

# Mechanical Degradation of PVC Films Monitored by Photoacoustic Spectroscopy\*

M. E. ABU-ZEID,<sup>†</sup> E. E. NOFAL, and L. A. TAHSEEN, *Department of Physics, University of Kuwait, Kuwait* and F. A. ABDUL-RASOUL, *Kuwait Institute for Scientific Research, Kuwait*

## Synopsis

PVC films were subjected to mechanical degradation at room and elevated temperatures and monitored by photoacoustic spectroscopy. Broken bonds in the main PVC chain result in the formation of "mechano-radicals," which in turn yield a zipper reaction and the formation of submicrocracks in the PVC samples. The mechanistic schemes based on the formation of the mechano-radicals are introduced and are successfully supported by the experimental results.

## INTRODUCTION

Fractures produced in varieties of solid polymers under tension have long been subjected to extensive investigation in order to understand their formations. Several models<sup>1-3</sup> have been introduced to explain the experimental results. These models together with other theoretical and experimental works were aiming towards understanding fractures on molecular levels. Unfortunately, due to several experimental constraints and due to the complication of the molecular structure of polymers in general, most of the research in this area can be considered as merely phenomenological in type. As a result, it seems that the formation of fractures in polymers is not clearly understood and that a lot of research is needed in order to facilitate the formation of a sound theoretical model based on experimental work free from any constraints.

In the past 20 years, various techniques were used to identify polymer degradations. These techniques are UV,<sup>4</sup> IR,<sup>5</sup> ESR,<sup>6</sup> EPR,<sup>7,8</sup> and, most recently, photoacoustic spectroscopy (PAS).<sup>9-12</sup> Of all these techniques, ESR and EPR were the only ones used for the study of mechanical degradation of certain polymers. This was because these two techniques could easily detect signals due to free radicals or unpaired electrons which are produced as a result of the rupture in polymers under suitable strains. The intensity of the ESR signal is proportional to the concentration of the free radicals and can be used to measure the relative number of free radicals formed as a result of broken bonds in the polymer main chain.

The first evidence for the formation of free radicals in polymers subjected to mechanical agitation was reported by Butyagin and his co-workers in early 1959.<sup>8</sup> Since then, several scientists<sup>1-3</sup> in different parts of the world

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<sup>†</sup> To whom correspondence should be addressed.

have carried out similar experiments which confirmed the work of Butyagin and his collaborators. Since these free radicals originated as a result of mechanical action, and in order to differentiate them from free radicals produced by other degradation processes, the term "mechano-radical" was used to mean free radicals produced by mechanical degradation.<sup>13</sup>

Although the work on mechano-radical carried out by various scientists revealed the original idea about their formation in some polymers such as PMMA, yet there were many experimental constraints in obtaining the information. One of the most difficult constraints was that the whole investigation had to be conducted under low temperature. No room temperature data have been reported that can throw some light on the mechanism of mechanical degradation of polymers. This is quite important since, in practical situations, mechanical degradation of polymers takes place at room and elevated temperatures. This article will be the first in a series of articles which will examine this problem using a different experimental approach that could lead to a realistic model of polymer rupture mechanism. We present here the first evidence of mechanical degradation of PVC monitored at room and elevated temperatures. No sample preparation or modification are required in this experiment, and the use of room and elevated temperatures enabled us to simulate the actual degradation in practical life.

## EXPERIMENTAL

### Photoacoustic Spectrometer

The photoacoustic spectrometer used in this experiment was described in detail in earlier publications.<sup>14,15</sup> A 1000-W xenon lamp was used as a source of excitation at 40 Hz modulation frequency. Air was used as coupling medium and carbon black was used as a reference (*R*) against which all the spectra were normalized. The exit slit of the monochromator was 2 mm in width at which the resolution of the spectrometer is 8 nm. The equipment is completely controlled and operated by a microprocessor.

The spectrum of a fresh non-creeped sample was taken as the blank (*B*). (*B*) was then subtracted from the spectrum of each creeped sample (*S*) to yield the net changes (*S-B*) in the creeped sample that might take place as a result of mechanical degradation. (*S-B*) was then normalized against (*R*) to give (*S-B*)/*R*.

### Samples and Sample Preparations

Commercial PVC powder was dissolved in cyclohexanone at 50°C for 24 h. The PVC was then precipitated by adding the PVC solution dropwise to methanol. The resulting PVC powder was washed several times by methanol and dried in a vacuum oven. This purified powder was once more dissolved in pure cyclohexanone to form a film 5 cm long, 1 cm in width, and 0.1 cm in thickness.

The PVC films were elongated by 20%, 40%, 60%, 80%, and 100% of their original length using the system shown in Figure 1. The samples were kept under load for 3 h after reaching the desired elongation at normal and elevated temperatures. Another set of PVC films were left under load

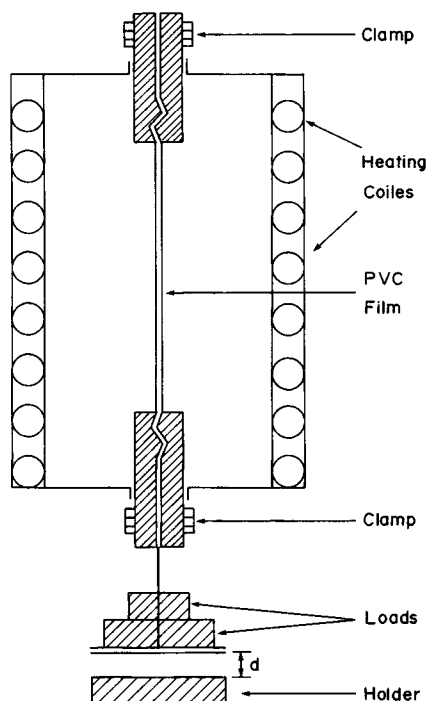


Fig. 1. Shows the system used to creep the PVC films in order to increase their lengths by the programmed distance  $d$ .

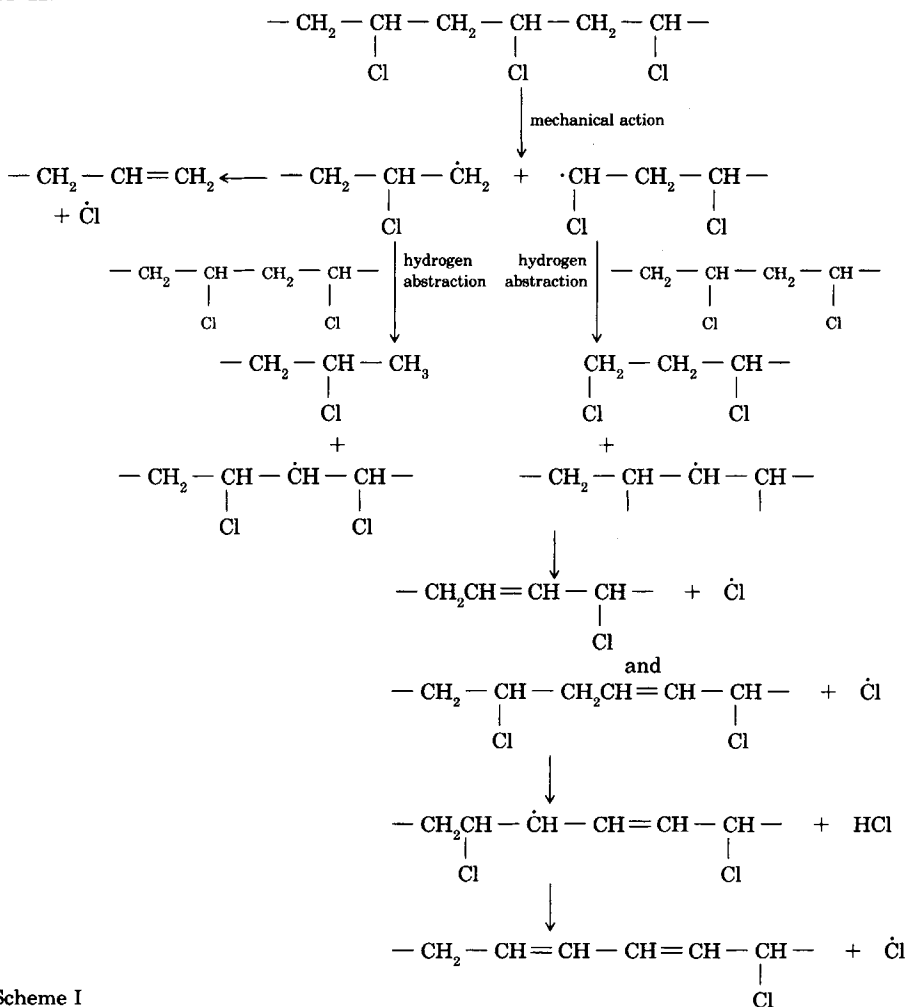
until the cutoffs occurred. A set of samples was prepared in each case and kept in a dark, dry container for further investigation. The elongation of the samples was monitored by measuring the length of the samples at different periods.

Three identical samples of dimension  $0.3 \times 0.5$  cm were cut from three different positions of the film, two from the terminals and the third from the middle. Three photoacoustic spectra (PAS) were recorded for the three samples and the average value of the PAS was recorded. In the case of cutoff, two samples were taken at the edge of rupture from both sides, and the PAS spectra were averaged for both samples. We should also mention here that the loads used were 3 kg in the case of the PVC film crept at room temperature, and 2 kg in the case of the PVC film crept at elevated temperature.

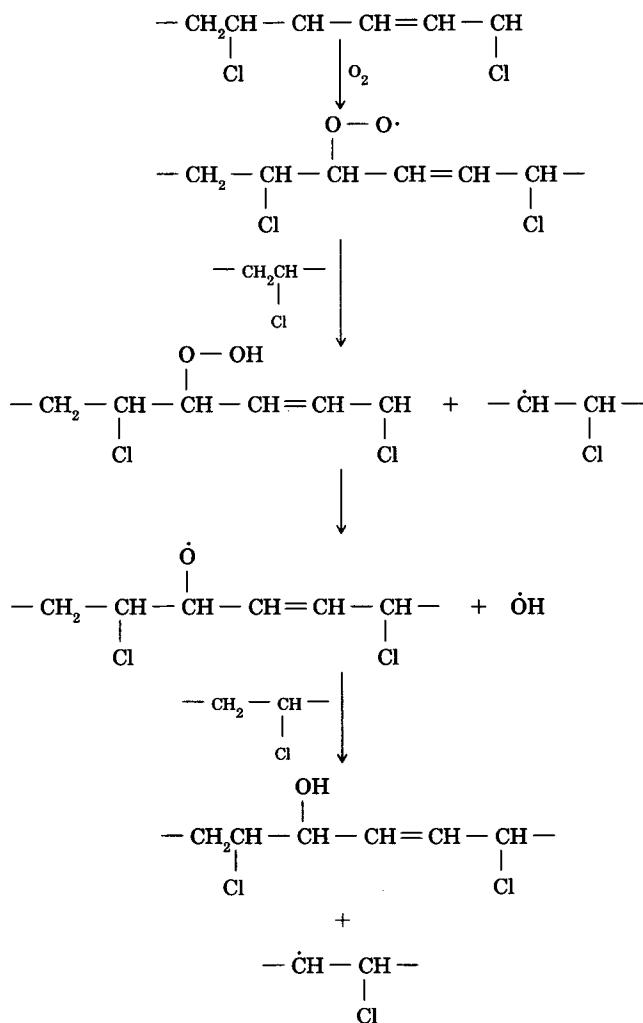
## RESULTS AND DISCUSSION

There are two main models used in studying the formation of mechano-radicals produced by large deformation of solid polymers. The first model is due to Peterlin.<sup>1</sup> This model, although simple and useful, can only be applied in the case of crystalline polymers. Since the polymer we are using in this experiment is PVC and X-ray analysis reveals it to be amorphous, the Peterlin model is of no use to us. The amorphous nature of PVC has also been confirmed by other scientists.<sup>16</sup> The second model, which is a general one, was introduced first by Zhurkhov and co-workers<sup>2</sup> and later developed by Kausch.<sup>3</sup>

In the second model, the formation of submicrocracks are initiated by broken bonds. The highly stressed molecule in the main polymer chain is broken first to form two end radicals. These end radicals abstract hydrogen from the nearest macromolecules in the polymer main chain and form stable ends. As a result of abstracting hydrogen from neighboring molecules, unpaired electrons exist at those particular sites of the molecular chains, which in their turn abstract hydrogen from their neighboring molecules and convert into stable ends, and so forth. During this zipper microcrack formation, free radicals are formed which can be detected by ESR technique. The concentration of the broken ends can be determined by IR. Zhurkov et al.<sup>2</sup> have estimated that for each microcrack, there are on the average 1000 stable ends in solid polymer under stress. Therefore, one may conclude from Zhurkov's model that once solid polymer is stressed, mechanical degradation could be initiated due to the formation of what is called mechano-radicals. Using Zhurkov's model, one can safely assume that when a PVC film is subjected to mechanical creep, mechano-radicals are formed which lead to its degradation in accordance with the mechanistic schemes I and/or II:



Scheme I



Scheme II

Figure 2 shows the PAS spectra of PVC under load that results in elongations of 20%, 40%, 60%, 80%, and 100% of its original length. It also includes the PAS spectra of the PVC sample at the cutoff point. All these spectra were measured at room temperature (25°C) and 5 min storing time after reaching the desired elongation. The drastic increase in the absorption spectra at the short wavelength  $\sim 230$  nm is due to the fact that C—C conjugated bond sequences are produced due to PVC mechanical degradation as per scheme I. The concentration of C—C conjugated bonds was increased by increasing elongation percentage. It reaches its maximum at the cutoff point. Furthermore, since PVC film was creeped in air atmosphere; it is expected therefore that the mechano-radicals produced might be scavenged by  $\text{O}_2$  (scheme II). This would lead to the formation of carbonyl and/or hydroxyl groups on the conjugated system. This effect was shown clearly in PAS spectra at 260 nm and to a certain extent at  $\sim 310$  nm wavelength. Figure 2 also shows a broad absorption band between 400 and

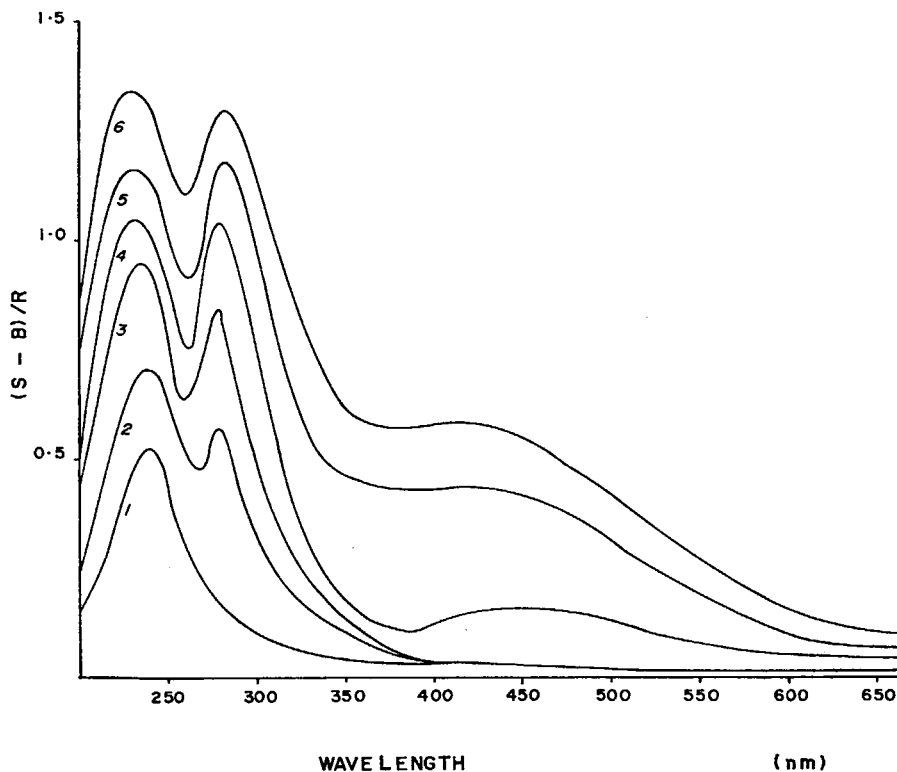


Fig. 2. Photoacoustic spectra of PVC films under load which resulted in the elongations 20% (1), 40% (2), 60% (3), 80% (4), and 100% (5) of the original lengths. Curve 6 represents the PAS spectra of a broken film. All spectra were measured immediately after reaching the desired elongation, and PVC film creep was done at room temperature.

500 nm, which is the more pronounced the higher the percentage of the film elongations. These are shown in curves 4–6 of the figure. This band is also assigned to the formation of the C—C conjugated bond sequence. Again the number of the formed C—C conjugated bond sequences is proportional to the percentage of the film elongations.

Since the degradation of PVC involves radical formation, it will lead to dehydrochlorination. As a result of that, the mechanism of PVC degradation is a zipper-type reaction, as mentioned previously. Therefore, one might expect that the degradation of PVC increases with the storage time. This is clearly shown in Figures 3–6. It is well known that the elimination of each subsequent HCl molecule from the macroradicals (mechano-radicals) produces a gain in conjugation energy of the residual chain.<sup>17</sup> This results in a decrease in the activation energy for the next dehydrochlorination step and the polyene chain is easily formed. This leads to a shift in the PAS absorption spectra of the mechanically degraded PVC from ~230 nm to ~260 nm, where it is amalgamated with C—O peak at ~310 nm as indicated clearly in curve 6 of Figure 3, curves 4–6 of Figure 4, and curves 3–6 of Figure 5 and 6.

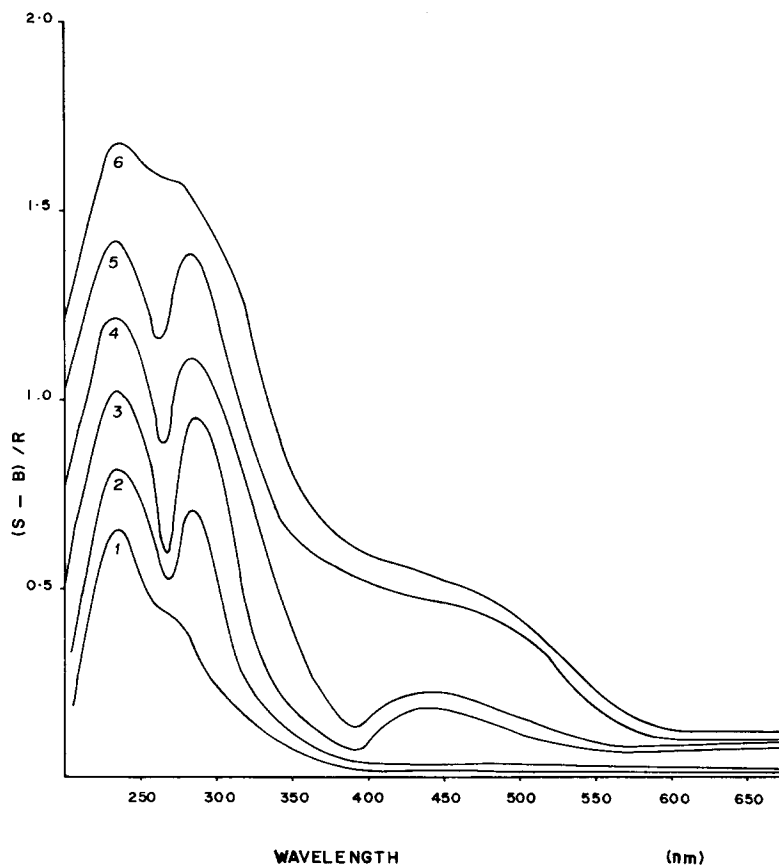


Fig. 3. Photoacoustic spectra of the PVC films of Figure 2 after one day storing time.

The broad absorption band between 400 and 500 nm was assigned to C—C conjugated bond sequence, as mentioned before. This is due to the formation of yellow coloration which requires a minimum of seven conjugated C—C bonds in a sequence. It was found that this yellow coloration increases with both elongation percentage and storing time as indicated by the relative increase in PAS absorption in wavelength region between 400 and 500 nm (see Figs. 3–5).

Similarly a combination of heat at 80°C and simultaneous 40% creep showed similar effects as a result of degradation (see Fig. 7). It is worth mentioning here that the rate of thermal degradation is higher than the rate of mechanical degradation. Therefore, the thermal degradation effects are much more pronounced in this case. Details of the thermal degradation of PVC was discussed by the authors in a previous publications.<sup>12</sup>

In conclusion, it was found that mechanical degradation of PVC can be successfully explained based on the formation of mechano-radicals, as per our schemes I and II. PAS was proved to be a very useful technique in the area of polymer creep which leads to mechanical degradation at room and elevated temperatures, in contrast to other conventional spectroscopic tech-

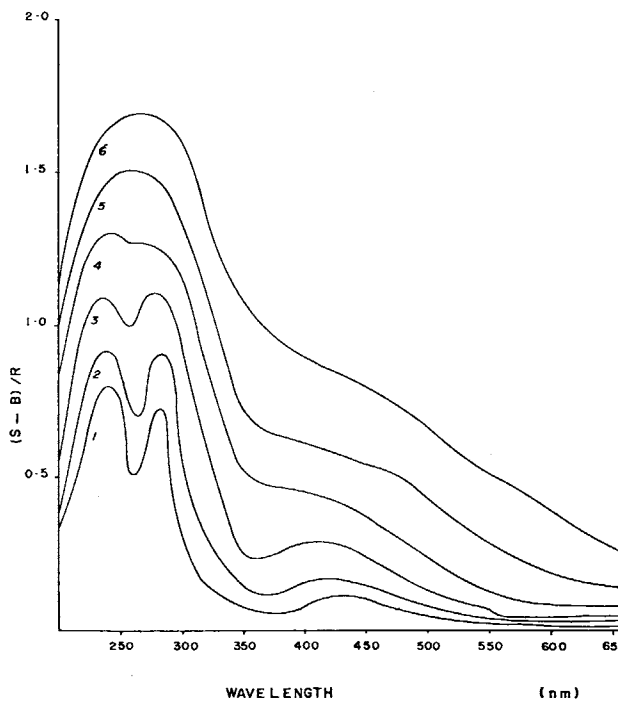


Fig. 4. Photoacoustic spectra of the PVC films of Figure 2 after 7 days storing time.

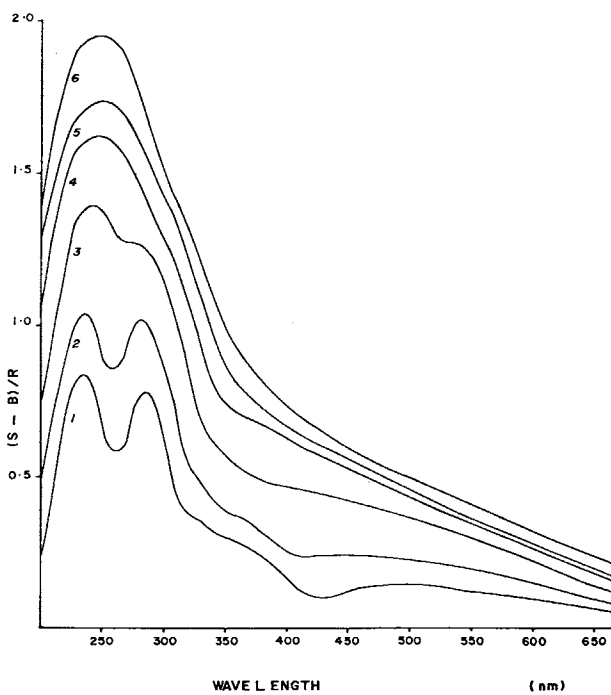


Fig. 5. Photoacoustic spectra of the PVC films of Figure 2 after 15 days storing time.



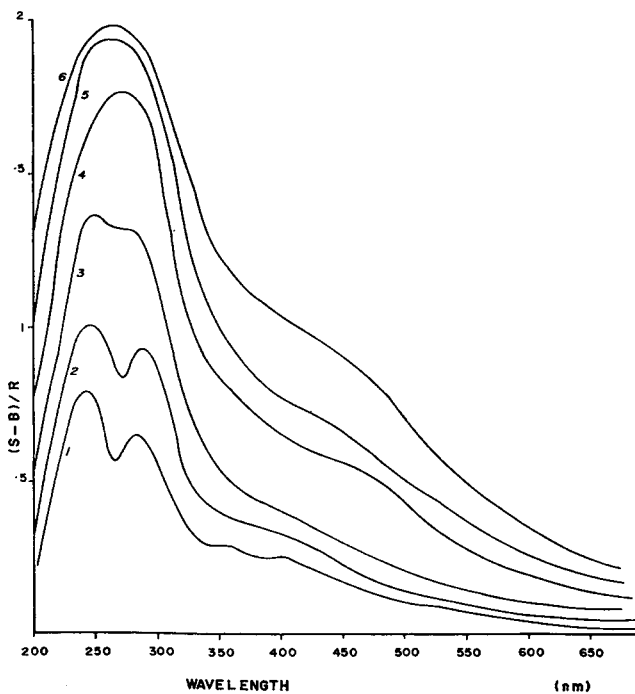


Fig. 6. Photoacoustic spectra of the PVC films of Figure 2 after 30 days storing time.

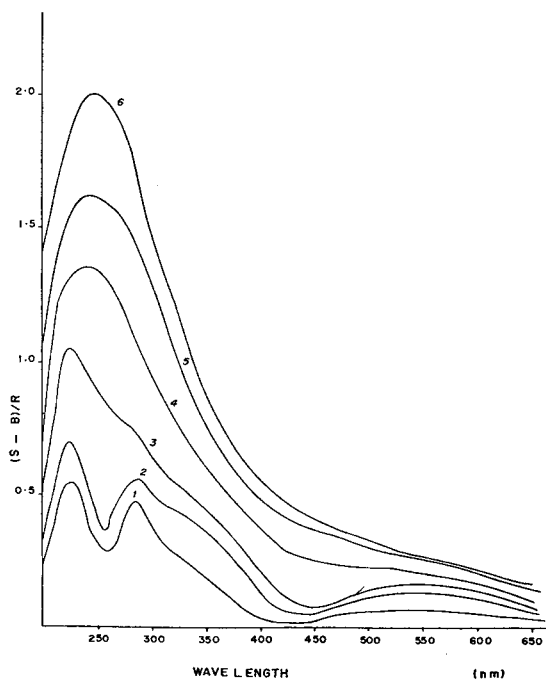


Fig. 7. Photoacoustic spectra of a PVC film elongated 40% of its original length at 80°C after the following storing times: immediately (1), one day (2), 4 days (3), 7 days (4), 15 days (5), and 30 days (6).

niques. The models of the formation of mechano-radicals have been developed by several authors.<sup>1-3</sup> We feel that these new studies will add additional information to the previous studies. We will next attempt, in this series of studies, to obtain direct information on the mechano-radical at room temperature for life loading of the PVC and other commercial polymers.

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