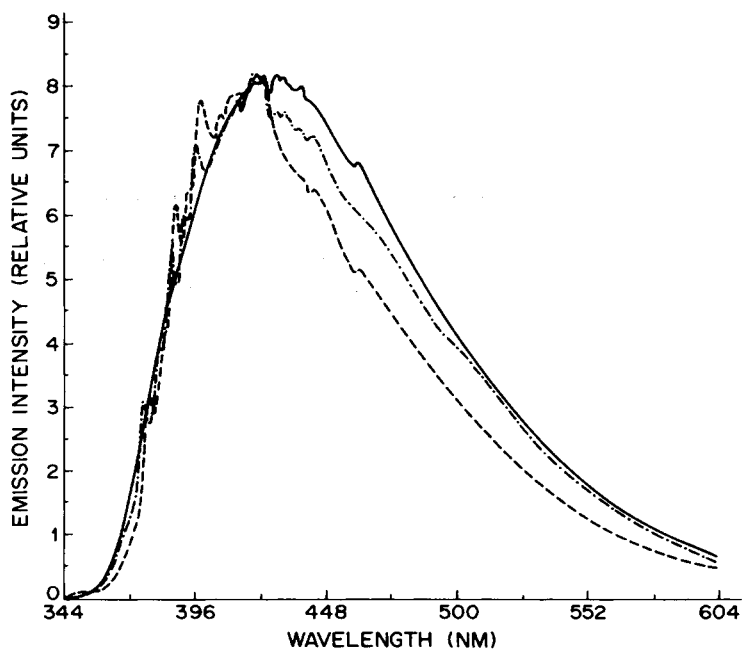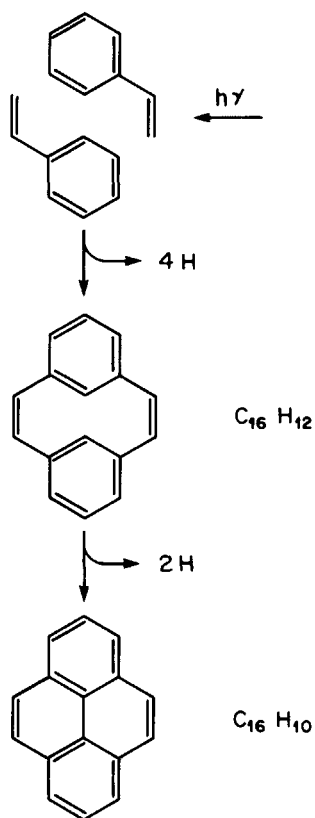


Fig. 10. Uncorrected emission spectra of 0.05 mm thick FR–S film excited with 337.1 nm wavelength: (——) at room temperature and in air; (---) at room temperature and in vacuum; (– · –) at 10 K.

Scheme 1.

For FR–S the situation was completely different. For example, we hardly could observe any pyrene emission from 0.37 mm thick film as is clear from Figure 9. Pyrene emission starts to appear for films of thicknesses < 0.05 mm in vacuum as indicated in Figure 10.

It is clear from the data presented here that pyrene is formed in all kinds of butadiene–styrene-based rubber used when subjected to UV irradiation such as the 337.1 nm wavelength of the main laser beam. The suggested mechanistic scheme leading to the formation of pyrene in these samples is shown in Scheme 1.

As a confirmation of pyrene formation, we took the spectrum of 0.06 mm thick stereon film and warmed it up from 10 K to room temperature. This is shown in Figure 5. As is shown in this figure the pyrene spectrum shows narrowing as the temperature rises, but it never ceases to exist even after we subject the sample to atmospheric pressure conditions. This means that once pyrene is formed inside the sample, it stays there, and this process is irreversible. For further confirmation that the developed peaks are due to pyrene, we carried out the following experiment: We excited our samples in vacuum with a wavelength that cannot be absorbed by pyrene (using Xe lamp, dye laser beam, or frequency doubling the dye laser beam), and no pyrene emission was observed.

There are two questions now that need to be tackled. The first question is: Why we do not observe pyrene emission when samples are excited at room temperature under atmospheric pressure especially for relatively thick films? In a previous article[8] we indicated that polybutadiene can be easily attacked by $O_2$ even at room temperature. This might lead to the formation of crosslinked diene chains containing conjugated carbonyl structures which have an absorption band around 350 nm with a shoulder around $\simeq$ 400 nm. This spectrum almost overlaps with the emission spectrum of pyrene which could result in radiative or nonradiative energy transfer[18,19] from pyrene to these species with almost the disappearance of emission from pyrene.

All butadiene–styrene-based rubber samples we used are almost transparent. When thin films are used, laser beam can easily penetrate through them, and the ratio of excited pyrene molecules to that of unexcited carbonyl group will be higher the thinner the film is. This is why, for relatively thin films, sometimes we can observe pyrene emission from samples excited in air. However, removal of $O_2$ prevents the formation of conjugated carbonyl groups, and reabsorption of pyrene emission is reduced to its minimum value.

The second question is: Why do we not observe any pyrene PAS absorption bands even for those pyrene films exposed to UV under vacuum for long time and their emission spectra clearly indicates pyrene formation? It turns out that pyrene has a high quantum yield,[20] and as a result its emission spectrum can be detected even for minute traces.[†] PAS signal, on the other hand, originates mainly from nonradiative processes that take place within the molecular energy levels of the sample. These processes compete with the radiative ones and as a result PAS spectrum of pyrene is expected to be negligible compared to that of polybutadiene or polystyrene molecules which have relatively low quantum yields.

As we mentioned before, although FR–S, Kraton and Stereon are all synthetic rubbers based on butadiene-styrene copolymer, yet they differ in their compositions. For example, FR–S is a random copolymer, Kraton is a block copolymer and Stereon is an alternate copolymer. This is why perhaps the rate of pyrene formation differs from one sample to another for films of the same thickness. For instance, it was found that FR–S exhibited the least tendency of all the copolymers to form pyrene when subjected to UV irradiation. In the case of Stereon, for every diene unit there are at least two styrene units on each side. These styrene units protect the diene from UV and at the same time can participate in pyrene formation. To the same extent, this is the case with Kraton where styrene blocks protect diene and participate in pyrene formation. FR–S is a random polymer and UV can attack easily diene and results in FR–S degradation. This is why perhaps FR–S has a relatively broader emission band than Kraton or Stereon, with less probability of pyrene formation.

[†] We were able to detect the emission of less than one part per $10^6$ parts by weight of pyrene in $n$-heptane at 10 K using 3371 Å laser line as the exciting wavelength.

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