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Spectroscopic Study of the Photodegradation Pathways of Silver-Backed Polyacrylonitrile Films

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ABSTRACT: Ultraviolet radiation in the regions $266 \leq \lambda \leq 400$ nm and $250 \leq \lambda \leq 400$ nm has been employed to study the oxidative photodegradation pathways for silver-backed polyacrylonitrile film. Measurements based on Fourier transform infrared reflection absorbance (FTIR–RA) spectroscopy were supported by electron paramagnetic resonance (EPR) studies. Isotopic ^{13}CN PAN was used to confirm some photodegradation products. Upon irradiation at wavelengths below 266 nm the polymer turns yellowish-brown and also increases in electrical conductivity, suggesting the presence of a chromophore system of the type $(>C{=}N-)_n$.

Introduction

Protective films have been used recently for photovoltaic solar energy conversion systems.[1-3] In particular, polymers have been applied to protect metallic surfaces from exposure to environmental degradation.[4-8] The photodegradation of the polymeric films remains an obstacle and the selection of the photostabilizers and photoinhibitors[9] is extremely dependent on the type of degradation, e.g., oxidative or nonoxidative. Therefore, an understanding of the photodegradation mechanisms of aluminum- or silver-backed polyacrylonitrile (PAN) films is important for their effective utilization in solar energy systems. There have been numerous studies of the thermal degradation and the mechanism of color formation in PAN (solid or liquid), of which several recent publications[10-15] are representative. However, there are a limited number of investigations[16,17] of the UV photodegradation of this polymer. Burlant et al.[18] studied the effect of high-energy radiation (1-meV electrons) on PAN films in the presence and absence of oxygen. But a fundamental and systematic study of the photodegradation of PAN/Ag films in the $250 \leq \lambda \leq 400$-nm region of the spectrum has yet to be accomplished. Fourier transform infrared reflection absorption (FTIR–RA) spectroscopy is a useful tool for obtaining analytical information on surface reactions. The technique is sensitive, reproducible, and nondestructive with high signal-to-noise (S/N) ratios achievable and with computer software enabling the digital subtraction of spectra. Several authors have used recently an FTIR technique to study the thermal degradation of PAN under vacuum, oxidative, and nonoxidative environments.[19-21]

Experimental Section

The spectrophotometer used for these experiments is a Digilab FTS-14B equipped with mercury cadmium telluride (MCT) and triglycine sulfate (TGS) detectors. Two controlled environment chambers were designed to fit the spectrometer sample compartment as shown in Figure 1. An earlier chamber[4,22] used to collect the infrared spectra of polymeric coatings on mirrors, while simultaneously undergoing exposure to UV and flowing ambient gases (e.g., O_2, N_2), was modified by attaching two thermistors, one on the film and the other on the reference mirror, to record the temperature achieved during the UV exposure. The second chamber[23] is vacuum tight and can be used to study both the degradative changes in the film as well as the gases produced during UV irradiation. These chambers were designed to maximize the sensitivity of the absorbing species to IR (the angle of incidence was kept at 78°).[24-26] The irradiation of the PAN/Ag film was accomplished through the quartz windows of the chambers by an SS-1000-2 solar simulator supplied by the Optical Radiation Co. (ORC). For these experiments, UV light with $266 \leq \lambda \leq 400$ nm (dichroic filter) at air mass one and $250 \leq \lambda \leq 400$ nm (without dichroic filter) were used. The spectral distribution of the ORC simulator at air mass one and without dichroic filter is given in Figure 2. The acrylonitrile polymer with an average molecular weight of 150 000 and intrinsic viscosity of 1.95 dL g^{-1} was obtained from E. I. duPont de Nemours and Co.

Experiments on the solubility of PAN in various solvents indicated dimethyl sulfoxide (Me_2SO) to be the most suitable solvent to yield thin films. Clear films of PAN, of approximately 4.4-μm thickness, were successfully drawn at a rate of 1 mm s^{-1} in nitrogen. The optimum concentration of PAN in Me_2SO was about 8% (w/v). The PAN-coated mirrors were dried in nitrogen and then in a vacuum oven at 72 °C for 48 h. The IR–RA spectra (Figure 3) of these films were consistent with the reference spectra of PAN[27-29] and our own spectra of the polymer. (It should be remembered that the relative intensities of absorption bands are dependent upon film orientation). There was no spectroscopic evidence for entrapped Me_2SO solvent in these films. As indicated by their IR spectra, the Ag-supported PAN films were of a very satisfactory quality for the study of polymer degradations. The irradiation of PAN was carried out under both oxidative conditions (dry purge air, oxygen-16, and oxygen-18) and a nonoxidative atmosphere (N_2) in both chambers described earlier. The flow rate of gases in the open chamber was maintained at 40 cm^3 s^{-1}. After stabilization of the xenon lamp for 25 min, the sample was exposed to UV radiation for a specific time. The IR spectra were collected during and after the period of exposure. The loss of the original bands in the polymer and the formation of new bands during the photodegradation were studied from the absorbance subtraction spectra. The maximum temperature reached during the irradiation of PAN/Ag samples as measured by the thermistors was 57 °C.

Results and Discussion

The PAN/Ag film was exposed to UV light of $266 \leq \lambda \leq 400$ nm (dichroic filter at air mass 1, Figure 2) for as long

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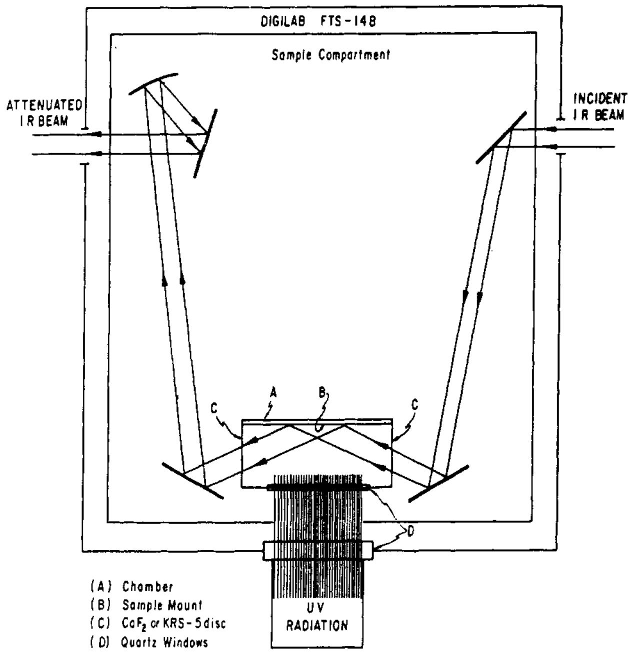


Figure 1. Schematic diagram of apparatus.

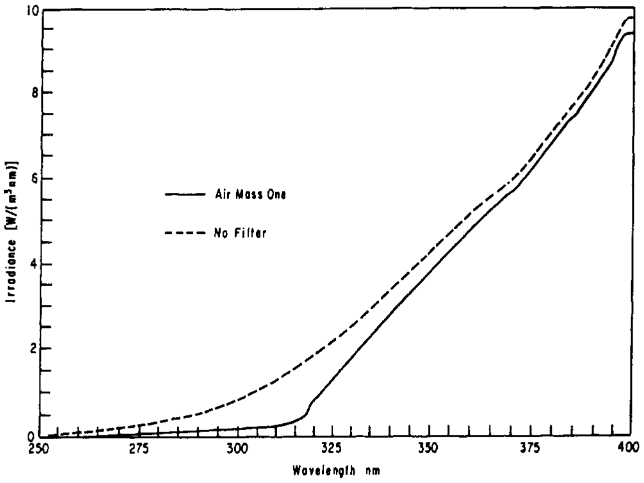


Figure 2. Spectral distribution for solar simulator.

as 15 h. The experiment was conducted with 450 torr of zero-air in the closed chamber. Formation bands (Figure 4) at 1300 (–OH deformation), 1140 (C–O str), 3330 (–OH and NH), and 1660 cm^{-1} (>C=O) were observed.[30-32] The presence of NH was confirmed by a separate experiment using nonoxidative conditions (Figure 5) in the presence of N_2 from the liquid N_2 tank. This figure also indicates the absence of the formation bands due to the oxygen-containing species assigned above. The gaseous products collected (Figure 6) in the closed chamber are[33] (i) H_2O (3600 cm^{-1} (str mode)), 1600 cm^{-1} (bending mode); (ii) CO_2 (2340 cm^{-1}); (iii) CO (2100 cm^{-1}); (iv) hydrocarbon (e.g., CH_4, 3100 cm^{-1}); (v) HCN (3300 cm^{-1}); (vi) NH_3 (1040 cm^{-1}). Furthermore, loss of –CH_2, –CH (2940 cm^{-1}), –C≡N (2245 cm^{-1}), and skeletal combination bands (1060 cm^{-1}) also was observed. To study the photodegradation of PAN below 1000 cm^{-1}, a chamber with KRS-5 windows was employed. The flow of purge air was maintained at 40 cm^3 s^{-1}. The formation of two additional bands at 940 (C–O str)[30] and 760 cm^{-1} (–OH def)[30] was observed (Figure 7).

To confirm the assignments of the formation bands at 1300 cm^{-1} and 1140 cm^{-1} as due to an oxygen-containing species, two more experiments were performed in the closed chamber with $^{16}O_2$ and $^{18}O_2$. The subtraction spectra (Figure 8) showed that the peaks at 1300 and 1140 cm^{-1} have shifted to lower frequency by 20 cm^{-1}, consistent with the previous assignments. In other words, the bands at 1300 (–OH)[30] and 1140 cm^{-1} (C–O str)[30] result from the

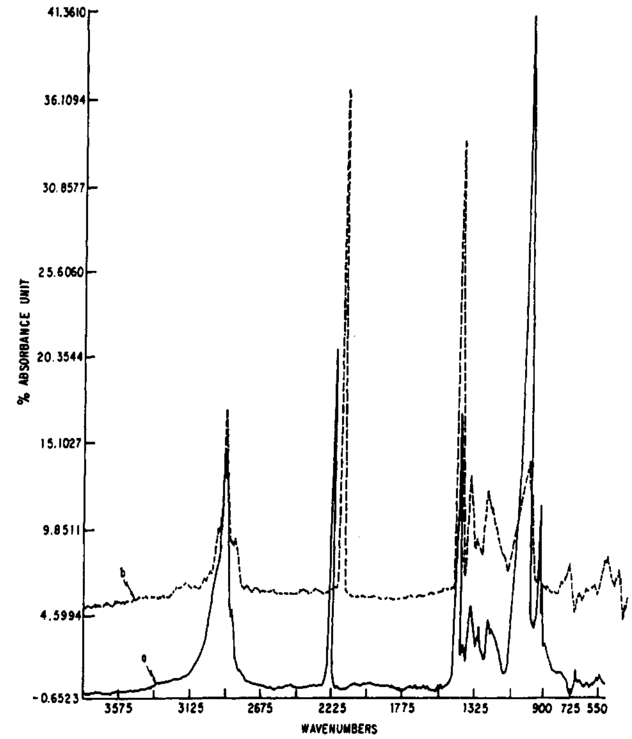


Figure 3. (a) FTIR–RA spectrum of PAN/Ag film. (b) FTIR absorbance spectrum of isotopic (^{13}CN) PAN polymer film.

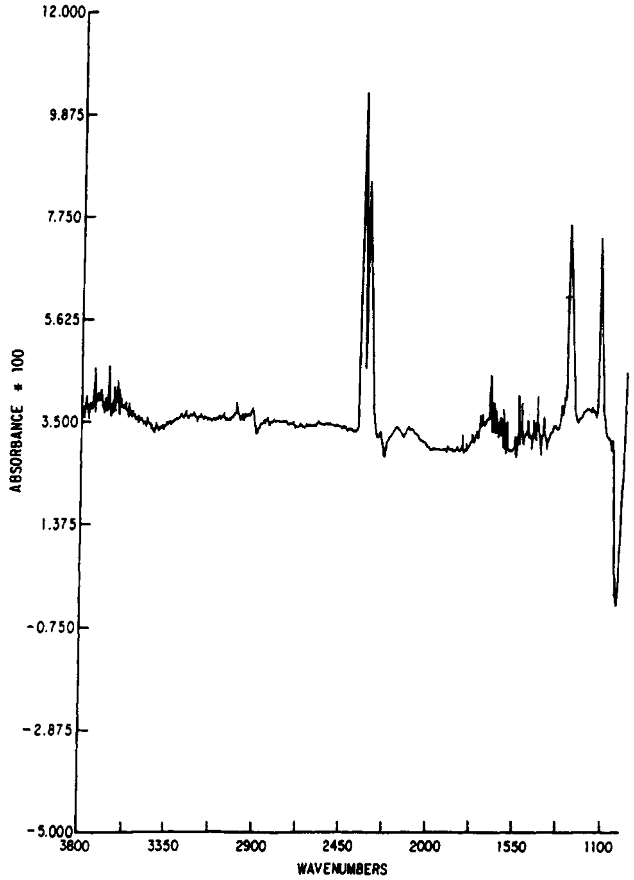


Figure 4. Subtraction spectrum of the original PAN/Ag film from one irradiated for 15 h under oxidative conditions, air mass one.

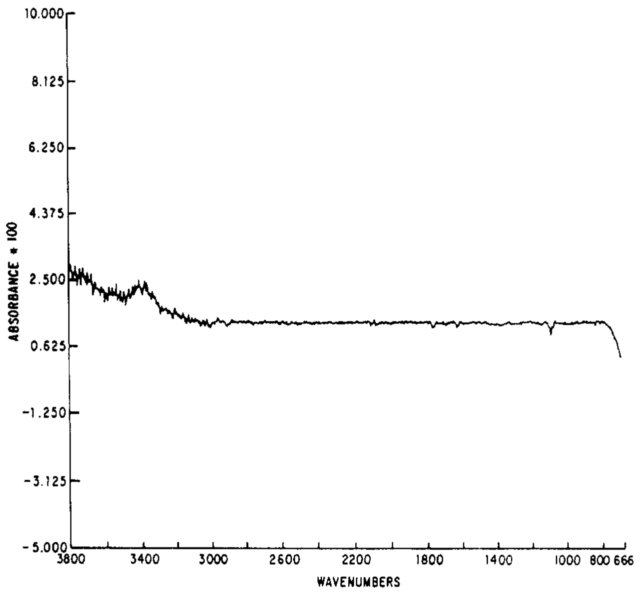


Figure 5. Subtraction spectrum of the original PAN/Ag film from one irradiated for 15 h under nonoxidative conditions, air mass one.

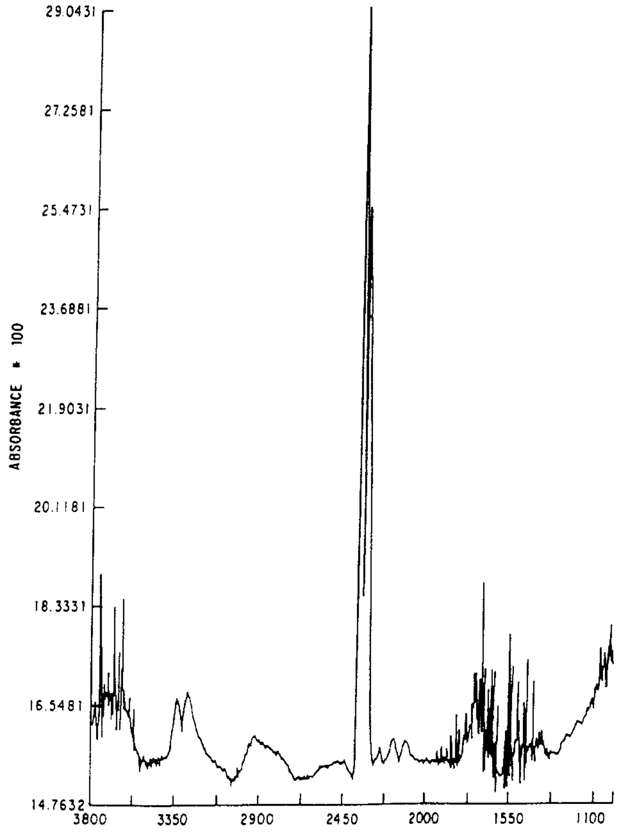


Figure 6. Gases produced during the irradiation of PAN.

formation of alcohols, carboxylic acids, hydroperoxides, or ethers.

To investigate the presence of radicals generated during the oxidative photodegradation of PAN polymer, electron paramagnetic resonance (EPR) studies were performed (using an E-9 X-band spectrometer coupled with a Varian 620/L100 microcomputer). The EPR spectrum of the unexposed polymer film (Figure 9a) showed no signal. However, the film when exposed to UV radiation ($266 \leq \lambda \leq 400$ nm) for 10 min, under oxidative conditions, gave a broad signal (Figure 9b). A broad EPR band of $g = 2.0037$ was observed (Figure 9c) when the PAN film was exposed to UV radiation ($250 \leq \lambda \leq 400$ nm) for 2 h, and it became yellowish brown. The g value was calculated by comparing with the g (2.0036) of a standard diphenylpicrylhydrazyl (DPPH). From the shape and g value of the spectrum, it can be inferred that (i) the g value indicates the presence of organic radicals;[34] (ii) the broad band is an indication of the presence of a mixture of organic radicals; (iii) the low power (0.2 mW) necessary for the spectrometer to give an optimum signal, for the exposed PAN film, is also characteristic of organic radicals. Inorganic radicals such as those of transition metals require a higher power between 5 and 10 mW for optimum signal. It also has been observed that radicals generated in PAN during the photodegradation are stable for a long period of time. However, when the exposed polymer was dissolved in Me_2SO the EPR signal disappeared but the color remained in the solution, indicating that these radicals are not the source of the color formation.

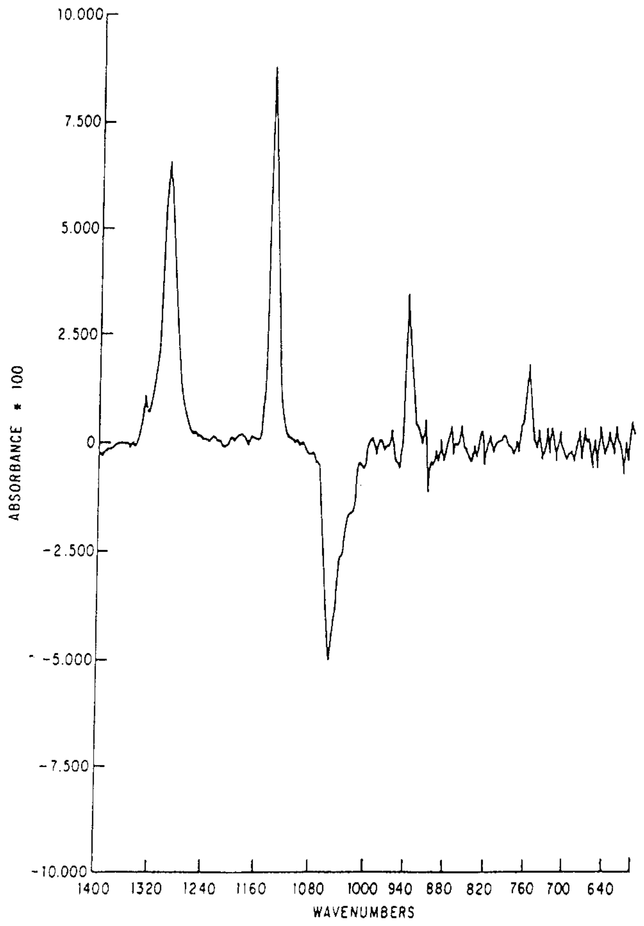
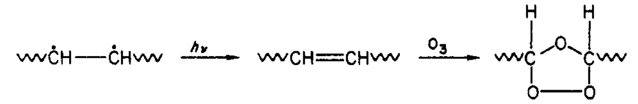


Figure 7. Subtraction spectrum after 15 h exposure to UV (air mass 1) using an open chamber.

Since, in the presence of this UV light, molecular oxygen is partially converted to ozone, a pathway involving the formation of ozonide cannot be excluded, although these experiments disclosed no evidence of its presence.



An ozonide band would escape detection because of overlap with the skeletal combination band of the polymer. Also, no infrared bands of the gaseous O_3 were detected because of its lower concentration and/or extreme reactivity toward the double bond. Further photodegradation studies of PAN/Ag with radiation components of higher energy (250

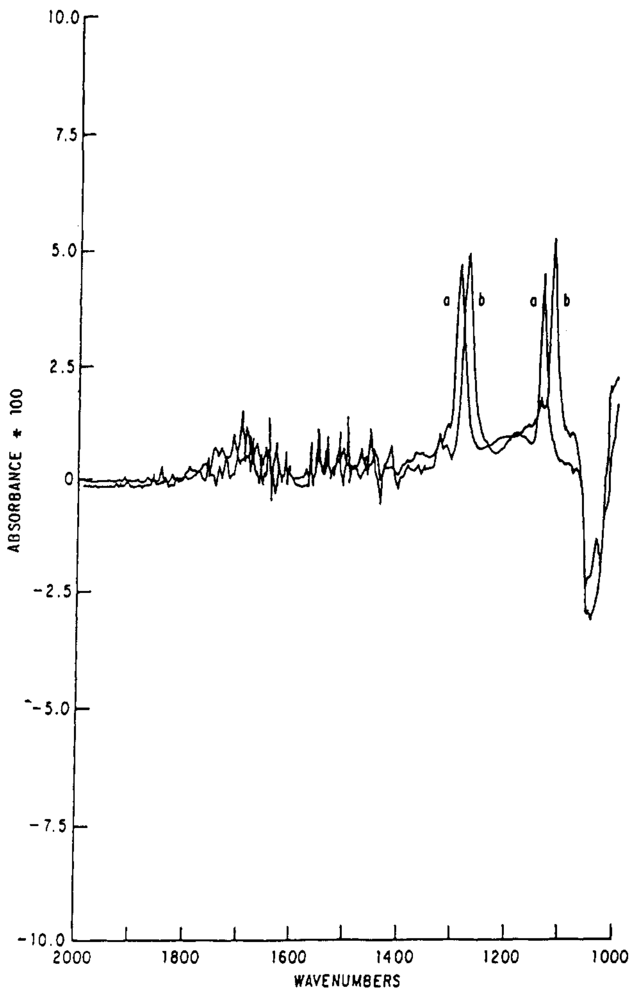


Figure 8. Subtraction spectra after 15 h exposure to UV irradiation (air mass 1), using 450 torr of oxygen-16 (spectrum a) and oxygen-18 (spectrum b).

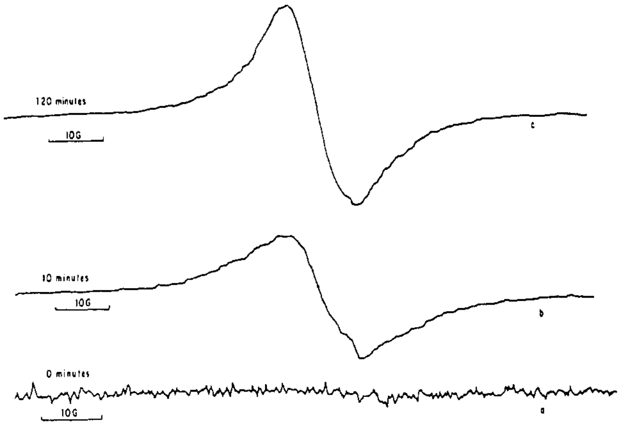


Figure 9. EPR spectra of PAN film; (a) unexposed to UV light; (b) exposed to UV 266 $\leq \lambda \leq$ 400 nm for 10 min (c) exposed to UV 250 $\leq \lambda \leq$ 400 nm for 2 h until it became yellowish brown.

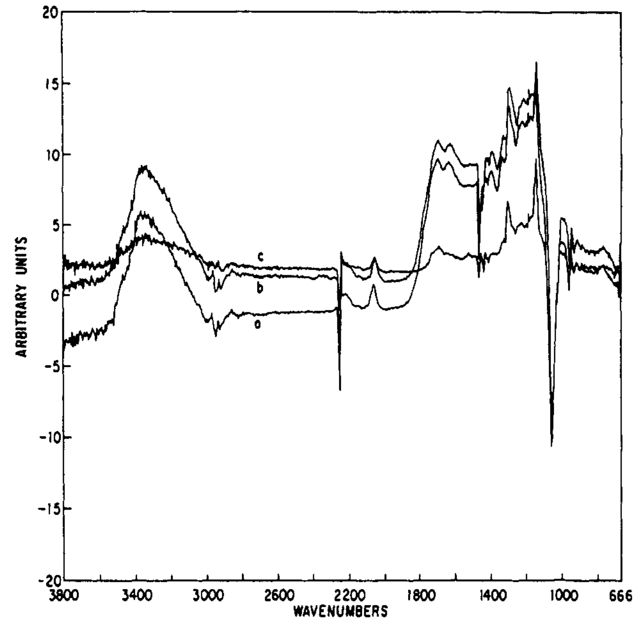


Figure 10. Subtraction spectra of the original PAN/Ag film from the irradiated one with 250 $\leq \lambda \leq$ 400 nm under oxidative conditions: (a) after 15-h exposure to UV; (b) after the sample was cooled to room temperature; (c) after 6-h exposure to UV.

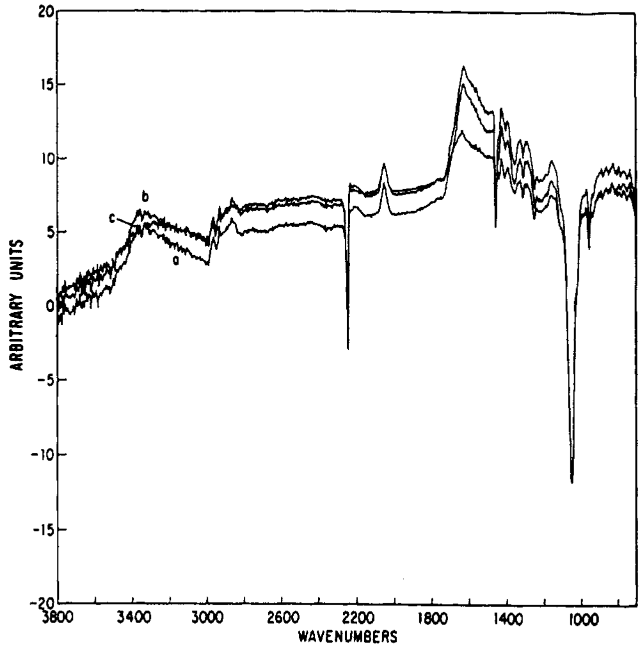


Figure 11. Subtraction spectrum of the original PAN/Ag film from one irradiated at 250 $\leq \lambda \leq$ 400 nm under an inert atmosphere: (a) after 15-h exposure to UV; (b) after 13-h exposure; (c) after 6-h exposure.

$\leq \lambda \leq$ 400 nm) were carried out under both oxidative and nonoxidative conditions in the open chamber. In addition to the bands observed at UV $\lambda \geq$ 266 nm under oxidative conditions, new formation bands were observed (Figure 10) as a result of the higher energy irradiation. The assignments are[30-32] (i) the broad envelope at 3330 cm^{-1} is due to both -OH and -NH; (ii) the band at 2050 cm^{-1}, present with aluminum- and silver-backed surfaces but absent in film only, can be assigned to $M(CN)_x$[31] formation (this band disappears when the substrate is coated with SiO); (iii) the band at 1620 cm^{-1} is due to the ($>C{=}NC{=}N-$) species. The polymer became yellowish brown after the UV irradiation under both oxidative and nonoxidative conditions. Furthermore, the electrical conductivity of the irradiated polymer was doubled [to 5.04 $\times 10^{-8}$ (Ω cm)$^{-1}$. This information indicates that the formation of a conjugated system, such as a ($>C{=}N-)_n$ polyimine structure, took place after the high-energy irradiation. The bands at 3330, 2050, and 1620 cm^{-1} in Figure 10 were the same as those obtained under nonoxidative conditions (Figure 11). Note that the broad band in the 3330-cm^{-1} region is of lesser intensity than that produced under oxidative conditions (Figure 10). The absence of the absorbance bands at 940 and 760 cm^{-1} under nonoxidative conditions further confirmed their assignments to the oxygen-containing species.

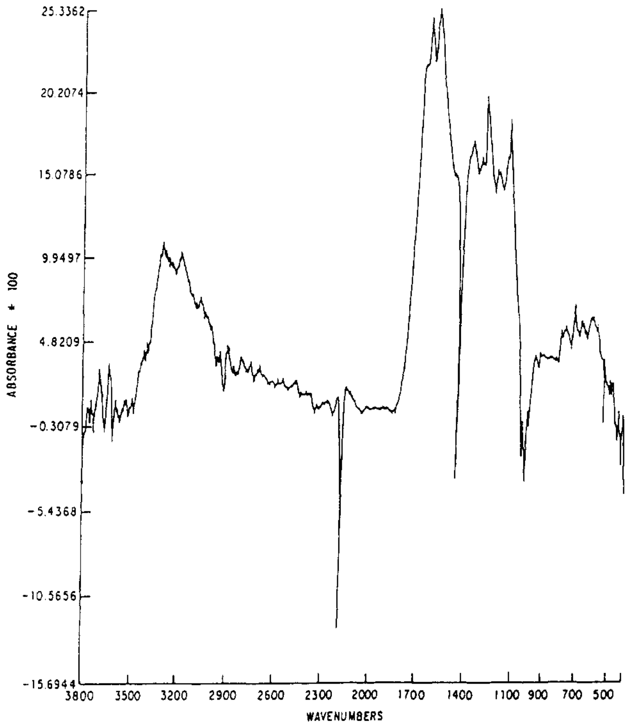


Figure 12. Subtraction spectrum of the original isotopic (^{13}CN) PAN film from one irradiated ($250 \leq \lambda \leq 400$ nm) under oxidative conditions.

Some authors,[10,35] as a result of thermal degradation studies, have assigned the 1620-cm^{-1} band and the coloration of the polymer to >C=C< conjugation. However, in this study, the small loss of $-CH_2$ at 2940 cm^{-1}, as compared with the formation of the 1620-cm^{-1} band, implies that no relationship exists between $-CH_2$ loss and the 1620-cm^{-1} formation band. However, if any $(>C=C<)_n$ formation occurs, it can easily react with O_3 to give ozonide, which absorbs in the 1065–1040-cm^{-1} region. In the opinion of other authors,[11,12] the chromophore responsible for the color in PAN is a conjugated nitrone system $[>C=N(\rightarrow O)]_n$. In this study, however, the coloration of the polymer also takes place in the absence of O_2. Furthermore, it can be seen from the subtraction spectra of PAN/Ag under oxidative conditions that no strong absorption appears in the 1150–1270-cm^{-1} region, which is assigned[36,37] to the N–O stretching mode.

To further explore the species formed during the oxidative photodegradation of PAN, isotopic studies were performed. PAN film of (^{13}CN) polymer was used for these experiments. The FTIR spectrum (Figure 3b) of the unexposed isotopic film shows a shift of the –CN band to lower wavenumber by 53 cm^{-1}. The subtraction spectrum of the ^{13}CN PAN film (Figure 12), irradiated at $250 \leq \lambda \leq 400$ nm under oxidative conditions, leads to the following observations:

(i) The formation band at 1620 cm^{-1} of the exposed ^{12}CN film, assigned to >C=N–, was shifted to 1600 cm^{-1} for the exposed ^{13}CN PAN. The shift of –20 cm^{-1} was in agreement with theoretical calculations using the harmonic oscillator model ($\Delta\bar{\nu} = -22$ cm^{-1}) and supports our assignment.

(ii) The band at 2050 cm^{-1} in the ordinary irradiated PAN/Ag film is absent in this irradiated PAN not backed by metal, thus confirming our independent observations that this band is due to the formation of an $M(CN)_x$ species. The gas-phase products collected during the UV irradiation of ^{13}CN PAN film are shown in Figure 13. Both $^{13}CO_2$ and $^{12}CO_2$ are formed, as shown by a –65-cm^{-1} shift, suggesting that the CO_2 is produced not only from the –CN functional group but from the skeletal backbone of PAN polymer as well. Furthermore, no shift was observed for the CO band (2100 cm^{-1}), suggesting that the carbon monoxide is generated only from the skeletal backbone of the polymer. It is difficult to measure shifts of other gaseous species like HCN because of their low concentration. However, their presence is very distinguishable in the gas-phase products collected from the ^{12}CN PAN film (Figure 6), which were present in much larger quantities.

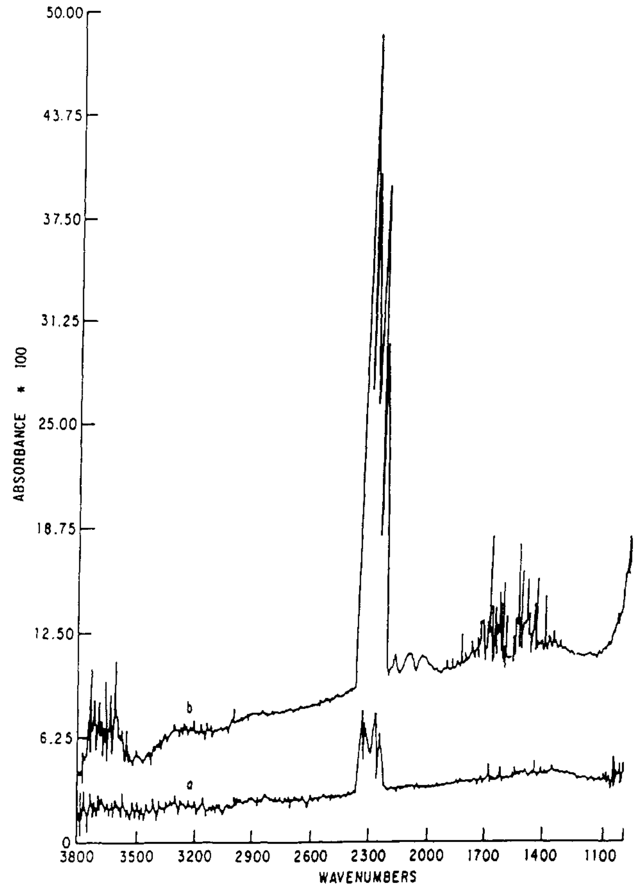


Figure 13. Gases produced during the irradiation of isotopic (^{13}CN) PAN: (a) with $266 \leq \lambda \leq 400$ nm; (b) with $250 \leq \lambda \leq 400$ nm.

On the basis of the FTIR spectroscopic information of the photodegradation products (gaseous and solids), EPR spectra, conductivity measurements, and isotopic studies, two separate oxidative photodegradation mechanisms are evident:

(i) For radiation $266 \leq \lambda \leq 400$ nm, cleavage at the α-carbon gives rise to four possible reaction paths (Figure 14). Terminal H and CN radicals lead to the formation of carboxylic group, CH_4, CO_2, H_2O, and CO under oxidative conditions while radical formation at the α-carbon gives CO_2 and NH_3 via peroxide and hydroperoxide formation. The scission of the α–β carbon bond produces tertiary alcohols and ethers. Reduction of the C≡N group gives primary amine.

(ii) For radiation $250 \leq \lambda \leq 400$ nm, in addition to the photodegradation products at lower energy (Figure 14), two more species, apparently $M(CN)_x$ and a polyimine structure, appear to be produced (Figure 15).

Conclusion

Oxidative photodegradation pathways are proposed for PAN/Ag film, with radiant energy of $\lambda \geq 266$ nm and $\lambda \geq 250$ nm (with and without dichroic filter). With the

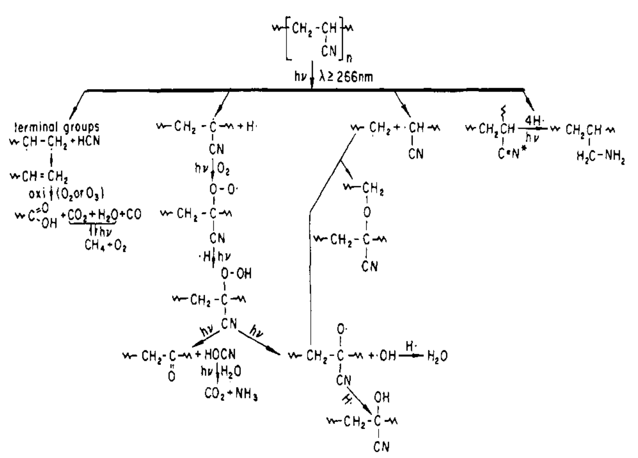


Figure 14. Some oxidative photodegradation pathways for PAN/Ag film with 266 ≤ λ ≤ 400 nm.

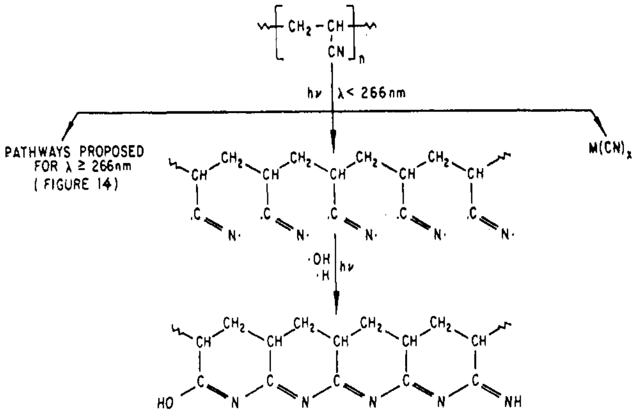


Figure 15. Some oxidative photodegradation pathways for PAN/Ag films with 250 ≤ λ ≤ 400 nm.

higher energy radiation, a conjugated system $(>C=N-)_n$ was found to be generated.

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Registry No. PAN, 25014-41-9; Ag, 7440-22-4.

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