From these observations it is concluded that oxidation below 110° is initiated by foreign particles. In the oxidation at 150° no local colored spots around foreign particles could be detected before the start of oxygen absorption (Figure 1).

A series of about 50 foreign particles which had a brown spot around them were investigated by means of laser microprobe analysis. Only iron was found to be present. A few of these particles were investigated by electron microprobe analysis (see Experimental Section). The particles contained iron and no oxygen or chlorine; therefore they probably are metallic in nature.

The particles are believed to originate from the production machines, in particular the pelletizer. Owing to corrosion by catalyst residues containing chlorine, and the large shearing forces in the extruder, small metal particles are torn out of the metal surfaces which are in contact with the polymer.

Conclusion

Machined polypropylene contains metal particles which initiate oxidative degradation. Especially at temperatures below 110°, the activity of the particles in the oxidation of unstabilized polypropylene is pronounced. Long before the end of the induction period (τ), the activity of these particles could be made visible, using sulfur dioxide as a coloring agent for oxidized areas in the polypropylene film. Deviations from the straight line in a plot of log τ against $1/T$ might well be due to the presence of these particles.

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Effect of Crystalline Form on the Electron Spin Resonance Spectrum of γ-Irradiated Acrylonitrile at 77°K. Observation of a Photosensitive Center in the Low-Temperature Phase[1]

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Recently it has been observed that the ^{14}N esr spectrum of γ-irradiated crystalline acetonitrile-d_3 at 77°K shows either a quintet[2,3] or triplet[4] hyperfine structure depending upon the conditions of sample preparation before irradiation. From reversible photobleaching studies[2] together with other evidence, these spectra have been assigned to two types of excess-electron centers. In the high-temperature phase prepared by quenching the crystallized sample from just below the melting point to 77°K, the unpaired electron interacts magnetically with two equivalent nitrogen nuclei; whereas in the other crystalline form prepared by slow cooling through the phase transition near 210°K, the hyperfine interaction is limited to only one nitrogen. The above assignments have been verified by parallel studies[5] on $CD_3C^{15}N$. These findings prompted us to carry out similar experiments with acrylonitrile, and here we report the discovery of a new paramagnetic species in this γ-irradiated monomer.

Experimental Section

Acrylonitrile (Matheson Coleman and Bell Co., chromatoquality grade) was washed successively with aqueous solutions of 10% NaOH, 10% H_2SO_4, 10% Na_2CO_3, and finally with distilled water. After standing overnight on Drierite, the monomer was distilled using a packed column, and the middle fraction was retained for sample preparation. Degassed samples were prepared in Spectrosil or Suprasil esr tubes by conventional vacuum-line techniques.[6] Two crystalline forms of acrylonitrile have been recognized.[7,8] In the present study, the high-temperature phase was formed by quenching the sample in liquid nitrogen, and the low-temperature phase was obtained by cooling the crystal slowly through a phase transition at *ca.* 140°K. The latter operation was usually carried out in the cold space above liquid nitrogen in an enclosed dewar.

All samples were γ-irradiated at 77°K for a total dose of 1 Mrad (6.2×10^{19} eV g^{-1}) at a dose rate of 0.2 Mrad hr^{-1}. The esr spectra were recorded using a Varian-4502 spectrometer with 100-kc field modulation and a modulation amplitude of 3.4 G. A low-power bridge was employed and the incident microwave power was usually *ca.* 0.01 mW. The samples were kept in the dark at 77°K during γ irradiation, transfer to the spectrometer, and the subsequent measurements. Photobleaching was carried out *in situ* by filtered light (Corning Filter No. 2030, λ >640 nm) from a 1-kW tungsten lamp. A lens was used to focus the light beam on the irradiation slots of the V-4531 cavity. Spectra were recorded at sample temperatures above 77°K through the use of the Varian V-4557 variable-temperature accessory.

Results and Discussion

In agreement with previous work,[7] we have observed that after γ irradiation of a quenched sample of acrylonitrile and subsequent measurement at 77°K in the dark, the esr spectrum is a quintet of which the three broad lines in the center are especially prominent with a hyperfine splitting of about 25 G. This esr spectrum has been assigned to the $CH_3\dot{C}HCN$ radical, and it has been reported[7] that in the temperature range from 83 to 121°K, this is the predominant radical present after γ irradiation of both quenched and annealed samples. However, we now find that when the annealed sample is γ irradiated *and measured* at *77°K*, the esr spectrum is significantly different.

In the upper spectrum of Figure 1, a relatively intense triplet structure with a hyperfine splitting of 10.5 G can be discerned. This is revealed very clearly by

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[1] This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-51.

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[3] M. A. Bonin, K. Takeda, and F. Williams, *J. Chem. Phys.*, **50**, 5423 (1969).

[4] K. Takeda and F. Williams, *Mol. Phys.*, **17**, 677 (1969).

[5] K. Takeda and F. Williams, unpublished work.

[6] J. Lin, K. Tsuji, and F. Williams, *J. Amer. Chem. Soc.*, **90**, 2766 (1968).

[7] R. Bensasson, A. Dworkin, and R. Marx, *J. Polym. Sci., Part C*, **4**, 881 (1964); see also the references to earlier papers by these authors.

[8] For reviews of the extensive work on the solid state polymerization of acrylonitrile, see the following articles: (a) Y. Tabata in "Advances in Macromolecular Chemistry," W. M. Pasika, Ed., Academic Press, New York, N. Y., 1968, p 283; (b) M. Magat, *Pure Appl. Chem.*, **10**, 413 (1965); (c) M. Magat, *Polymer*, **3**, 449 (1962).

comparison with the lower spectrum recorded after the sample was photobleached with red light (λ >640 nm). In contrast to the esr spectrum of the quenched sample which showed no change on illumination with visible light and little or no angular dependence in the magnetic field, the esr spectrum of the slowly cooled sample exhibited changes due to magnetic anisotropy both before and after photobleaching. By selecting the particular orientation which offered the best resolution, it has been found that the difference between the spectra taken before and after photobleaching gives a triplet spectrum having approximately 1:1:1 intensity ratios. From the results of several such experiments with aligned samples, the triplet hyperfine splitting is determined as being between 10 and 11 G. Hence it is clear that a different paramagnetic species is produced by γ irradiation of the low-temperature phase. The parallel with the triplet spectrum[4] for the low-temperature phase of CD_3CN is very striking, and the magnitude of the nitrogen hyperfine splitting is almost identical in the two systems. Also both centers are photobleached by red light. Recent work[5] with aligned samples of $CD_3{}^{13}CN$ has revealed an isotropic ^{13}C splitting of *ca.* 60 G which strongly implies that the excess-electron center in the low-temperature phase of acetonitrile is the anion radical with appreciable spin density in an sp^2 orbital on the carbon atom of the nitrile group. A similar assignment of the triplet spectrum for acrylonitrile to the anion radical is therefore suggested by the correspondence in the spectra.

Previous work[7,8] has not succeeded in identifying the active species responsible for initiating the "in-source" polymerization of acrylonitrile in the low-temperature phase. No evidence for free radical propagation has been obtained from esr studies between 83 and 121°K, and it has been frequently suggested that the anion radical is formed and initiates anionic polymerization. Hitherto, the failure to detect the anion radical could be attributed to its reactivity in polymerization or to the lack of sufficient resolution in the esr spectrum. In the present study we have observed that the triplet spectrum largely disappears if the sample either is allowed to stand for 2 days at 77°K in the dark, or is warmed to 93°K (this was the lowest temperature obtainable in this series of experiments with our variable-temperature equipment), and the resulting spectrum is very similar to the one recorded after photobleaching.

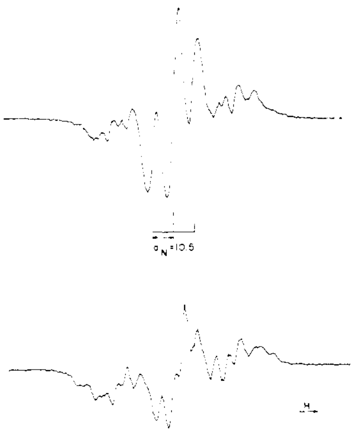
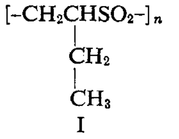


Figure 1. Electron spin resonance first-derivative spectra of γ-irradiated acrylonitrile in the low-temperature phase at 77°K. The hyperfine splitting is in gauss. Upper and lower spectra were recorded at the same microwave power (0.016 mW) and at the same spectrometer gain settings before and after photobleaching with filtered light (λ >640 nm) from a tungsten lamp (Corning filter No. 2030). The γ-irradiation dose was 1 Mrad (6.2×10^{19} eV g^{-1}).

Communications to the Editor

The Degradation of Poly(butene-1 sulfone) during γ Irradiation

This communication presents preliminary results of a study of the effect of γ radiation on poly(butene-1 sulfone) (I), a regularly alternating copolymer of butene-1 and sulfur dioxide.



$$[-CH_2\underset{\underset{CH_3}{|}}{\underset{CH_2}{\underset{|}{C}}}HSO_2-]_n$$

I

The polymer is shown to degrade rapidly under irradiation. Cross-linking is relatively unimportant, no gel being formed, even at quite high doses. Sulfur dioxide is the main volatile product at 0°, together with some butene-1, hydrogen, methane, and ethane. The gas yield increases rapidly with increasing irradiation temperature and approaches equimolar proportions of sulfur dioxide and butene-1, indicating depropagation.

Electron spin resonance studies of the radiolysis of poly(olefin sulfones) at −196° by Ayscough, Ivin, and O'Donnell[1] indicated preferential scission of C–S bonds. Also, initial C–S bond scission was shown to be the predominant effect in the radiolysis of dialkyl sulfones (RSO_2R).[1] These bonds are weak and bond cleavage is evidently energy selective. However, it was not clear whether both C–S bonds were broken, either simultaneously or successively, as the final radiolysis products were not determined.

No other information on the effects of γ radiation on poly(olefin sulfones) has been reported. However, Eaton and Ivin,[2] in an experiment involving the grafting of styrene on to poly(butene-1 sulfone) with X-rays, showed that the poly(butene-1 sulfone) was degraded.

Poly(butene-1 sulfone) is the first soluble polymer in the olefin series,[3] hence the first for which changes in molecular weight can be followed. Also, the olefin (bp −6.3°), if produced during radiolysis, can be

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(1) P. B. Ayscough, K. J. Ivin, and J. H. O'Donnell, *Trans. Faraday Soc.*, 61, 1110 (1965).

(2) E. C. Eaton and K. J. Ivin, *Polymer*, 6, 339 (1965).

(3) H. A. Ende, K. J. Ivin, and G. Meyerhoff, *ibid.*, 3, 129 (1962).