rpm must be ascribed to the low viscosity of the solution (0.0077 P). The rate of crystallization of this polymer at 88.2° did not vary within a wide range of stirrer speeds, but the unstirred solution was found to crystallize at a considerably slower rate. In the course of this experiment it was noticed that comparatively small crystals were formed which sedimented on the bottom of the dilatometer. The slow crystallization of this unstirred solution may therefore be due to the accumulation of growing crystals and the consequent reduction of the growth face area available to the dissolved molecules in the remaining part of the system.

This interpretation is substantiated by the observation that at 50% transformation the high molecular weight polyethylene sample crystallized about 15 times more slowly in a wide-gap dilatometer where the flakes were seen to deposit than in the narrow-gap dilatometer where they remained uniformly distributed throughout the solution.

Finally, some remarks should be made regarding the experimental observation that laminar shear flow and the Taylor vortices in the low molecular weight polyethylene solutions apparently have no effect on the folded chain crystallization. One might have anticipated an increase in rate of crystallization with stirrer speed in view of the possibility that the shear stresses might cause fracturing of the platelet-like single crystals[4] and generate screw dislocations.[5] Although it remains to be ascertained by morphological observations whether or not these growth accelerating processes take place under the present conditions of flow, the information on the growth rate at least suggests that they do not vary within the range of stirrer speeds employed.

Apparently the rate of folded chain crystallization is controlled by the interfacial process and not influenced by the transport of polymer molecules to the growth faces; this would be in line with the predictions based on the kinetic theories of polymer crystallization.[6]

Acknowledgment. The authors are greatly indebted to Professor A. J. Kovacs Strasbourg for valuable suggestions in designing the dilatometer.

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(4) V. F. Holland and P. H. Lindenmeyer, *J. Polym. Sci.*, **57**, 604 (1962).

(5) J. M. Peterson, *J. Appl. Phys.*, **37**, 4047 (1966).

(6) J. D. Hoffman, J. I. Lauritzen, Jr., E. Passaglia, G. S. Ross, L. J. Frolen, and J. J. Weeks, *Kolloid-Z.*, in press.

Initiation Process in the Oxidation of Polypropylene[1]

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Accelerated tests are used for the prediction of the useful lifetime of polymers. Acceleration is most frequently obtained by elevation of temperature.

For polypropylene the time is measured to the occurrence of mechanical failure, or the time to the onset of oxygen absorption (induction period). Results obtained at high temperatures (110–150°) are extrapolated to the temperature of interest by an Arrhenius plot. However, this method leads to errors, especially when extrapolations are extended to temperatures below 70°.[2]

The length of the induction period depends on the initiation process. In order to get more information about this process, a study of what happens during the induction period was undertaken. The present paper describes the use of a color reaction in detecting early signs of oxidative degradation in thin films of polypropylene.

Experimental Section

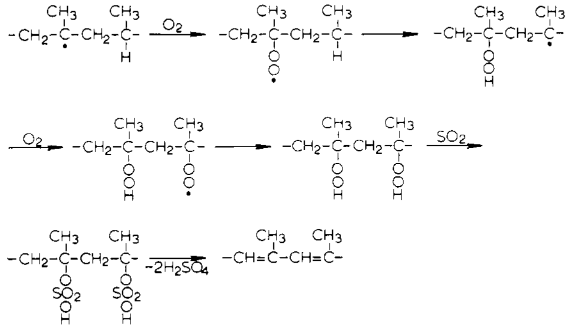
A clear, blown film of polypropylene, $[\eta] = 2.60$, decalin, 135°), thickness 0.05 mm, was used for most experiments. The residue after ashing was 0.025%. The film contained 15 ppm Ti, >25 ppm Al, 8.5 ppm Fe, 0.09 ppm B, 6 ppm Si, 2 ppm Mg, 0.03 ppm Mn, 0.08 ppm Pb, 0.09 ppm Cr, 0.5 ppm Mo, 0.2 ppm Ni, 1 ppm Zn, >25 ppm Na, 0.4 ppm Cu, 3.5 ppm Ca, 0.08 ppm Sn. Traces of K and Cl were also present. Other polypropylene types showed similar behavior. Stabilizers were extracted successively with *n*-hexane at about 20° and a boiling mixture of methanol and ethyl acetate (1:1). The residue of phenolic stabilizer was less than 1 ppm as determined by glpc analysis. The oxidation was followed by measuring the absorption of oxygen.

Laser microprobe analysis was carried out with a LMA-1 instrument (Carl Zeiss, Jena).[3] An ARL-EMX instrument (Metal Research Institute TNO, Delft) was used for electron microprobe analysis. Both sides of the polypropylene film were covered with a layer of aluminum about 500 Å thick. Particles suitable for analysis could be located using a microscope. However, the particles which are embedded in a nonconductive polymer film started to move during the analysis, probably owing to a buildup of static charge. Therefore electron and X-ray pictures could not be taken. However, point analyses at short time intervals showed the presence of iron. Chlorine and oxygen were not present.

Color Reaction. Oxidized polypropylene film turned brown on treatment with sulfur dioxide at room temperature. Heating at 100° intensified the coloration.

Sulfur dioxide transformed hydroperoxides, which are the first products of oxidation, into alkyl sulfates.[4] Decomposition of these alkyl sulfates led to conjugated systems of double bonds, as shown in Scheme I.

Scheme I



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(1) Presented at the IUPAC Symposium on Macromolecular Chemistry, Budapest, August 25–30, 1969.

(2) (a) J. W. Tamblyn and G. C. Newland, *J. Appl. Polym. Sci.*, **9**, 2251 (1965); (b) H. J. Oswald and E. Turi, *Polym. Eng. Sci.*, **5** (3), 152 (1965).

(3) H. Moenke and L. Moenke-Blankenburg, "Einführung in die Laser-Mikro-Emissionsspektralanalyse, Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig, 1968.

(4) J. Mitchell, Jr., and L. R. Perkins, *Appl. Polym. Symp.*, **4**, 167 (1967).

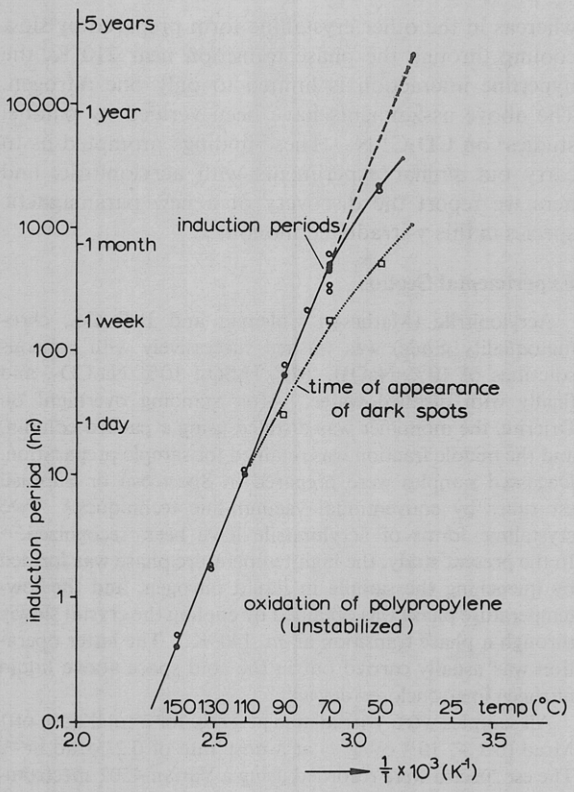

Figure 1.

Results and Discussion

Induction periods (τ) of the unstabilized polypropylene film at 1 atm of oxygen were determined in the temperature range 50–150° by measuring the oxygen absorption. Plotting of log τ against $1/T$ (K^{-1}) gave a straight line only between 80 and 150°. Deviations from this behavior began at 70°. Experimentally, the induction period at 50° was 3 months, while the extrapolation method predicted 10 months (Figure 1).

Oxidation of the polypropylene film was interrupted at different times. Treatment with sulfur dioxide showed that the film had not been oxidized homogeneously. Parts of the film were still colorless while others were deeply colored and brittle. Microscopic examination of the film showed the presence of circular dark brown spots, located around foreign particles. The spots varied in diameter between 1 and 200 μ, the particles in the center between 0.1 and 50 μ. In some instances cracks were observed in these colored spots. Figure 2 shows the order of appearance of different visible phenomena of oxidation in the course of time. When oxidation at temperatures below 110° was interrupted at an early stage, long before the end of the induction period, only a few (*e.g.*, two per 100 cm² of film) of these spots were detected in otherwise colorless film (Figures 3 and 4). Larger parts of the film could be colored when oxygen absorption became easily measurable (Figure 5). Comparison of the infrared spectrum obtained by the MIR technique (multiple internal reflection) with a normal infrared spectrum showed that oxidation took place predominantly in the surface areas of the film. On further oxidation, the film became brittle. Treatment with sulfur dioxide resulted in an overall dark brown coloration.

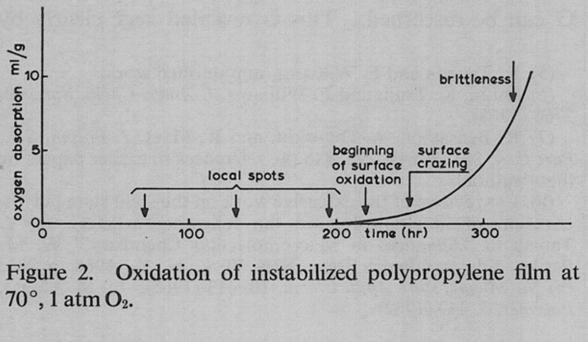

Figure 2. Oxidation of instabilized polypropylene film at 70°, 1 atm O_2.

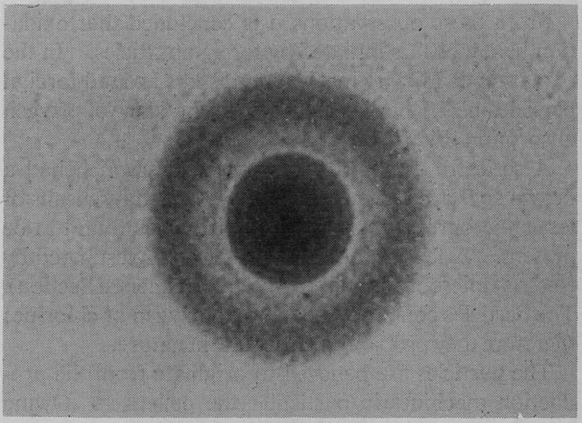

Figure 3. 50-μ polypropylene film, stabilizers extracted, oxidized at 50°, treated with SO_2, particle 15 μ, spot 200 μ.

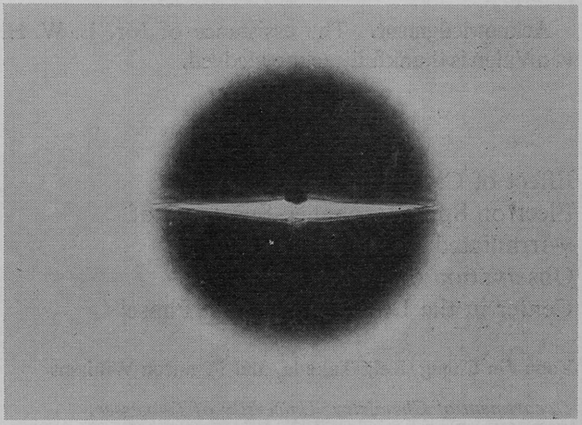

Figure 4. 50-μ polypropylene film, stabilizers extracted, oxidized at 70°, treated with SO_2, particle 20 μ, spot 200 μ.

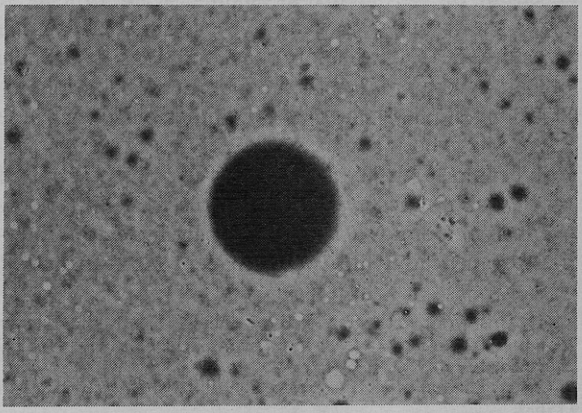

Figure 5. After prolonged oxidation at 70° and treatment with SO_2, particle 10 μ, spot 200 μ.

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, $\lambda > 640$ 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.

(2) M. A. Bonin, K. Tsuji, and F. Williams, *Nature*, **218**, 946 (1968).

(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).