

# Accelerated Degradation of Poly(vinyl Chloride) (PVC) Monitored by Photoacoustic Spectroscopy\*

M. E. ABU-ZEID, E. E. NOFAL, M. A. MARAFI, and L. A. TAHSEEN,  
*Department of Physics, University of Kuwait, Kuwait, F. A. ABDUL-RASOUL, Kuwait Institute for Scientific Research, Kuwait, Kuwait, and A. LEDWITH, Department of Inorganic, Physical and Industrial Chemistry, Donnan Laboratories, The University of Liverpool, Great Britain*

## Synopsis

Poly(vinyl chloride) film shows substantial changes in its photoacoustic absorption spectra (PAS) on either irradiation or heating in the presence of O<sub>2</sub> or N<sub>2</sub>. These spectral changes are due to the conjugation structures and carbonyl (group formation), formed during photo- and thermal degradation. In this paper interpretations of the PAS and of the decomposition mechanism of PVC are presented.

## INTRODUCTION

The wide application of poly(vinyl chloride) (PVC) as a construction material in building and machine industries required stability for several years.<sup>1</sup> PVC suppliers are stepping up their development of improved materials for outdoor applications, and processors are applying window-frame extrusion technology for a growing range of construction elements.<sup>2</sup> It is very important to check the role of different external factors, such as thermal and photochemical degradation of solid PVC. It is well known that ultraviolet irradiation of PVC causes formation of conjugated polyene structures, chain degradation, and crosslinking.<sup>3-10</sup> During this reaction hydrogen chloride is formed and the polymer samples become colored, gradually turning to reddish-brown. The reactions mentioned above are considered to follow free radical mechanism. The mechanism of formation of conjugated polyene structures was explained by Rabek et al.<sup>1</sup> Furthermore, it is worth mentioning that since PVC contains only C—C, C—H, and C—Cl bonds, it is expected that PVC should not absorb UV light of wavelength longer than 190 nm. Measurements of UV absorption spectra of PVC show an increased rapid absorption below 220 nm and a low absorption at 320 nm.<sup>3</sup> The observation that free radicals are formed by either UV irradiation at a wavelength of 250 nm or heat at 70°C indicates the presence of some kinds of chromophores.<sup>1</sup> Also, small quantities of external impurities which were not removed in the purification process may be responsible for the absorption of light above 190 nm. The most probable chromophores present in PVC are carbonyl groups distributed randomly and in small amounts on PVC chain.<sup>1,3</sup> This chromophore may have been formed during the polymerization process in the presence of air. Rabek and Ranby<sup>1,3</sup> suggested that extremely small amounts of carbonyl groups (e.g., one carbonyl group

\* This research is supported by Kuwait University Research Council Grant No. SP 015.

for 100–1000 mers) could be responsible for a photoinitiation process through the triplet state level of the carbonyl group.

Several conventional spectroscopic techniques<sup>1–3</sup> have been used for the study of PVC degradation. Although these techniques yield useful information, they are subjected to many technical constraints which limit their applicability to the study of PVC degradation. For example, completely opaque or transparent samples cannot be used with conventional absorption spectrometers for obvious reasons. Also most of the conventional spectrometer signals could be distorted by light reflection and light scattering. All these inconvenient factors and others have been eliminated in our experiments through the use of the photoacoustic spectroscopy (PAS) technique.

The basic principle of PAS is that when a modulated light beam falls over a sample, part of it is absorbed by the molecules of the sample. The light absorbed is then dissipated either radiatively or nonradiatively. The nonradiative part is emitted from the sample surface in a form of heat pulses of the same frequency as those of the modulation frequency of the incident light beam. These pulses then cause a vibration in a column of gas between the sample and a sensitive microphone. The microphone detects these vibrations whose amplitude is proportional to the power of the light absorbed by the sample.

The theoretical and experimental background of PAS has been worked out by several scientists. This technique besides having several advantages over conventional spectroscopic techniques, as mentioned before, is less expensive, faster, and more accurate than most of the other spectroscopic techniques. We found PAS technique to be very useful not only in the study of polymer degradation,<sup>11,12</sup> but for many other applications.<sup>13–16</sup>

## EXPERIMENTAL

**Sample and Sample Preparation.** Pure powder PVC were dissolved in dioxane and from the solution a thin film (thickness 0.5 mm) was prepared at 50°C. In preparing such a thin film, special precautions were taken to prevent air bubbles from being trapped inside the film. These air bubbles could produce a non-PVC photoacoustic signal specially when operating our spectrometer at low modulation frequencies. The thin film was then kept in a vacuum oven at the same temperature of 50°C to complete its dryness.

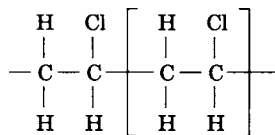
Identical samples whose dimensions are  $2 \times 3 \times 0.5$  mm were prepared from the thin film. These samples were then heated in a calibrated oven for a period of 15 min, in groups of three samples at a time, at the following temperatures: 60°C, 80°C, 100°C, 100°C, and 200°C. The heat-treated samples were stored in light tight dry containers for further use in our experiment. Other samples were heated and stored in the same way as mentioned before but in gases other than air in order to study the effect of these gases on the process of PVC thermal degradation.

For photodegradation a Spectra-Physics CW Ar<sup>+</sup> Laser Model 171 was used. The PVC samples were exposed to the 335 nm laser beam whose cross-section area is 12.6 mm<sup>2</sup> and its power is 40 mW. The exposure periods were 1, 2, 3, 4, or 5 min. A specially designed cell container was used to facilitate sample irradiation in the presence of gases other than air as will be indicated later.

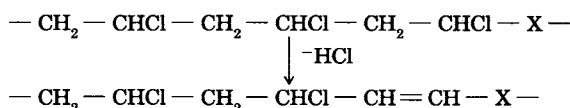
**Photoacoustic Spectrometer.** The photoacoustic spectrometer used in this work was discussed in detail in earlier publications.<sup>11-16</sup> The excitation source is a 1000 W xenon lamp. Any variation in the lamp intensity is automatically compensated for by a pyroelectric detector. The spectral range of the equipment is from 200 to 2600 nm. The xenon lamp can be modulated at any frequency between 10 Hz and 2 K Hz. The optimum modulation frequency for the spectrometer is 40 Hz. This is the frequency at which our experiment was performed. The scanning rate of the spectrometer could vary from one to 200 nm/min. The exit slit of the scanning monochromator is 2 mm in width, which results in a resolution of 8 nm. The sample cell is made of high quality quartz and accepts samples of size 5 × 8 × 2 mm in liquid or solid phases. Air was used as a coupling media between the sample and the microphone. The equipment is completely controlled and runs by a Model U62-TMS 9900 Microprocessor and utilizes the capabilities of PAR Floppy Disk Model 6001/97. Carbon black was used as reference (R) against which all spectra were normalized. A fresh nonexposed sample was used as a blank (B) and its PAS spectrum was subtracted from all the spectra of the exposed samples (S).

## DISCUSSION

If PVC in reality did correspond to the idealized concept of regular repeating units such as

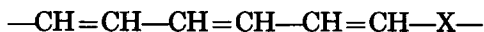


and nothing else, it would be expected to be a polymer of remarkable inherent stability, as evidenced by thermogravimetric analysis and other studies made on similar low-molecular-weight model compounds such as 1, 3, 5-trichlorohexane.<sup>17,18</sup> The fact that the commercial PVC does not perform in a manner as predicted by the model system led investigators to examine other model systems representative of the various end groups illustrated, as well as other possible structures that might logically be expected to be present in PVC. These studies have shown that internal allylic chlorides are the least stable (most susceptible to replacement) of all the groups examined, followed in order by tertiary chlorides, terminal allylic chlorides and secondary chlorides.<sup>19</sup> From this and from other evidence, it is postulated that the degradation of PVC is due initially to a loss of hydrogen chloride, which commences at a site on the molecule either containing a or adjacent to a tertiary or allylic chloride atom, either of which can function as an activating group as follows:

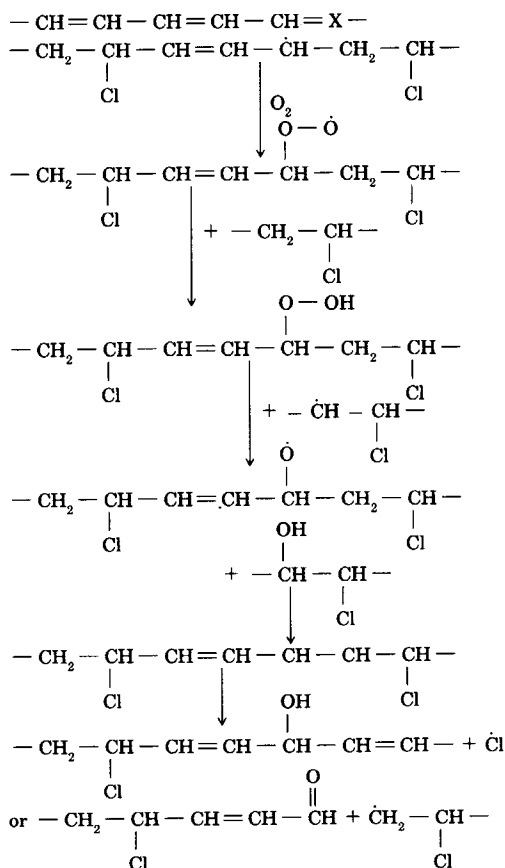


where X indicates the activating group.

The elimination of the first molecule of hydrogen chloride and the subsequent formation of an unsaturated double bond on the PVC chain then activates the neighboring chlorine atom, which is now structurally located as an allylic chlorine, and thus facilitates the subsequent elimination of another hydrogen chloride molecule, with the process continuing to repeat itself. This progressive dehydrochlorination proceeds quite rapidly, soon leading to a chain segment of polyunsaturation as follows:



**Thermal Degradation of PVC.** The general mechanism of the thermal degradation of PVC is illustrated in the above equations. The photoacoustic absorption spectra of PVC samples heated for 15 min in air at temperatures 60°C, 80°C, 100°C, and 150°C are shown in Figure 1. The polymer films were stored in air for 3 h before the PAS were taken. The dramatic increase in the absorption at the short wavelength is due to the carbon-carbon conjugated bond sequence. Furthermore, since the pvc samples were heated in air, the possibility of formation carbonyl and/or hydroxyl groups on conjugated system is very likely. This effect was shown in PAS at 260 nm and at 300–320 nm. The following equation expresses this mechanism very clearly.



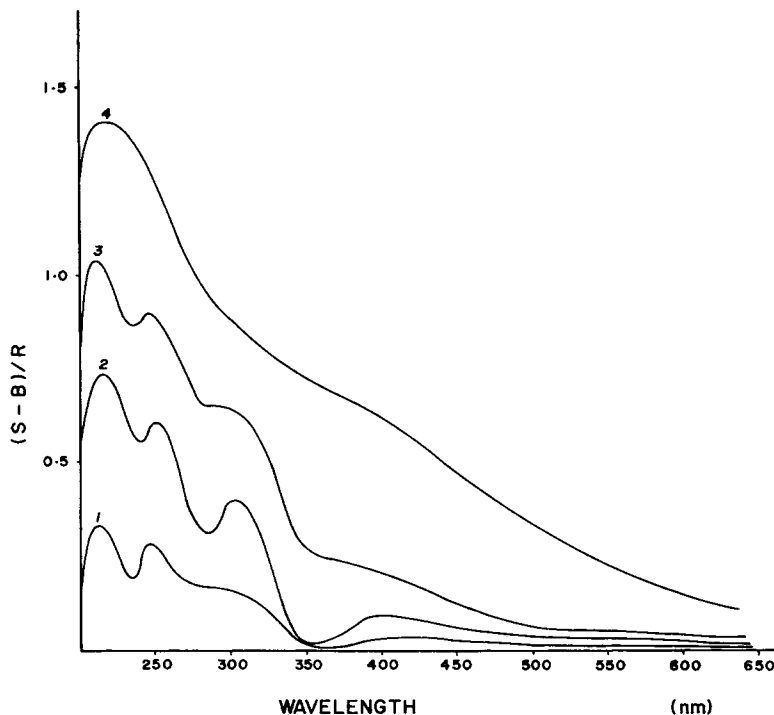


Fig. 1. PAS spectra of PVC samples heated in air for 15 min at 60°C (1), 80°C (2), 100°C (3), and 150°C (4) and stored for 3 h in air before recording their spectra.

Furthermore, due to yellow coloration, an absorption in PAS at 400–500 nm was also recognized, and it was increased by raising the temperature due to increased formation of conjugation.

Figure 2 shows the effect of storing time on PAS absorption. This figure proved that the dehydrochlorination is a "zipper"-type reaction. The yellow coloration requires a minimum of seven conjugated double bonds in sequence. The PAS absorption maxima moves towards larger wavelengths with increasing number of conjugated double bonds.<sup>20,21</sup> This is very typical since the elimination of each subsequent HCl molecule from the micro radical leads to a gain in conjugation energy of the residual chain. This results in a decrease in the activation energy of the next dehydrochlorination step, and the polyene chain is easily formed. The above reasons could be ascribed to the shift in the PAS absorption of thermally degraded PVC towards longer wavelengths, as was shown in Figures 1 and 2, respectively.

The effect of oxygen on the thermal degradation of PVC was also studied. Samples of PVC which were heated in a N<sub>2</sub> atmosphere and stored in N<sub>2</sub> for 5 min up to 15 days show only typical absorption of the conjugated double bands sequences, and the shift towards the visible region is due to the increased number of conjugation (Fig. 3). However, for PVC samples heated in N<sub>2</sub> stored in O<sub>2</sub>, PAS spectra show very clearly the formation of carbonyl and/or hydroxyl groups absorption at wavelength 300–350 nm. It was noticed from the comparison of Figures 2 and 3 that the PAS absorption

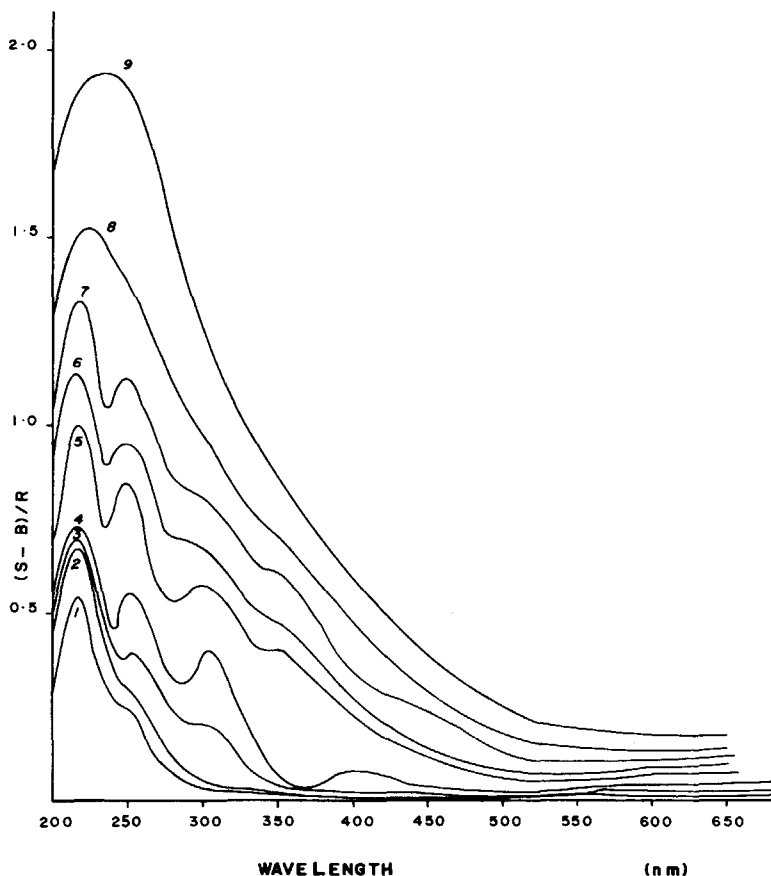


Fig. 2. PAS of PVC heated at 80°C for 15 min in air. The storing periods in air before measuring each spectrum are: (1) 5 min; (2) 1 h; (3) 2 h; (4) 3 h; (5) 10 h; (6) 40 h; (7) 70 h; (8) 150 h; (9) 300 h.

of thermally degraded PVC stored under  $O_2$  atmosphere shows absorption at wavelengths 220 nm and 260 nm. These peaks might be referred to the formation of conjugated carbonyl groups. However, the PAS of PVC samples heated in a  $N_2$  atmosphere and stored in  $N_2$  (Fig. 3) show an absorption at wavelength 245 nm which might be attributed to the formation of carbon-carbon conjugated bond sequence. On the other hand, storing of PVC samples, which were heated in  $N_2$  atmosphere, in  $O_2$  will not cause a change in the PAS absorption at the short wavelength (245 nm) but another peak was formed at wavelength 300–350 nm, which might be related to the carbonyl group formation.

**Photochemical Degradation of PVC.** During UV irradiation of PVC, degradation processes take place, (Figs. 4 and 5). In addition, hydrogen chloride and conjugated polymers are formed. The dehydrochlorination reaction changes the PAS absorption spectrum of PVC. The formation of conjugated polymer structure is responsible for coloration of PVC and can be explained by the following mechanism:



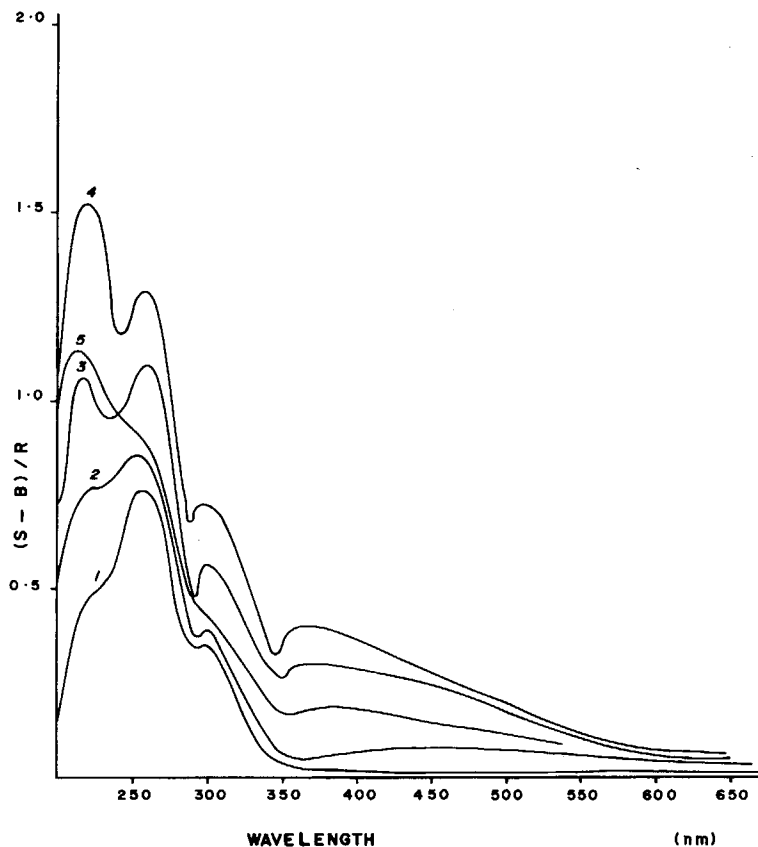
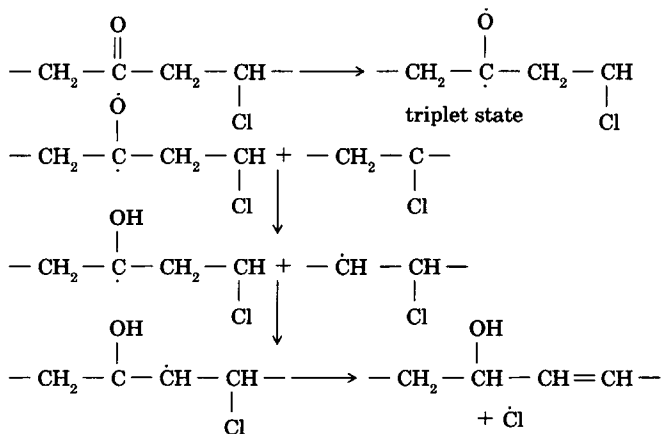
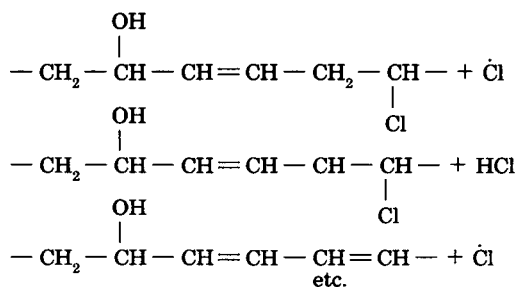


Fig. 4. Effect of UV irradiation on PVC. Samples were exposed to UV for the following periods: (1) 1 min; (2) 2 min; (3) 3 min; (4) 4 min; (5) 5 min (as explained in the text). Each PAS spectrum was measured 3 h after irradiation with UV.

triplet state easily abstracts hydrogen atoms from neighboring molecules as indicated by the following mechanism:







This mechanism explains the rapid formation of conjugated double bonds and of polyenyl radicals during UV irradiation of PVC.

In the presence of  $\text{O}_2$ , peroxy radicals are formed rapidly, and this reaction in the solid state is a diffusion-controlled process. Hydroperoxide groups

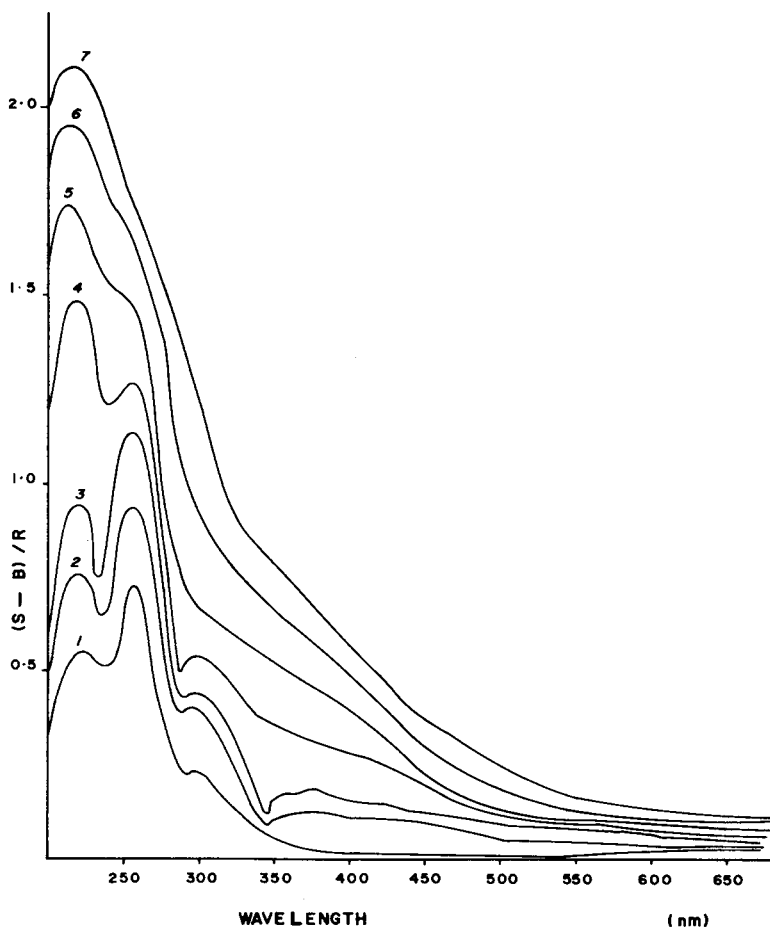
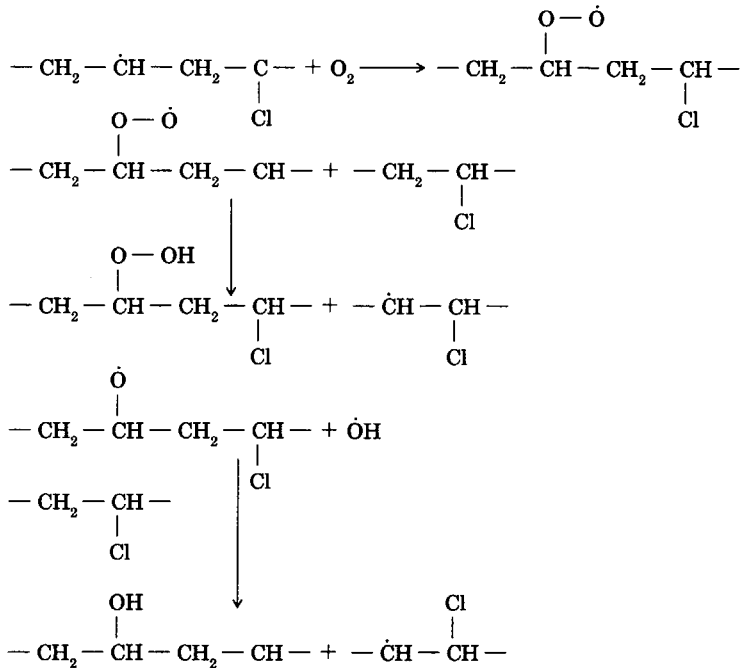
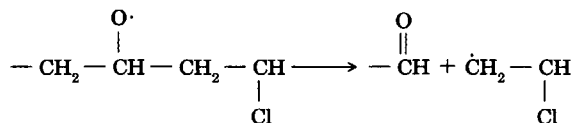


Fig. 5. PAS spectra of UV irradiated PVC for 4 min. The storing periods before measuring each spectrum are: (1) 5 min; (2) 30 min; (3) 60 min; (4) 3 h; (5) 24 h; (6) 100 h; (7) 150 h.

can only be formed in the presence of air by addition of molecular oxygen, and hydrogen abstraction (thermal and photochemical):



For prolonged UV irradiation or heating carbonyl group was formed which gives IR absorption at  $1740 \text{ cm}^{-1}$ : The photoacoustic absorption spectra of PVC films irradiated by a Spectra-Physics  $\text{Ar}^+$  laser at wavelength 335 nm in air for 1,2,3,4 and 5 min are shown in Figure 4. The polymer films were stored for 3 h before the PAS were measured. Two peaks at wavelengths 220 and 260 nm were observed which might be attributed to the carbon-carbon conjugated bond sequence and carbonyl and/or hydroxyl groups on conjugated systems. It was noticed that these peaks increased by increasing the irradiation time as well as the storage time (Fig. 5). Another peak at wavelength 300–320 nm was observed which was attributed to the formation of carbonyl and/or hydroxyl groups. Furthermore, an extended tail in PAS absorption at wavelength 400–500 nm was drastically shifted to the visible region due to an increase in number of conjugation by irradiation time and storage time (Figs. 4 and 5). However, for PVC samples irradiated by the same UV source in  $\text{N}_2$  atmosphere and stored in  $\text{N}_2$  for 1–30 days, the PAS absorption spectra show peaks at wavelength of 225 nm which might be due to pure carbon-carbon conjugated bond sequence. Also an extended tail up to 500 nm was observed (Fig. 6).



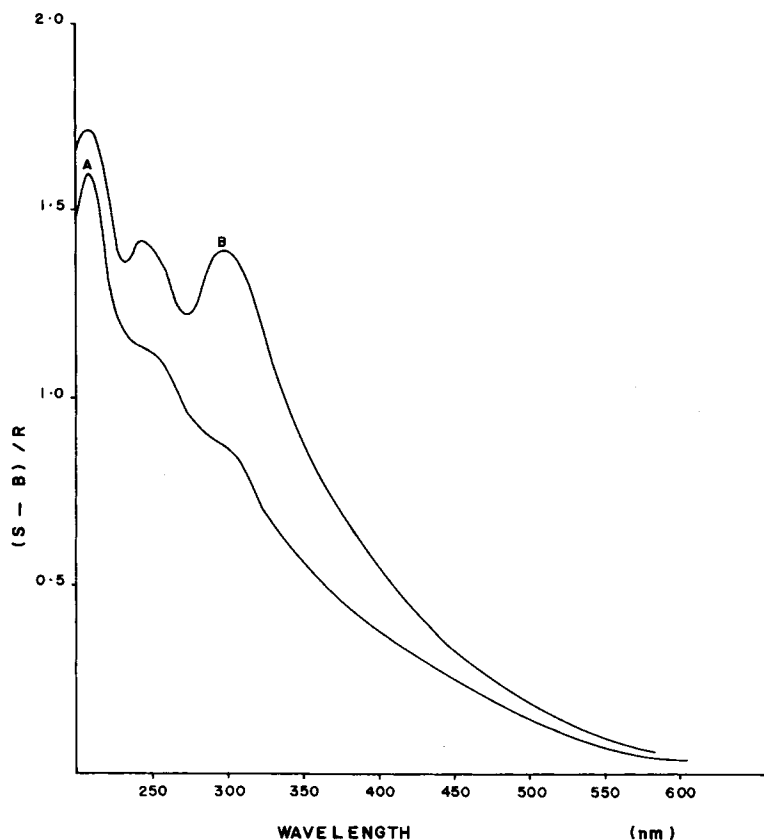


Fig. 6. PAS spectra of UV irradiated PVC for 4 min in  $N_2$  atmosphere, and stored for 360 h in  $N_2$  atmosphere (A) and  $O_2$  atmosphere (B).

On the other hand changing the storage medium from  $N_2$  to  $O_2$  causes an absorption in PAS at wavelength 300–320 nm (Fig. 6). Furthermore, another peak at 260 nm starts to appear after 7 days of storing in both  $N_2$  and  $O_2$ , but it is more pronounced in  $O_2$  atmosphere.

It was noticed also from the comparison of Figures 2 and 5 that the peak at 220 nm for the thermally degraded PVC samples is more pronounced and stronger than the same peak for the photochemically degraded PVC samples. However, the peak at 260 nm for the photochemically degraded sample became less strong by increasing the storage time (Fig. 5). This might be attributed to the formation of different decomposition species in both cases.

### References

1. J. F. Rabek, G. Canback, J. Lucky, and B. Ranby, *J. Polymn. Sci., Polym. Chem. Ed.*, **14**, 1447 (1976).
2. *PVC Moves into New Outdoor Applications*, Anomance, Modern Plastics International, March 1981.
3. B. Ranby and J. F. Rabek, *Photodegradation, Photo Oxidation and Photostabilization of polymers*, Wiley, New York, London, 1975.

4. W. H. Gibb and R. I. MacCallum, *Eur. Polym. J.*, **7**, 1231 (1971).
5. W. H. Gibb and R. I. MacCallum, *Eur. Polym. J.*, **8**, 1223 (1972).
6. W. H. Gibb and R. I. MacCallum, *Eur. Polym. J.*, **9**, 771 (1973).
7. W. H. Gibb and R. I. MacCallum, *Eur. Polym. J.*, **10**, 529 (1974).
8. K. P. S. Kwei, *J. Polym. Sci., A-1*, **7**, 237 (1969).
9. K. P. S. Kwei, *J. Polym. Sci., A-1*, **7**, 1075 (1969).
10. M. R. Kamal, M. M. El-Kaissy, and M. M. Avedesian, *J. Appl. Polym. Sci.*, **16**, 83 (1972).
11. M. E. Abu-Zeid, N. A. Marafi, E. E. Nofal, and A. A. Anani, *J. Photochem.*, **18**, 347 (1982).
12. M. E. Abu-Zeid, E. E. Nofal, F. A. Abdul-Rasoul, M. A. Marafi, G. S. Mahmoud, and A. Ledwith, *J. Appl. Polym. Sci.*, **28**, 2317 (1983).
13. M. E. Abu-Zeid, G. S. Mahmoud, A. A. Anani, A. F. Halasa, and A. A. Mobasher, *J. Photochem.*, **16**, 279 (1981).
14. M. E. Abu-Zeid, M. A. Abu-Elgheit, G. S. Mahmoud, and M. A. Marafi, *J. Photochem.*, **18**, 277 (1982).
15. N. M. Moussa, A. Laham, M. S. El-Ezaby, N. Al-Salem, M. E. Abu-Zeid, G. S. Mahmoud, A. Kabarity, and S. Mazrooei, *J. Inorg. Biochem.*, **17**, 185 (1982).
16. S. S. Issa and M. E. Abu-Zeid, *SEPARATUM-IMEKO 9th World Congr.* **5**, 141 (1982).
17. J. H. P. Standing, *Plast. Progr.*, **9**, 15 (1953).
18. H. V. Smith, *J. Rubber Int. Plast.*, **138**, 966 (1960).
19. M. Asahina and M. Onozuka, *J. Polym. Sci., A2*, 3505 (1964).
20. F. Sondheimer, D. A. Ben-Efraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).
21. B. Ranby, J. F. Rabek, and G. Canback, *J. Macromol. Sci. Chem.*, **A12(4)**, 587 (1978).

Received May 13, 1983

Accepted December 15, 1983