Communications to the Editor

Mechanism of Propylene Polymerization on Single Crystals of α-Titanium Trichloride

In a recent publication[1] we have shown that the polymerization of propylene in the gas phase on dry single crystals of α-$TiCl_3$ activated with aluminum trimethyl vapor occurs along growth spirals, on lateral faces, and on surface defects of the α-$TiCl_3$ crystals. Initially, the polymer growths appear globular with a diameter of 200–500 Å. As growth continues these globules elongate into fibrils of approximately the same diameter with striations approximately perpendicular to the fibril axis. This work has now been extended to elucidate the mechanism of fibrillar growth.

Experimental Section

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 room temperature. Propylene gas was admitted from a storage cylinder kept at low temperature to provide propylene pressure at 150–350 Torr. Polymerization was allowed to continue for a period of 10–60 min. The reaction vessel was then evacuated and a carbon replica of the catalyst surface was made. After removing the glass plate from the vacuum chamber, the catalyst was dissolved in methanol at 25° and the replica floated off on water. No attempt was made to remove the polypropylene from the replica. The mounted replicas were observed in a Philips EM-200 electron microscope.

Larger amounts of polymer were synthesized in an evacuated glass tube containing about 2 g of α-$TiCl_3$. The polymer was washed initially with 1% HCl in methanol at 25° and then several times with pure methanol. About 50 mg of polymer could be produced at one time in this manner. This polymer was used for dsc studies after it was shown by electron microscopy that it contained similar fibrillar structures.

Results and Conclusions

The electron micrographs show a large number of polymer fibrils on the lateral edges of the catalyst crystal (see Figure 1). These fibrils are up to 15,000 Å in length and 400–600 Å in diameter. The fibrils grow on a broad base which is usually 1000–1500 Å in diameter (Figures 1 and 2). Most fibrils show striations making angles of 75–90° with the fibril axis and with a periodicity of 100–150 Å. This is approximately the repeat distance expected for a folded chain crystal of polypropylene. These fibrils appear to have a structure similar to those described by Blais and Manley[2] prepared by slurry polymerizations. Figure 2 shows some fibrils which broke roughly perpendicular to the fibril axis. This has an important bearing on the growth mechanism. The periodicity of the striations and the appearance of the broken fibrils suggest that the fibrils are composed of stacked highly crystalline lamellae.

Figure 1. Polypropylene fibrils growing on the lateral edges and on surface defects of the α-$TiCl_3$ crystal. Carbon replica. Electron micrograph.

Morrow[3] has reported the existence of three crystal forms of polypropylene. α-PP [$T_m(\alpha) = 165°$] is monoclinic and is produced by melt or solution crystallization. This form contains chain folded lamellae. β-PP [$T_m(\beta) = 150°$] is hexagonal and is produced by (i) crystallization within a narrow temperature range (~100–130°) or (ii) crystallization with nucleating agents. γ-PP [$T_m(\gamma) = 150°$] results from melt recrystallization at elevated pressure and is triclinic in form. There are two states; the stable state contains extended chain segments and the metastable state contains some chain folded lamellar crystals. A dsc run shows a doublet at 152° due to γ-PP and a single peak at 160° due to the transition $\gamma\text{-PP} \rightarrow \alpha\text{-PP}$.

Our studies of fibrillar polypropylene show a single dsc peak at 162–165.5° which is indicative of the α form, *i.e.*, chain-folded lamellae. No evidence was found for extended chain crystallization. The heat of fusion ΔH_f for the polymer was obtained from the area of the melting peak and was found to be 25.7 cal/g. Wilkinson and Dole[4] estimate the heat of fusion for 100% crystalline isotactic polypropylene to be 35 cal/g.

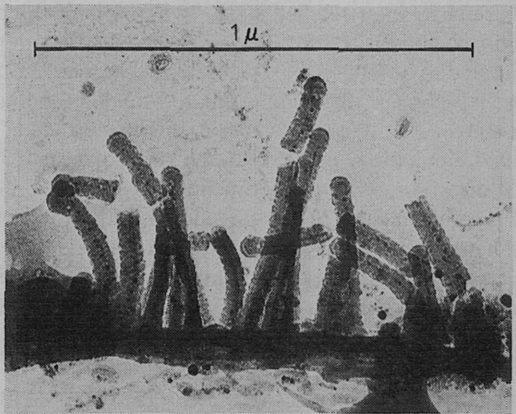

Figure 2. Fractured polypropylene fibrils. Carbon replica. Electron micrograph.

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

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[4] R. W. Wilkinson and M. Dole, *J. Polym. Sci.*, **58**, 1089 (1962).

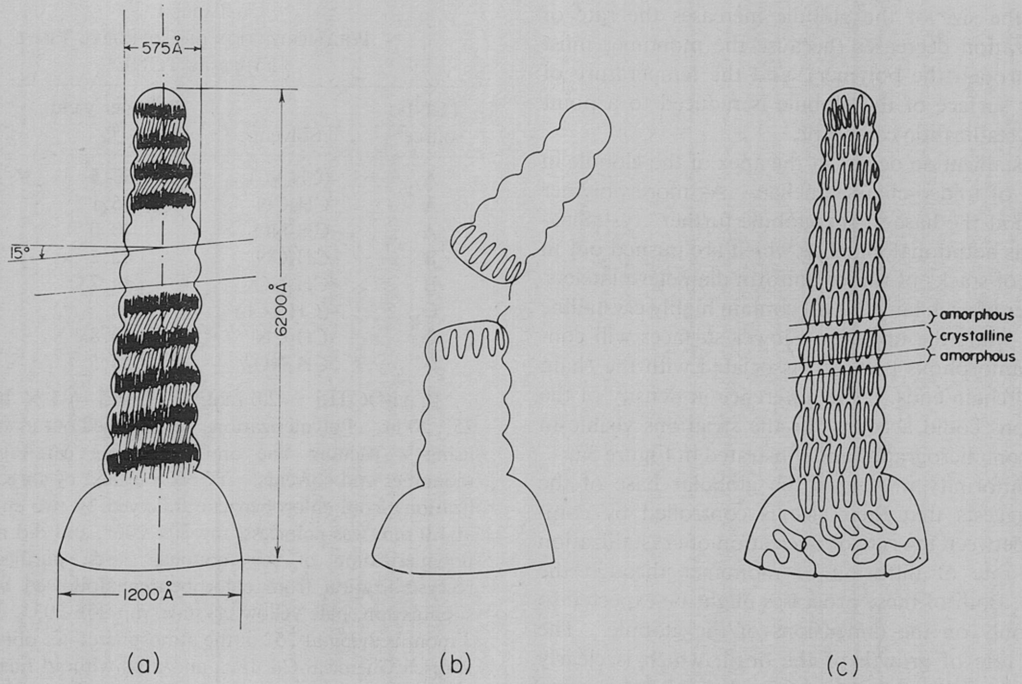

Figure 3. (a) The appearance of a typical fibril in the electron micrographs; (b) a fractured fibril; (c) proposed structure of the fibrils.

Hence, the overall crystallinity of our fibrils is estimated at about 73%.

Since there was no evidence of the β-PP form in our fibrils and the dsc melting peak occurred at 165° the fibrillar material appears to have a structure similar to that of polypropylene crystallized at a temperature greater than 125°.

Using X-ray and electron diffraction Blais and Manley[2] found that the molecular orientation was approximately parallel to the fibril axis. Low-angle X-ray analysis revealed a long spacing of around 100 Å which corresponded to the striation repeat distance in the fibrils. Since the polymer molecules are much longer than 100 Å, the fibrils were presumed to contain folded chains. The similarity in major structural features suggest that the fibrils prepared by our method have a similar orientation.

The electron micrographs show that most of the polymeric material formed is fibrillar in structure. It appears therefore that the fibrils consist of stacks of platelets or lamellae consisting of chain-folded molecules growing on top of one another as shown in Figure 3c.

Several authors[5–7] have described polyolefin fibrils arising from crystallization of stirred solutions of polyolefins and from nascent polymerization in slurry systems. These consist of lamellar platelets strung out at more or less regular intervals along an extended-chain central filament in a co-called "shish-kebab" arrangement. Such a structure seems inappropriate in the present instance for the following reasons.

1. The fracture patterns shown in Figure 2 are not consistent with the presence of a core of extended chain crystals.

2. There is no evidence of the γ form of polypropylene (characteristic of extended chain or high melting material).

3. While in principle it may be possible to devise a growth mechanism which would give a core of extended chain polymer, in the present catalytic situation there is no appropriate way to account for the growth of folded-chain overgrowths, as would exist in a shish-kebab structure.

On the basis of Figure 3 we propose the following mechanism for polymer growth, illustrated in Figure 4.

1. Polymer growth occurs at one or more active sites at defects on the $TiCl_3$ crystal surface. The rate of polymerization is initially more rapid than the rate of crystallization and hence the initial structure formed is a hemispherical mass of amorphous polymer. The temperature of the polymer close to the active site may be quite high because of the exothermic nature of the polymerization process ($\Delta H_p \simeq -25$ kcal mol^{-1}).[8]

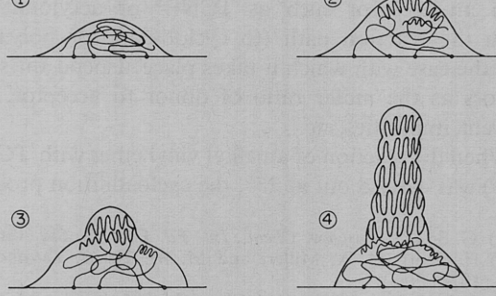

Figure 4. Proposed mechanism for fibril growth.

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2. As the size of the globule increases the rate of polymerization decreases (because the monomer must diffuse through the polymer), and the temperature of the outer surface of the globule is reduced to a point where crystallization can occur.

3. Crystallization occurs at the apex of the globule in the form of folded-chain lamellae. As more polymer is formed at the base of the globule further crystallization forms additional lamellae which are pushed out in the form of stacks of rather uniform diameter platelets. The center of each lamella will contain highly crystalline polymer, while the upper and lower surfaces will contain the amorphous polymer associated with the chain folds and chain ends. The difference in density of the two regions could account for the striations visible in the electron micrographs and illustrated in Figure 3a.

The uniformity in size of the globular base of the fibrils suggests that their size is controlled by competition between the rate of nucleation of crystallization and the rate of diffusion of monomer through the globule. Both of these processes might be expected to depend only on the dimensions of the globule. The absolute rate of growth of the fibril, which is clearly different at different locations on the catalyst surface (Figure 1), may depend on the number or activity of the catalyst sites located at the base of the fibril.

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Polymerization of Alkyl Vinyl Ethers by Tricyanoethenol in Tetracyanoethylene

Vinyl monomers containing electron-donating substituents are known to polymerize in the presence of an organic electron acceptor *via* a charge-transfer mechanism of initiation. Tetracyanoethylene (TCNE) is a strong electron acceptor[1] which has been reported to initiate the polymerization of N-vinylcarbazole[2,3] and ketene diethyl acetal.[4] TCNE also affords cyclobutane derivatives in reactions with N-vinylcarbazole[3,5] and alkyl vinyl ethers.[5]

Both the initiation of the polymerization of N-vinylcarbazole and the formation of the cyclobutane derivative have been postulated to take place through a charge-transfer complex of the N-vinylcarbazole donor with an acceptor such as TCNE[3] or acrylonitrile.[6] Both the reaction path (to cyclobutane or polymer) and the ease with which it takes place depend on such factors as the molar ratio of donor to acceptor, the solvent, impurities, etc.

When the reaction of an alkyl vinyl ether with TCNE (2:1) was carried out at 25°, the cycloaddition product was obtained. The red-orange color of the charge-transfer complex appeared immediately and, from the rate of disappearance of the color, it was observed that the rate of cyclobutane formation followed the order $C_2H_5- < (CH_3)_2CH- < t\text{-}C_4H_9-$. The reaction in a polar solvent, acetonitrile, was faster than in a nonpolar solvent, toluene.

TABLE I
POLYMERIZATION OF ISOPROPYL VINYL ETHER BY TCNE[a]

TCNE source[b]	Solvent	Polymer yield, %	η_{sp}/C[c]
A	$(CH_2)_2Cl_2$	63.4	0.31
A	CH_3CN	85.1	0.10
A	CH_3NO_2	70.0	0.11
B	CH_3CN	42.2	
B	CH_3NO_2	39.7	
C	$(CH_2)_2Cl_2$	0	
C	CH_3CN	10.8	
C	CH_3NO_2	4.5	

[a] $[C_3H_7OC_2H_3] = 2.0$ mol/l., $[TCNE] = 5 \times 10^{-3}$ mol/l., 25°, 20 hr. Polymerizations were carried out in an ampoule using a vacuum line and employing carefully purified monomer and solvents. TCNE purified by three recrystallizations from chlorobenzene followed by two sublimations at 1.0 mm was colorless, mp 205–206°, and did not initiate polymerization of the monomer. [b] A, purified by one recrystallization from chlorobenzene followed by vacuum sublimation, pale yellow crystals, mp 201–203°; B, A after 3 months aging at 25° in the atmosphere; C. obtained from Aldrich Chemical Co. Inc., and used without further purification, light brown crystals, mp 197–200°. [c] Determined in benzene at 30° ($C = 0.5$ g/dl).

Highly purified TCNE would not initiate polymerization, even in polar solvents such as acetonitrile and nitromethane. However, when a catalytic amount of TCNE which was incompletely purified was added ([TCNE]/[alkyl vinyl ether] = 1:400) polymerization took place, depending on the solvent and purity of the TCNE. The polymerization of isopropyl vinyl ether, as well as *n*-butyl, isobutyl, and *t*-butyl vinyl ethers in polar solvents, was found to be initiated by incompletely purified TCNE. The results of polymerization of isopropyl vinyl ether are given in Table I.

This effect of impurities on the polymerization is similar to that found for the polymerization of N-vinylcarbazole initiated by *p*-chloranil. In this case, the initiator was found to be an acidic impurity, 3,5,6-trichloro-2-hydroxy-1,4-benzoquinone, in the chloranil.[7]

In these polymerizations, the red-orange color of the charge-transfer complex did appear immediately on mixing the TCNE and isopropyl vinyl ether in acetonitrile, but disappeared within a few seconds. Precipitation of the polymer from the solvent, however, did not occur until 10–30 min after mixing and polymerization continued in the colorless media. Thus it appears that the charge-transfer complex is not responsible for polymerization, since the color of the complex is not present throughout the polymerization, and it is unlikely that any cationic species formed *via* the charge-

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