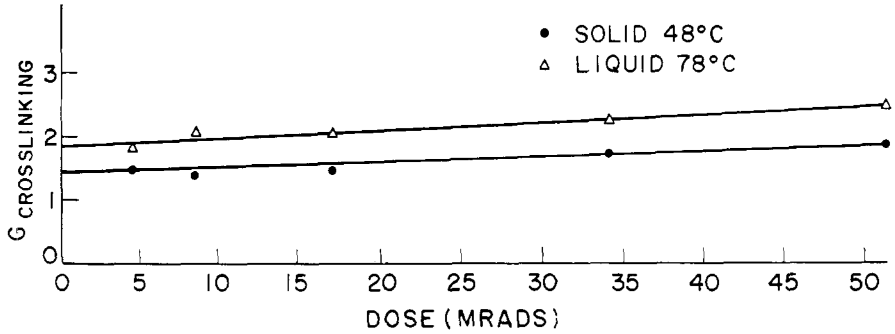

Figure 7. Cross-linking yields in irradiated *n*-pentatriacontane.

paraffins with 35 or 36 carbon atoms suggests that packing of the paraffin molecules may differ in the two linear alkanes just above the melting point.

The variation in total cross-linking yield with phase on irradiation of an orthorhombic long chain paraffin has been reported for *n*-heptadecane (C_{17}) where G_{dimer} equals 1.6 for liquid and 1.1 for solid, as determined by gas phase chromatography.[6] Similarly, cross-linking yields in *n*-eicosane (C_{20}) differ widely in solid and liquid states, both from gas phase and gel permeation chromatographic analyses.[2a]

Conclusions

Cross-linked products resulting from the irradiation of long chain linear paraffins are resolved from parent alkanes and yields determined by gel permeation chromatography. For irradiated solid and liquid *n*-pentatriacontane and solid *n*-hexatriacontane, the *G* values of cross-linking at zero dose are 1.4, 1.8, and 1.1, respectively. Gel permeation chromatograms of irradiated liquid *n*-hexatriacontane indicate an additional, presumably multiply cross-linked, product corresponding to 25% of the total dimer area, regardless of dose. The same product distribution is observed in liquid state radiolyses of *n*-hexatriacontane purified by the removal of an olefinic impurity on recrystallization.

An increase in cross-linking yield with dose observed in irradiated *n*-C_{35} paraffin is reminiscent of a similar effect inferred from solubility studies on irradiated polyethylene.[8] The marked effect of physical state and crystalline packing on cross-linking yields suggests complex cross-linking in polyethylene with regions of varied order and packing.

Acknowledgments. We acknowledge with gratitude R. K. Eby for the sample of *n*-tetranonacontane, J. P. Luongo for infrared analyses, and H. E. Bair for differential scanning calorimetry.

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Communications to the Editor

The Effect of Oxidation Products on the Photostability of Polypropylene Films

The formation of oxidation products during processing has frequently been cited as a source of the instability of polyolefins to near-ultraviolet radiation.[1,2] A detailed study of the possible photodegradative processes involving these products may lead to improved methods of stabilizing polymers against exposure to sunlight. The recent work of Guillet and Heskins[2] on solutions of ethylene–carbon monoxide copolymers has shown the photolysis of carbonyl groups by a Norrish type II reaction to be a major source of chain scission. This paper is a description of some effects of carbonyl groups on the photostability of polypropylene in the solid phase.

Films of unstabilized, isotactic polypropylene (Hercules Profax 6801) were prepared by heating the resin in air to 225° on a quartz plate for a controlled period (1–5 min) followed by rapid cooling. The oxidized polymer was transferred to a nitrogen atmosphere, and briefly squeezed between quartz plates at 50 psi in a press preheated to 225°. The films were then quenched in a Dry Ice–methanol slurry and stripped from the quartz; samples of controlled, uniform thickness (15–130 μ) and high optical clarity were obtained. The extent of oxidation of each film was determined by infrared (ir) spectrophotometry (*e.g.*, Figure 1), which shows that the products of oxidation at 225° are simple in comparison[3] with the products of low temperature (less than 100°) thermal oxidation or of photooxidation. The ir spectra of films oxidized at 225° showed a relatively sharp ketone carbonyl peak at 1721 cm^{-1} together with some absorption at 1645 cm^{-1}, indicating C–C unsaturation but no detectable absorption at 3560–3370 cm^{-1} for hydroperoxide. The oxi-

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(1) A. W. Pross and R. M. Black, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **69**, 113 (1950).

(2) M. Heskins and J. E. Guillet, *Amer. Chem. Soc., Div. Polym. Chem., Preprints*, **9**, 370 (1968); *Macromolecules*, **1**, 97 (1968).

(3) Low-temperature oxidation gives a broad carbonyl band, (1675–1790 cm^{-1}, Figure 1) and a large hydroperoxide content. Thermal and photooxidation products are identical, however, under suitably chosen conditions of temperature and irradiation wavelength.

TABLE I
CONDENSABLE PRODUCTS FROM IRRADIATED, OXIDIZED POLYPROPYLENE[a]

Product	Mol %	Products less than 0.2%	Products less than 0.01%
CH_3COCH_3	75	H_2O	HCOOH
CH_3CHO	12	i-$C_4H_9COCH_3$	n-C_3H_7CHO
CH_3COOH	5	$CH_3CH(CH_3)CHO$	n-C_3H_7COOH
$CH_3COC_2H_5$	3	C_4H_9CHO	i-C_4H_9OH
C_2H_5CHO	2	i-C_3H_7OH	$CH_3CH(CH_3)CH_2CH(CH_3)CH_3$
C_2 hydrocarbons	1.5	C_5 hydrocarbons	$CH_2{=}CHCH_2CH(CH_3)CH_3$
C_3 hydrocarbons	0.75	$CH_2{=}CCH_3CH_2CH_2CH_3$	
C_4 hydrocarbons	0.5		
C_2H_5COOH	0.5		

[a] Film and irradiation conditions are identical with those used in the determination of $\phi_{\text{polychromatic}}$; total product collected (15 hr irradiation) = 0.68×10^{-6} mol.

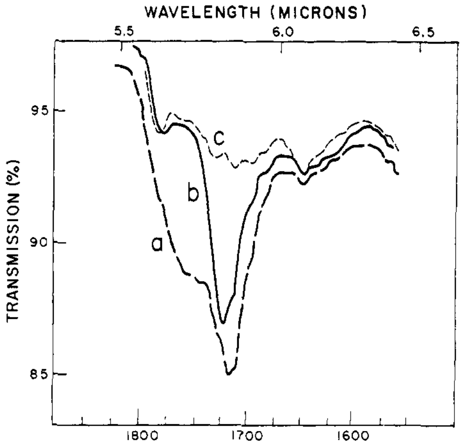


Figure 1. Infrared spectra of polypropylene films: a, 18-μ film after thermal oxidation at 74°; b, 35-μ film, resin air oxidized for 3 min at 225° before pressing; c, film b after 20-hr irradiation with 2400–4000-Å light.

dation products could not be extracted with boiling acetone or hexane and, therefore, are not low molecular weight species.

To investigate the role of carbonyl groups in the photodegradation of polypropylene, films of the oxidized polymer (about 14 cm^2) were suspended from a Cahn RG electrobalance and irradiated under mercury-free conditions, with continuous pumping at 10^{-5} mm. The optical systems used included a super-pressure mercury lamp (Osram HBO 200 W) collimated with quartz optics to give a parallel beam through a 10-cm water filter and Corning filters, and a Bausch & Lomb high-intensity monochromator (Osram HBO 200 W source). Light intensities were determined with a calibrated Eppley thermopile. On irradiation, the films showed a loss in weight due to the formation and removal of volatile products. Typical weight loss–time curves are shown in Figure 2. The production of volatiles was accompanied by a proportional decrease in the carbonyl absorption with virtually complete loss of the 1721-cm^{-1} band (Figure 1) on irradiation to constant film weight. On prolonged irradiation of the thicker film samples, a very slow residual weight decrease was detected. This is believed to be due partly to the direct photolysis of polypropylene (to give hydrogen and traces of methane, C_2, C_3 and C_4 hydrocarbons) and partly to the slow photolysis of traces of esters and carboxylic acids in the film. The total weight loss of each sample per mole of carbonyl substituents was found to be independent of film thickness up to 130 μ. The initial rate of weight loss was independent of film thickness below 60 μ, at constant carbonyl concentration, and was directly proportional to carbonyl concentration (up to 0.026 mol/l.) at constant film thickness (40 μ). The rate of weight loss was also found to be directly proportional to the incident intensity.

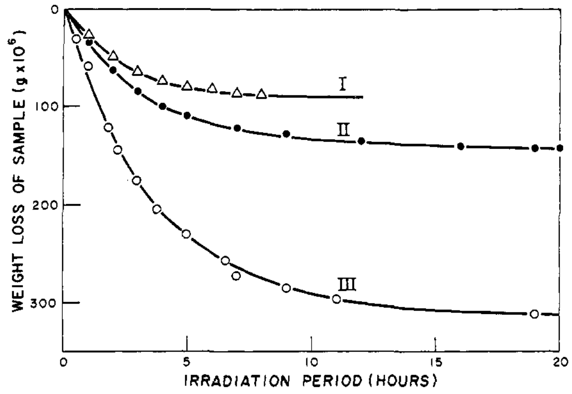
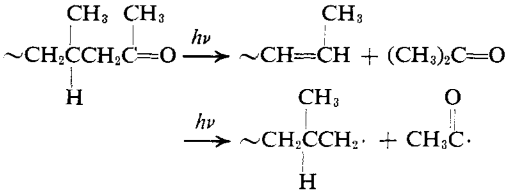


Figure 2. Weight loss curves for irradiated polypropylene films; Osram HBO 200-W lamp used without color filters; sample temperature 30 ± 2°; incident intensity $\cong 6 \times 10^{-6}$ kcal sec^{-1} cm^{-2}: I, 0.0215 g of 16-μ film, OD (1721 cm^{-1}) reduction during irradiation 0.022; II, 0.0468 g of 35-μ film, OD (1721 cm^{-1}) reduction during irradiation 0.036; III, 0.060 g of 57-μ film, OD (1721 cm^{-1}) reduction during irradiation 0.072.

In separate experiments, the volatile products from film samples irradiated under vacuum were condensed in liquid nitrogen and analyzed by gas chromatography and mass spectrometry. An experimental product distribution is shown in Table I. Analysis of products collected at different stages of an irradiation showed that the product distribution was constant up to complete loss of the carbonyl substituents. If it is assumed that the ir extinction coefficient for the carbonyl group (in aldehydes and ketones) is 200 l. mol^{-1} cm^{-1},[4] then the electrobalance curves indicate the loss of 54 ± 10 g of volatiles per mole of carbonyl initially present in the film. This value agrees well with the analytical results which show acetone to be the major product.

(4) J. F. Heacock, *J. Appl. Polym. Sci.*, 7, 2319 (1963).

The analytical results indicate that the dominant degradative process is a Norrish type II cleavage of the excited singlet or triplet state of a methyl ketone[5] (eq 1). The main product of oxidation at 225° must



$$\sim CH_2C(CH_3)(H)CH_2C(CH_3){=}O \xrightarrow{h\nu} \sim CH{=}CH(CH_3) + (CH_3)_2C{=}O \quad (1)$$

$$\xrightarrow{h\nu} \sim CH_2C(CH_3)(H)CH_2\cdot + CH_3\overset{O}{\overset{\|}{C}}\cdot \quad (2)$$

be a ketone group situated at a chain end and is probably produced by the β-scission of an alkoxy radical[6] formed after the oxidation of a tertiary C–H group. This is indicated by a typical change in intrinsic viscosity[7] from 5.60 to 0.63 on oxidation of the polypropylene, but negligible change (from 0.63 to 0.60) on subsequent complete photolysis. The occurrence of a type II process during photolysis was further supported by the change in the 1645-cm^{-1} unsaturation band which indicated an increase in unsaturation equal to the loss of ketone ($\epsilon_{C=C}$ was taken as 20 l. mol^{-1} cm^{-1} [8]). The formation of unsaturated end groups was not detected, probably because of the large number of strong polypropylene bands in the 800–950-cm^{-1} region. Acetaldehyde may possibly be a secondary product from a Norrish type I cleavage (eq 2).

With allowance for the slow, residual degradation of the thicker films, the weight loss curves all fit the first-order rate expression

$$\log \frac{[>C{=}O]_t}{[>C{=}O]_{t=0}} = -\phi_{\text{polychromatic}} \frac{lt}{V} \sum_{\lambda_1}^{\lambda_2} I_\lambda \epsilon_\lambda$$

which is valid for films of low absorption. $[>C{=}O]_t$ is the residual carbonyl concentration at time t, $\phi_{\text{polychromatic}}$ is the quantum yield, I_λ is the incident light intensity on the sample of volume V and thickness l, and ϵ_λ the molar extinction coefficient[9] for the carbonyl group in the wavelength region λ_1 to λ_2. In all determinations of $\phi_{\text{polychromatic}}$ using 35-μ films, the maximum absorption at any wavelength was less than 0.5% of the incident intensity. In the region 2400–4000 Å (Corning C.S. 7-54 filter) at an intensity of 5.3×10^{-6} kcal sec^{-1} cm^{-2}, $\phi_{\text{polychromatic}}$ for the production of acetone was estimated to be 0.10 ± 0.05 mol einstein^{-1}. With the monochromator, similar quantum yields were found at 3000, 3130, and 3650 Å.

Collectively these results indicate that, under our conditions of high processing temperature and high vacuum, carbonyl-initiated photodegradation results in the loss of terminal groups but does not cause scission along the polymer backbone. Trozzolo and Winslow[10] have proposed that, in the presence of oxygen, quenching of the carbonyl triplet may occur to give singlet oxygen, which may then give rise to hydroperoxide groups on the polymer chain. The efficient decomposition of a carbonyl group from its activated singlet (which is not quenched by oxygen) would, however, reduce the importance of the carbonyl group during the photodegradation of polypropylene, except possibly in the very early stages of exposure. After the formation of a very low hydroperoxide concentration, the photolysis of hydroperoxide is likely to dominate subsequent degradative processes. This possibility is now being investigated.

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[10] A. M. Trozzolo and F. H. Winslow, *Macromolecules*, **1**, 98 (1968).

[11] National Research Council of Canada Postdoctoral Fellow, 1967–1968.

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Polymerization of Propylene on Single Crystals of α-Titanium Trichloride

In spite of intensive research carried out over the last 10 years on the mechanism of Ziegler catalysis of olefin polymerization, the exact chemical constitution of the active site responsible for stereospecific polymerization is still, to a large extent, unknown. Further, there is as yet no general agreement as to the order of magnitude of the absolute rate constant for propagation (k_p) for the polymerization of propylene on heterogeneous Ziegler catalysts such as the metal alkyl activated α-$TiCl_3$ system. This is due to an uncertainty in the radiochemical determination of the number of active sites present on the surface of the heterogeneous catalyst and has been discussed in an earlier paper.[1]

We wish to report electron microscopic studies of the stereospecific polymerization of propylene on single crystals of α-$TiCl_3$ which we believe have an important bearing on both of these questions.

In a recent publication, Rodriguez and van Looy[2] used electron microscopy to show that the polymerization of propylene in the gas phase on dry Ziegler catalysts occurs along the growth spirals, on lateral faces, and on surface defects of α-$TiCl_3$ crystals. We have used a similar technique, but have extended the polymerization to obtain an estimate of rates of the various processes involved and the morphology of the nascent polymer.

The polymerizations were carried out in a modified Balzers Micro-BA3 high vacuum coating unit. α-$TiCl_3$ was sublimed onto a thin glass plate and allowed to react with aluminum trimethyl vapor at 25°. Propylene

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