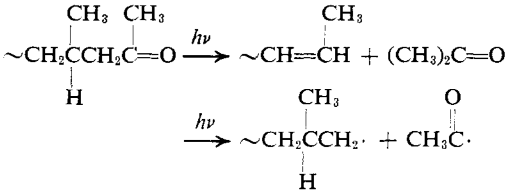
The analytical results indicate that the dominant degradative process is a Norrish type II cleavage of the excited singlet or triplet state of a methyl ketone[5] (eq 1). The main product of oxidation at 225° must



$$\sim CH_2\overset{CH_3}{\underset{H}{C}}CH_2\overset{CH_3}{C}{=}O \xrightarrow{h\nu} \sim CH{=}\overset{CH_3}{C}H + (CH_3)_2C{=}O \quad (1)$$

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

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.

Acknowledgments. The authors are grateful to Dr. J. C. Clunie, Canadian Celanese Co., and to Dr. G. N. B. Burch, Hercules Inc., for gifts of unstabilized polypropylene resin. Thanks are due Mr. J. D. Cooney, Mr. M. E. Bednas and Mr. L. M. King for technical assistance.

(11) National Research Council of Canada Postdoctoral Fellow, 1967–1968.

(12) National Research Council of Canada No. 10362.

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Received May 7, 1968

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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(5) J. Calvert and J. N. Pitts Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966; P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(6) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).

(7) Intrinsic viscosities were determined from measurements in decalin solution at 135°, under nitrogen and with phenyl-β-naphthylamine stabilizer.

(8) F. M. Rugg, J. J. Smith, and R. C. Bacon, *J. Polym. Sci.*, **13**, 535 (1954).

(9) ϵ_λ was assumed to be the same as in model ketones, *i.e.*, ~16 l. mol^{-1} cm^{-1} at 2800 Å.

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

(1) H. W. Coover Jr., J. E. Guillet, R. L. Combs, and F. B. Joyner, *J. Polym. Sci., Part A-1*, **4**, 2583 (1966).

(2) L. A. M. Rodriguez and H. M. van Looy, *ibid., Part A-1*, **4**, 1971 (1966).

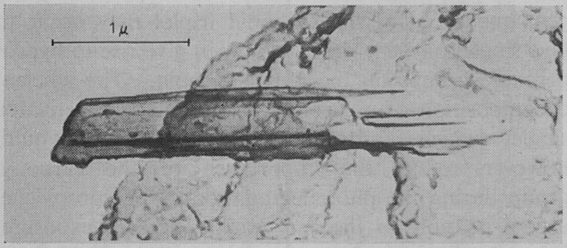

Figure 1. Electron micrograph showing the edge of an α-$TiCl_3$ crystal illustrating the oblique faces of the crystal edge (carbon replica).

gas was admitted from a storage cylinder kept at Dry Ice temperature (143 mm pressure) and polymerization was allowed to continue for a period of up to 60 sec. The reaction vessel was then evacuated and a carbon replica of the catalyst surface was made without breaking the vacuum. After the glass plate was removed from the vacuum chamber, the catalyst was dissolved in alcohol and the replica was floated off on water. Adhering polymer was removed by washing the replica with hot *p*-xylene. The replicas were mounted on grids and observed in a Phillips EM-200 electron microscope.

Sublimed α-$TiCl_3$ crystals obtained by this procedure are frequently regular hexagonal platelets 1–4 μ across and about 0.5 μ in thickness. The lateral faces of the crystal are at an angle of 62° to the basal plane. This is clearly demonstrated in the electron micrographs shown in Figures 1 and 2.

After reaction with $AlMe_3$ and polymerization of propylene for a few seconds, the polymer is seen to form as uniform dots or globules concentrated on the lateral faces, and on the crystallographically equivalent dislocation steps and growth spirals of the crystals (Figure 2). The (001) basal plane of the crystal is totally inactive as was also demonstrated by Rodriguez and van Looy.[2]

Thus it seems likely that the necessary condition for polymerization is a Ti–C bond on a titanium atom accessible through a chlorine vacancy which is found only on the lateral faces and in perturbed regions of the α-$TiCl_3$ crystals. The (001) basal plane is inactive because it contains no accessible titanium atoms.

If a model of the crystal structure of α-$TiCl_3$ is constructed with oblique lateral faces (similar to Figure 1), it is seen that three alternate lateral faces (the 101, $0\bar{1}1$ and $\bar{1}11$) contain accessible titanium atoms (and hence chlorine vacancies) which are inherent in the crystal structure. However, polymer growth appears to take place on all lateral faces, and it appears likely that in a real crystal these vacancies must exist on the other sides as well (*i.e.*, the $1\bar{1}1$, $\bar{1}01$ and 011 planes). These may possibly result from reaction with the aluminum alkyl.

At first the polymer growths appear to be globular, with a diameter of 300–500 Å, spaced relatively uniformly along the lateral faces or at crystal dislocations. As growth continues these seem to elongate into fibrils of approximately the same diameter. This is clearly shown in Figure 3. In some cases dark centers are seen in the fibrils which suggest that they may possibly be hollow, but because of the uncertainties involved in the replication process this possibility can be considered as only tentative until stronger confirmatory evidence is obtained.

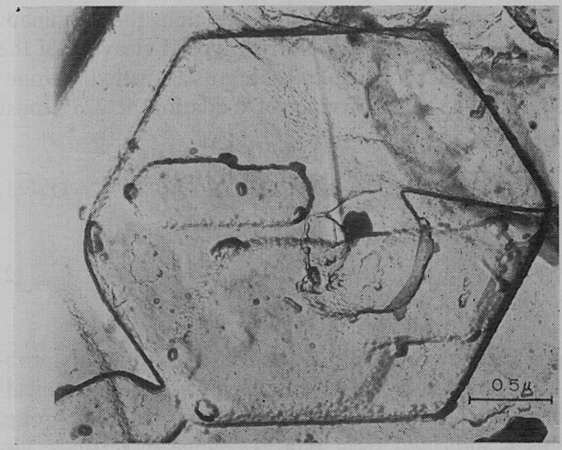

Figure 2. Electron micrograph showing hexagonal crystal of α-$TiCl_3$ after exposure to aluminum trimethyl vapor and propylene. Globules of polypropylene are seen along the lateral faces of the crystal and at dislocation steps (carbon replica; Pt shadowed).

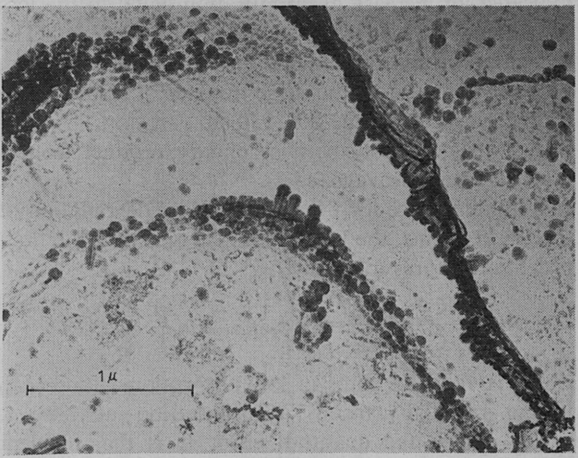

Figure 3. Electron micrograph showing incipient formation of fibrillar polypropylene on lateral faces of α-$TiCl_3$ crystals (carbon replica; Pt shadowed).

The fibrils have striations perpendicular to their axis with a repeat distance of 70 Å, which is approximately the repeat distance expected for a folded chain crystal of polypropylene. This is seen more clearly in the long fibril shown in Figure 4. There seems to be little doubt that these are morphologically the same structures described by Blais and Manley,[3] who observed long fibrils with the same diameter and with striations of 100 Å periodicity in crystalline polypropylene and polystyrene prepared with heterogeneous Ziegler catalysts in slurry systems. Our data now confirm that these are indeed formed on the solid surface of the catalyst as part of the growth mechanism of the polymerization. These must grow by a root-growth process similar to that frequently involved in the growth of ceramic or metallic "whiskers." Because of the polymerization conditions in the present case, it is possible that each fibril might be a single molecule.

(3) P. Blais and R. St. John Manley, *J. Polym. Sci., Part A-1*, 6, 291 (1968).

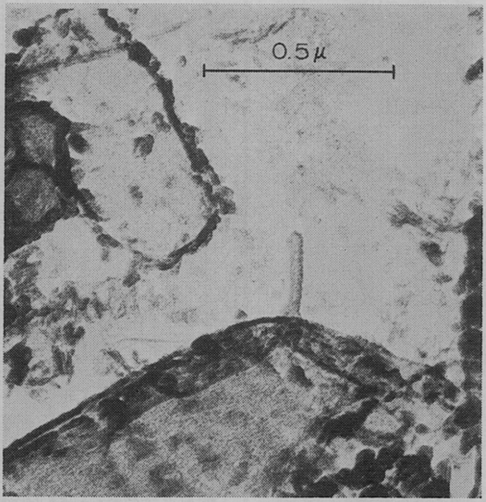

Figure 4. Electron micrograph of a single polypropylene fibril growing from lateral face of α-TiCl$_3$ crystal (carbon replica; Pt shadowed).

The rate of polymerization may be estimated from the size of the fibrils and the time of polymerization. In the calculation it is assumed that the fibrils have the density of isotactic polypropylene and that each fibril is attached to only one active site. The rate of polymerization is given by $R_p = k_p[C^*][M]$ where $[C^*]$ is the number of active sites and is taken as 1 mol and [M] is the concentration of monomer. The rate of polymerization was found to be $R_p = 2 \times 10^4$ mol sec^{-1} per mole of active sites of the monomer and the absolute rate constant was calculated to be $k_p = 2.5 \times 10^6$ l. mol^{-1} sec^{-1}. By comparison, Coover, *et al.*,[1] obtained $k_p = 48$ l. mol^{-1} sec^{-1} for the polymerization of propylene with α-TiCl$_3$–AlEt$_3$ catalyst in a slurry system. The discrepancy by a factor of 5×10^4 seems to be outside the usual limits for experimental error.

The first assumption which might be questioned is whether growth comes only from a single active site. This seems an attractive assumption, since all the globules are the same size and do not completely cover the available surface. If many sites were involved in the production of each globule one might expect a distribution of sizes and a more uniform surface coverage. The number of titanium atoms covered by the base of a globule or fibril is approximately 2000. It would seem that the maximum number of sites which could possibly be involved could not exceed this number, hence the minimum value for k_p must be about 1000 l. mol^{-1} sec^{-1}, or about 20 times the highest value reported previously for this catalyst system. A similar conclusion is reached if one assumes extended chain growth from a large number of sites at the base of the fibril. In this case the cross-sectional area of the polypropylene chain is 34.8 Å^2 and about 2000 would be accommodated in a fibril with a diameter of 300 Å.

Until the number of growth sites per fibril can be established unequivocally, the absolute value of k_p must remain in doubt, but it seems most likely that it lies between 1×10^3 and 3×10^6 l. mol^{-1} sec^{-1}. The lower values observed in slurry systems at higher conversions must surely be due to the fact that monomer must diffuse through a polymer film or a matrix of fibrils in order to reach the catalytic surface, and the rate is diffusion controlled under such conditions.

Certain other conclusions may be deduced from these data. If the area of an active site is that surrounding a single titanium atom this would be approximately 16 Å^2. With a propylene pressure of 143 mm, the rate of impact of propylene molecules on such a surface area can be calculated from the kinetic theory of gases to be 3.7×10^6 molecules per second. The fibrils grow at a rate of 2×10^4 molecules (of propylene) per second which is considerably slower and is obviously not controlled by the rate of gaseous diffusion to the uncovered surface of the catalyst. On the other hand, a simple calculation assuming Fick's law of diffusion and a diffusion coefficient of 10^{-6} cm^2 sec^{-1} for propylene through crystalline polypropylene suggests that if a single active site were at the center of the base of a fibril, the rate-controlling step could be the rate of diffusion of propylene through the polymer to the active site. Alternatively if the site is not occluded by the base of the fibril, a simple Langmuir treatment suggests that the rate-controlling step could be the rate of adsorption of monomer on a chlorine vacancy adjacent to a titanium atom in the crystal. The solution of these two possibilities must await the results of further research now in progress.

Acknowledgment. The authors wish to acknowledge the support of the National Research Council of Canada and the Petroleum Research Fund of the American Chemical Society.

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Received May 27, 1968

Diels–Alder Polymers. Polyimides from a Biscyclopentadienone and Bismaleimides

The well-known 1,4-cycloaddition reaction of a 1,3-diene to a dienophile to form a six-membered adduct, commonly known as the Diels–Alder reaction, is one of the most useful synthetic organic reactions. Although this reaction usually provides a high yield of adduct, there are few reported syntheses of polymers which employ it as a step-growth reaction.[1] Most of these syntheses afford low molecular weight polymers due to the ease with which reverse reactions take place[2] and a high frequency of side reactions, such as chain-growth polymerization of the diene.[2,3] The rigid, ring-containing polymer which is formed may also precipitate from the reaction medium resulting in an early termination of the polymerization.[4]

Substituted cyclopentadienones are particularly interesting dienes, since their adduction to a dienophile is accompanied by the loss of carbon monoxide, and therefore the reverse reaction is prevented. Different substituents on the cyclopentadienone ring guide the course of the cycloaddition reaction. Certain tetrasubstituted cyclopentadienones with small substituents

(1) J. K. Stille, *Fortschr. Hochpolym. Forsch.*, **3**, 48 (1961).
(2) J. K. Stille and L. Plummer, *J. Org. Chem.*, **26**, 4026 (1961).
(3) R. W. Upson, U. S. Patent 2,726,232 (Dec 6, 1955).
(4) W. J. Bailey, J. Economy, and M. E. Hermes, *J. Org. Chem.*, **27**, 3295 (1962).