

Effect of Surface Characteristics on Polymer Growth on Titanium Trichloride Catalyst

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Synopsis

Large sublimed leaflets of titanium trichloride have been observed over a wide range of magnification both by optical and electron microscopy under conditions such that ethylene polymerization was slow enough so that its progress could be observed in detail. After treatment with triethylaluminum, a network of cracks develops on which polymer grows upon introducing ethylene. Polymer also appears on steps, crushed areas, and cleaved edges but not on as-grown edges. The polymer appearing on lateral surfaces was nodular in character while that growing on basal surfaces was fibrous. The physical properties of these two forms may be different, and methods for favoring one or the other are suggested.

INTRODUCTION

The opportunity for microscopically observing the behavior of the active portions of Ziegler catalysts has not been extensively exploited. They have most often been observed in a finely divided form, and the polymeric product rather than the catalyst itself has been the focus of attention.^{1,2} Only rarely has the actual catalyst surface been examined in detail.

In one such study, Hargitay and co-workers³ used optical microscopy to observe the growth of ethylene polymer on the catalyst surface. The solid phase consisted of large, sublimed single leaflets of titanium trichloride which had been previously reacted with aluminum alkyl. Both aluminum alkyl and ethylene were added in the gas phase. The authors stated, a priori, that active sites may form at various locations on the solid surface: (a) at any point on the basal surface, (b) at places where titanium ions are exposed, and (c) at places where single imperfections occur. They then proposed that polymer growth should occur on a surface, along lines, or in spots, the three cases corresponding to the three active site locations. The polymer was observed to form along lines, and it was concluded that active site formation required a titanium ion which was accessible to the surface and that this was most likely to be the case on lateral surfaces.

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In a more recent study, Rodriguez and co-workers^{4,5} used an electron microscope to observe polymer formation on finely divided titanium trichloride. As in Hargitay's study, aluminum alkyl and monomer were added in the gas phase. Dots that were believed to be traces of polymer were observed on hexagonal faces of TiCl_3 leaflets. They were localized along a spiral which the authors believed to be a crystal growth spiral. Thus, they also concluded that the lateral faces produced the active sites.

In view of these successes, it seems that additional information concerning the action of heterogeneous catalysts in general and Ziegler catalysts in particular can be obtained by this approach. The observation of the same type of crystal with both optical and electron microscopy might yield valuable insight. The effects of various catalyst surface features and of various forms of mechanical treatment of the crystals on polymer growth might be observed. In addition to these relatively obvious sources of information, more subtle features might also be discernible.

Large, sublimed leaflets of titanium trichloride are well suited for use as the solid phase in making such observations. Much is known about the crystallographic nature of TiCl_3 . Also, sublimed crystals are of such a size that they can easily be observed by electron microscopy. Thus, they can be studied over a very wide range of magnifications. The optical studies are most valuable for a general view of a large area, while electron microscopy is useful for observing particular areas of interest. In addition, their size permits various forms of mechanical treatment to be administered under controlled conditions. The leaflets, for example, can be cleaved in any desired direction (perpendicular to the basal plane). When monomer is added, large sublimed crystals are covered with polymer much more slowly than finely divided material, and various stages of this process can thus be followed with little difficulty.

Accordingly, the solid catalyst formed by reacting large, sublimed leaflets of titanium trichloride with triethylaluminum (TEA) in a hydrocarbon solvent was chosen for use in this research. This catalyst was used to polymerize ethylene monomer dissolved in hydrocarbon solvent. The crystals were observed before, during, and after the addition of triethylaluminum and ethylene using both optical and electron microscopy. Observations were recorded in the form of photomicrographs, and are subjected to analysis in the light of known theory and hypothesis. Because of the slow polymer growth rate on large crystals, it was possible to record a number of interesting phenomena which confirm existing theories on Ziegler-type catalysts as well as add new insights concerning the mode of polymer growth on the catalyst.

EXPERIMENTAL

Preparation of Titanium Trichloride Crystals

Anhydrous, hydrogen-reduced, nonactivated, powdered TiCl_3 (Anderson Chemical Division of Stauffer Chemical Company) was used in preparing

large leaflets. All manipulations of TiCl_3 were carried out under a nitrogen atmosphere in a dry box. The powder was sublimed in a sealed 19-mm fused quartz tube (Lamp Glass Dept., General Electric, Inc.) 9 to 12 in. long. Sublimation and recrystallization were carried out in a gradient furnace. The subliming portion of the tube was maintained at 880° to 900°F , and the condensing portion, at 680° to 700°F . The tube was rotated periodically during the process. Leaflets of adequate size formed in about three days. The growing period was terminated by removing the tube from the furnace. In the dry box, the leaflets were removed from the tubes and placed in small, open sample bottles. These small bottles were placed in larger bottles which contained a small amount of phosphorus pentoxide. The larger bottles were tightly capped and stored in the dry box.

Optical Microscopic Observations

A polymerization reactor designed for ease of microscopic viewing was constructed of a short brass cylinder as shown in Figure 1. The lid was a

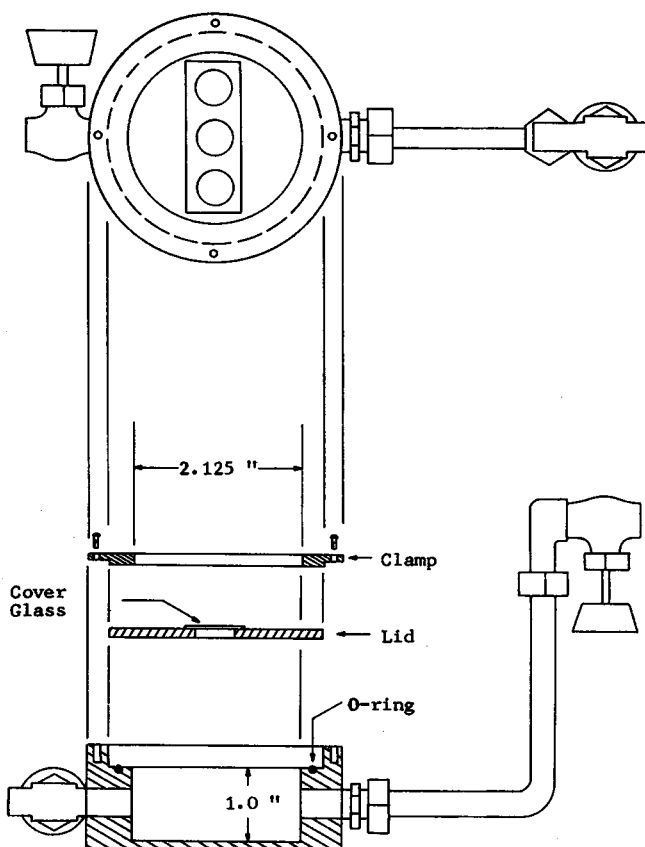


Fig. 1. Polymerization reactor.

brass disk with three $\frac{3}{8}$ -in. holes drilled through it. A #2 micro cover-glass was cemented to the lid such that the holes were covered. The TiCl_3 crystals were viewed through these holes. The reactor lid was inverted, and a very short cylindrical spacer (0.313 in. \times 0.372 in. \times 0.025 in.) was placed inside each hole so that it rested against the cover glass. A titanium trichloride leaflet was then placed inside the spacer so that it, too, rested on the cover glass. A circular piece of copper screen slightly larger than $\frac{3}{8}$ in. in diameter was then forced into the hole in the lid with a brass rod. When the lid was turned over and placed on the reactor, the screen supported the titanium trichloride leaflets just below the cover glass.

When the crystals were to be observed before adding the co-catalyst, the reactor was filled with carefully dried n-heptane or decalin. After observations had been made (or, on occasions when co-catalyst was added immediately), the reactor was filled with co-catalyst, a 25% solution of triethylaluminum (TEA) in n-hexane, obtained from Texas Alkyls, Inc.

Polymerization was initiated by bubbling ethylene (C.P. grade from The Matheson Company, Inc.) through the liquid in the reactor. Enough ethylene to eventually cover three large titanium trichloride leaflets with polymer would easily dissolve in the TEA-hexane solution.

Two optical microscopes were used to observe the titanium trichloride crystals. A Bausch & Lomb Stereo Zoom, Model KVB-73, was used for observing the gross morphology of the crystals and polymer. The microscope used in recording most of the data was a Carl Zeiss Epi-E. A Zeiss Ikon 35-mm camera and beam splitter were used with both microscopes. Kodak High Contrast Copy Film and D-19 Developer were used with the Zeiss microscope. With the Bausch & Lomb microscope, Kodak Plus-X Pan Film and Microdol-X Developer were used.

Electron-Microscopic Observations

Platinum-shadowed carbon replicas of the leaflets were prepared in a vacuum evaporator and observed with the electron microscope. The leaflets were transported from the dry box to the evaporator in a modified form of the polymerization reactor. A glass microscope slide was placed on a platform in the reactor such that the slide was parallel to and about $\frac{1}{4}$ in. below the reactor lid. The leaflet to be replicated was placed on this slide. When a fresh leaflet was to be replicated, it was transferred directly from a recrystallization tube onto the glass slide. When a leaflet was to be reacted with TEA before being replicated, it was placed in a sample bottle half filled with the alkyl and kept in the dry box. Ethylene was bubbled through the liquid in the sample bottle when polymer was to be observed. After removal from the TEA solution, the leaflet was washed in carefully dried decalin and placed on the glass slide. The lid was then placed on the reactor, and the reactor was evacuated. It was then removed from the dry box and placed in the vacuum evaporator. After the bell jar had been evacuated, the evaporator shutter lever was used to lift the lid from the reactor. After the replica had been prepared, the evaporator was opened

and the leaflet was picked up and immersed in water. This separated the replica from the leaflet, the replica floating free on the water. Polyethylene present at this time tended to adhere to the replica rather than the TiCl_3 . No attempt was made to remove it, and it caused no problem if the electron beam intensity in the microscope was kept low. The replica was removed from the water on adhesive-coated copper grids, allowed to dry, and stored in gelatin capsules. Observations were made using a Japan Electron Optics Laboratory Co. electron microscope (Model JEM 150). An accelerating voltage of 80 kV was employed. Images were recorded on Kodak Projector Slide Plates and developed in Dektol Developer.

OBSERVATIONS AND CONCLUSIONS

Observations of the titanium trichloride crystals can conveniently be divided into three categories: (a) freshly grown crystals, (b) crystals after the addition of triethylaluminum, and (c) crystals after the addition of triethylaluminum and ethylene. Each group will be discussed separately.

The polymer, as it grew on the surface of the crystal, did not reflect light as well as the crystal. Thus, when viewed through the Zeiss microscope, it appeared dark and the TiCl_3 surface appeared light. This coloring is the opposite of what one sees using the Bausch & Lomb microscope or the naked eye. So that the photographs look more like what one would expect to see, all Zeiss photomicrographs are printed as negatives. The contrast also appeared reversed in electron photomicrographs; therefore, they are also printed as negatives.

Freshly Grown Crystals

The freshly grown crystals were magenta in color and normally joined together to form flat leaflets about 0.1 mm thick. Some were so thin that one could see through them, while others were quite opaque. They were irregularly shaped but with straight edges and hexagonal angles (often 120° , occasionally 60°) in evidence. Their diameters ranged from 1 to 10 mm or larger.

The microscope revealed a number of characteristic features. Usually, large areas of the crystals were flat and smooth. Such areas were broken by linear steps appearing singly or in groups. Often, these steps intersected to form 60° angles, 120° angles, or (less commonly) equilateral triangles.

Crushed or damaged areas were very noticeable. Tapping a crystal with the end of a glass rod produced defects of the type shown in Figure 2.

Spirals which were almost surely growth spirals were sometimes seen. Both rectilinear and round-edge spirals were observed (Fig. 3).

They were not seen on very fresh crystals, but seemed to appear only after the crystals had been stored for several days or treated with alcohol. This suggests that some form of limited attack of titanium trichloride is



Fig. 2. A damaged area of a titanium trichloride crystal. Optical photomicrograph. 350x.

necessary before growth spirals can be seen. Rodriguez and associates^{4,5} have also reached this conclusion.

Crystals After the Addition of Co-catalyst

The most noticeable change effected by the TEA was the appearance of random "cracks" in the TiCl_3 surface. They usually formed networks, sometimes quite loose and sometimes dense. The time required for the cracks to become visible (at 320 \times) after the addition of TEA to the system varied between several minutes and several days.

As would be expected, when cracks first became visible in an area of a crystal, only a few were present. As the time of contact between the crystal and TEA increased, the cracks increased in size and number. This latter increase was much more noticeable. That is, in many instances the change in size of a crack with time was almost imperceptible. The change in number of cracks in an area, however, was always readily observable.

One other feature, which was apparently the result of the TiCl_3 -TEA interaction, sometimes appeared on the crystal surfaces. This was a number of small "humps" that usually appeared soon after the addition of TEA to the reactor. Their nature was difficult to ascertain. In many instances, they did not appear to be an integral part of the surface, but only adhered to it. They did not seem to affect in any way the subsequent formation of cracks or growth of polymer in the area. Generally, they became less and less noticeable as time progressed and as cracks appeared.

All of the above effects can be seen in Figure 4. This sequence of photomicrographs records the formation of a network of cracks. The first

photograph shows a titanium trichloride crystal in heptane. In (b), the same surface is shown after 5 hr in TEA; in (c), after 113 hr in TEA; and in (d), after 136 hr in TEA.



(a)



(b)

Fig. 3. Growth spirals on sublimed TiCl_3 crystals. Optical photomicrographs. 350x.

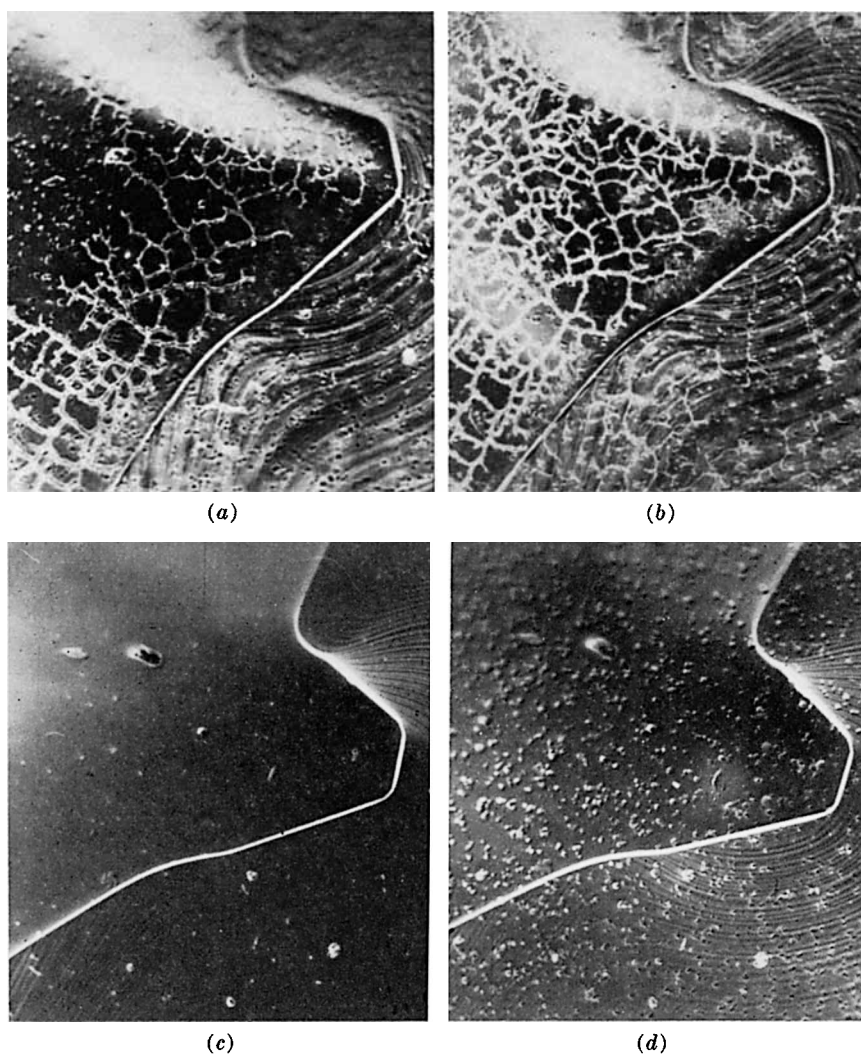


Fig. 4. Formation of large "cracks" on a TiCl_3 surface. Optical photomicrographs. 350x.

In many instances, the formed cracks were much thinner and the network mesh much finer than those shown in Figure 4, and some areas appeared to be devoid of cracks. These facts suggest that even finer cracks might have been present which could not be seen with the optical microscopes. Electron photomicrographs were obtained to resolve this issue. All replicas of the catalyst crystals produced after the crystal had been contacted with TEA appeared very similar to the one shown in Figure 5 and demonstrate that cracks form very soon after adding TEA. It seems reasonable to conclude that very fine cracks always form when the titanium trichloride crystals are contacted with triethylaluminum.

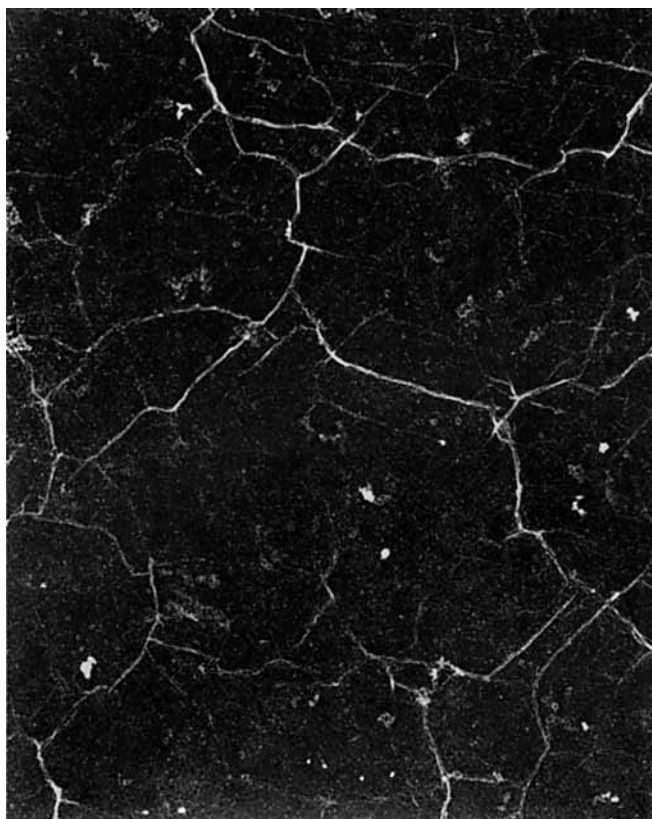


Fig. 5. Electron photomicrograph of a titanium trichloride surface after being contacted with triethylaluminum for 2 hr. 3700x.

Hargitay and co-workers³ observed "cracks" similar to those presented here on sublimed titanium trichloride crystals after they had been reacted with gas-phase aluminum alkyls. In their electron microscope observations, however, Rodriguez and co-workers^{4,5} could detect no change in finely divided TiCl_3 after reaction with trimethylaluminum.

Several conclusions concerning the titanium trichloride-triethylaluminum reaction are apparent: (a) the reaction does effect a microscopically visible change in the titanium trichloride surface, at least when large sublimed crystals constitute the solid phase; (b) this change, the appearance of random lines resembling cracks, affects a large portion of the total surface area; (c) the crack size varies over a wide range; and (d) the time required for the cracks to become visible at $320\times$ varies over a considerable range.

Very little can be definitely stated, however, about the nature of the cracks themselves. One possibility is that they are traces of polyethylene. It has been experimentally observed⁶ that small amounts of polymer are formed by the reaction in question. It is also possible that the cracks are, in fact, cracks. These could be formed in any of several ways. The fix-

tion of the aluminum alkyl in the solid phase might cause fissures or other surface imperfections already present to expand. The TiCl_3 -TEA reaction does exert mechanical forces on the crystals. When the reaction is carried out using very thin crystals, we have observed considerable buckling and bending of the crystals in question. It is also known that two adjacent Cl layers in an alpha-titanium trichloride crystal are only weakly bound together. Therefore, starting at an existing imperfection, it could be relatively easy to "peel back" several layers of the crystal.

A similar situation could also arise even when no surface imperfection is initially present. The titanium alkyl compound initially formed by the titanium trichloride-triethylaluminum reaction is to some extent unstable

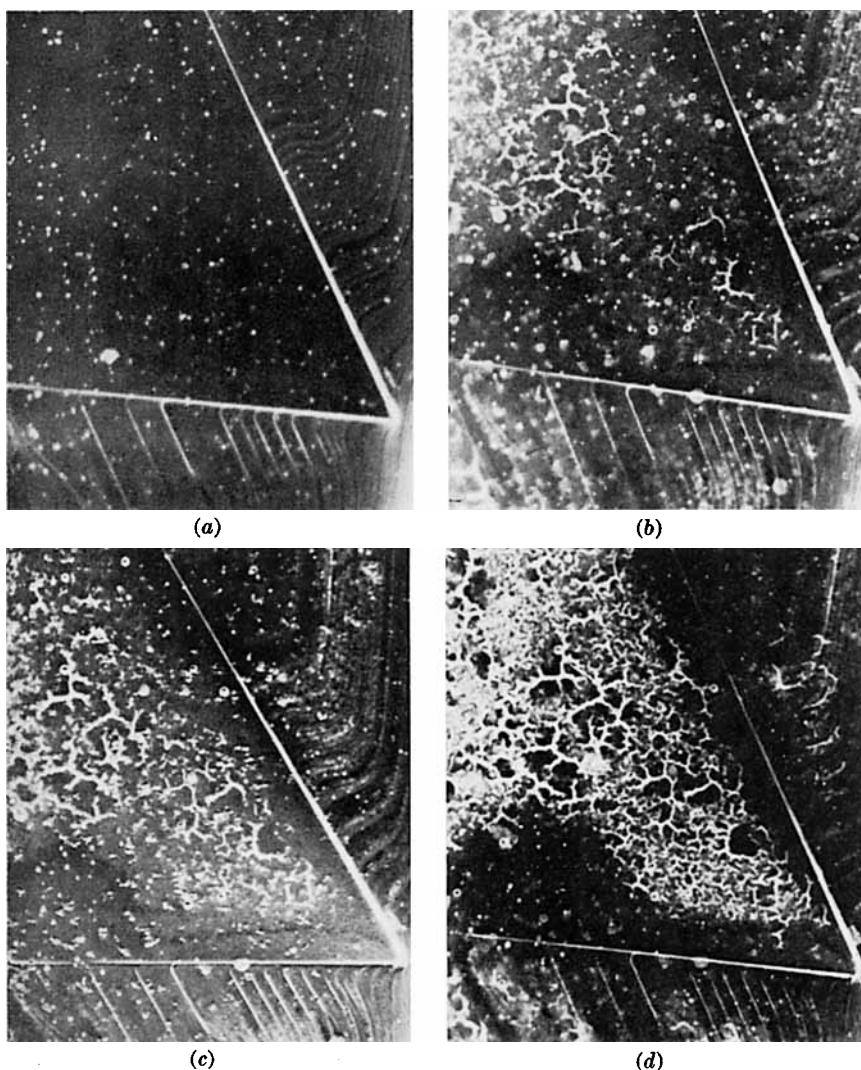


Fig. 6 (continued)

and tends to decompose before it can add a trialkylaluminum molecule.⁶⁻⁸ Relative rates of decomposition and aluminum fixation appear to depend strongly on reaction conditions. When triethylaluminum is the alkylating agent, decomposition is favored in the 20° to 65°C range.⁶ Thus, in the reactions carried out in this research, a large number of basal Cl vacancies are likely.⁶ The creation of basal Cl vacancies would expose inner Ti ions and could lead to alkylation of and aluminum fixation to ionic layers below the uppermost. This rather violent event could produce cracking or peeling of the crystal surface. The failure of Rodriguez and colleagues to

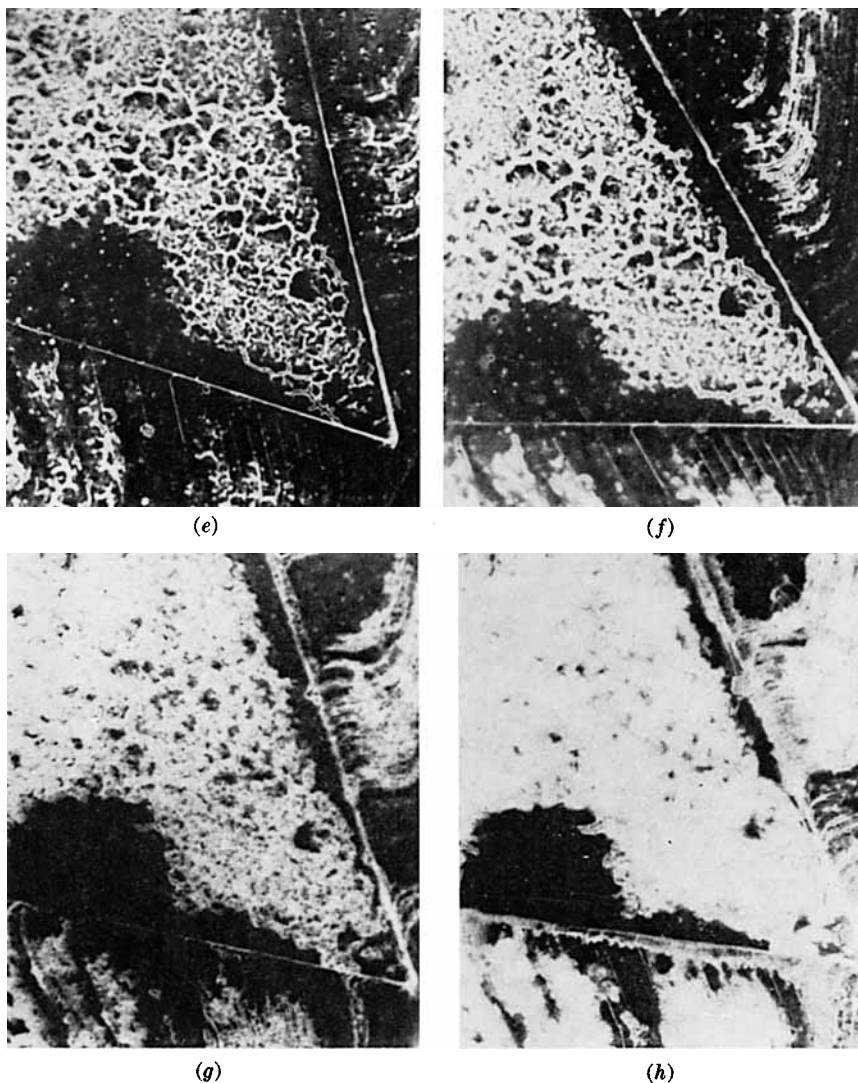


Fig. 6. Crack formation and growth of polymer on a catalyst crystal. Optical photomicrographs. 350x.

observe similar cracks can be explained by the relative stability of the titanium-methyl bond under the conditions of their reaction.

Crystals after the Addition of Monomer

In all reactions observed, dramatic changes in the catalyst surface occurred soon after the addition of ethylene. Polymer was always observed within 2 hr.

Since a number of observations are to be described and a number of points discussed in this section, it will be divided into several subsections. Each subsection will be concerned with polymer growth of a particular form or associated with a particular surface feature.

Buckling of the Crystals

Buckling of the crystals during polymer growth has been observed previously.⁹ When the thinner crystals were used, buckling and curling, especially at the edges, occurred early in the reaction. With thicker crystals, these effects were not noticeable to any great extent until after large amounts of polymer had formed.

Polymer Growth Along Cracks—Optical Microscopy

When cracks were visible in an area before the addition of ethylene, polymer formed along them. Figure 6 is a sequence similar to that shown in Figure 4. In this test, ethylene was added to the reactor after 141 hr of activation. The sequence shows (a) a fresh crystal in heptane, (b) the same surface area after 112 hr in TEA, (c) after 116 hr in TEA, (d) after 123 hr in TEA, (e) 40 min after the addition of ethylene, (f) 135 min after the addition of ethylene, (g) 9 hr 40 min after the addition of ethylene, and (h) 23 hr after adding ethylene.

Growth of polyethylene can be observed most profitably on fine cracks that are not so densely packed. Figure 7 not only shows the growth of polymer on small cracks, but also provides a study of the changes taking place during the initial stages of polymerization. Part 7a is a photograph taken after 22 hr of contact with TEA solution. After this activation time, ethylene was bubbled into the reactor, and the remaining photomicrographs were obtained: 7b, 15 min after the addition of ethylene; 7c, 36 min after the addition of ethylene; 7d, 51 min after the addition of ethylene; 7e, 85 min after the addition of ethylene; and 7f, 127 min after ethylene addition.

Apparently it is reasonable to conclude that when "cracks" are visible in an area before monomer is added, polymer forms along the cracks. This is evidenced by a "fuzziness" and general widening of the cracks. These effects become noticeable soon after monomer addition. In some instances, definite cracks were not visible at 320 \times in an area before the addition of monomer, but when polymer grew in such areas, it had the appearance of polymer growing on fine, closely, packed cracks.

Poly Growth Along Cracks—Electron Microscopy

Electron photomicrographs of replicas prepared after polymerization has begun show in finer detail essentially the same polymer growth patterns as indicated by the optical photomicrographs. That is, on a crystal surface that initially appears flat and smooth, the polymer forms along lines which

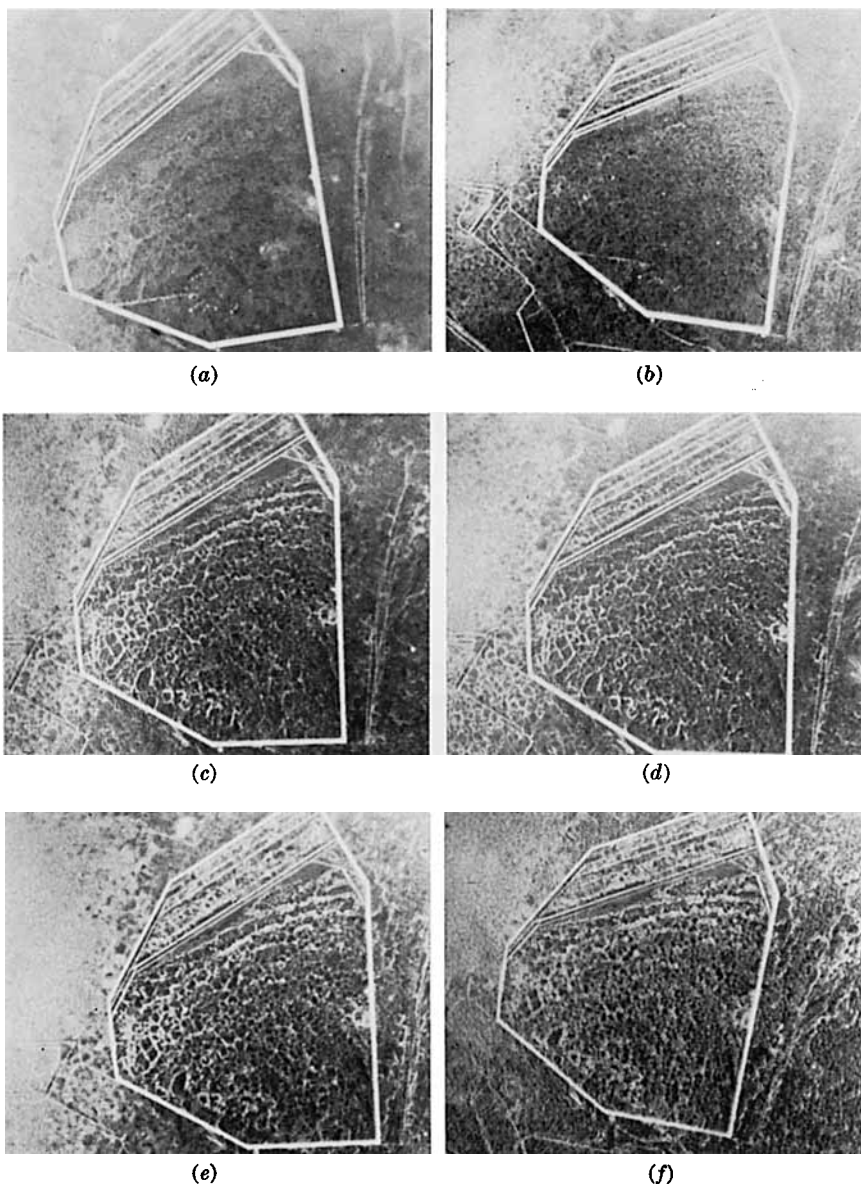


Fig. 7. Polymer growth on fine cracks after short activation time. Optical photomicrographs. 350x.

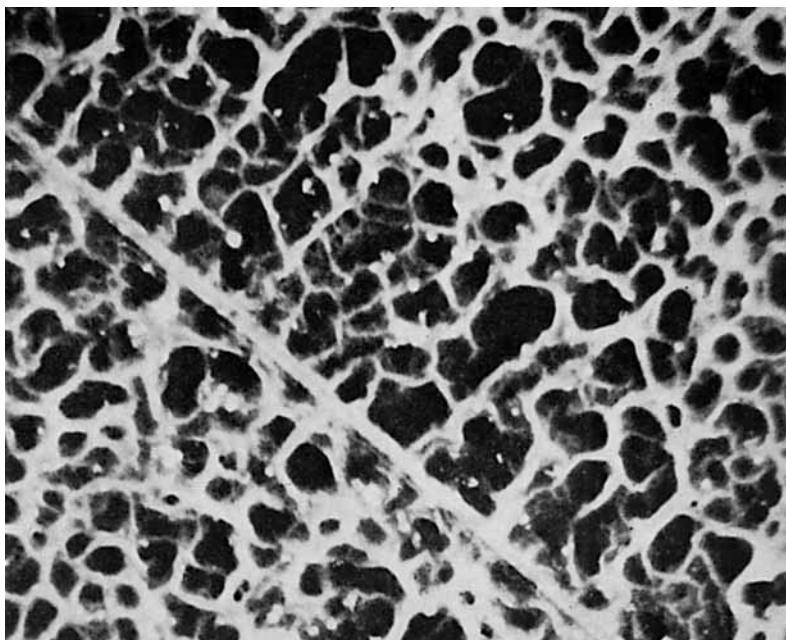


Fig. 8. Electron photomicrograph of polymer on a catalyst crystal. 4400x.

are present as a result of the activation reaction, as shown in Figure 8. In all such photomicrographs, polymer formations appear much the same as they did at lower magnifications, except that the higher magnifications reveal many fine lines of polymer growth. We are thus led to conclude that when polymer forms in an area apparently void of cracks, at low magnification, it is actually forming on very small cracks which are not resolved by the microscope being used.

The replica used to obtain Figure 8 was prepared after relatively large amounts of polymer (for electron-microscopic observations) had formed on the catalyst crystal. The crystal used to prepare the replica was removed from a recrystallization tube and contacted with TEA in a small sample bottle for nine days. Ethylene was then bubbled through the liquid for 15 sec, and the crystals were left in the liquid for an additional 4 min. They were then removed, rinsed in decalin, and replicated.

Polymer Growth on Lateral Surfaces

A very striking difference between the optical and electron-microscopic observations was noted on replicas prepared before large amounts of polymer had formed. Photomicrographs of such replicas are shown in Figures 9 and 10. The crystals used to prepare these replicas were contacted with triethylaluminum for 130 min before monomer was added for 30 sec. They then remained in the liquid for 1 min before being removed, rinsed, and replicated.



Fig. 9. Electron photomicrograph obtained after only a small amount of polymer had formed. 5200x.

In Figure 9, polymer growth along the cracks is not obvious. What is seen is a series of nodules. One group appears to be attached to a surface step. A second group does not seem to be associated with any visible surface characteristic, but each member does lie along a line parallel to the above step. Such nodules were observed often on replicas prepared during the early stages of polymerization. Their absence on replicas of fresh crystals leads to the conclusion that these nodules are polymer particles. This in turn supports the hypothesis that active sites form directly on lateral surfaces.

The nodular character of these formations might well be attributed to highly active sites. Wunderlich¹⁰ suggests that very rapid polymer growth imposes diffusional limitations on the inner core of growing polymer. The outer chains, which are growing faster, fold because the chain ends most remote from the growth site have crystallized. Further, he states that it is also possible that fast-growing strands can become entangled and also cause nodular polymer formations.

In Figure 10, more polymer growth has occurred. Nodules still appear along the steps, but polymer along the random lines has become noticeable.

In fact, it appears as if it might overshadow the nodular growth. Thus, the line which is apparently a step in Figure 8 is somewhat forced into the background by the polymer forming on cracks. On closer observation, one sees that this line appears to be covered by polymer nodules that have grown together.

This suggests that we examine lateral surfaces (steps, spirals, edges) in the optical photomicrographs for polymer growth. A careful study of all such photographs revealed the following:

1. Polymer did often appear on steps (see Fig. 6, for example). The polymer does have the appearance of nodules that have grown together. In other cases there did not seem to be polymer growth on steps (see Fig. 7).
2. In some instances, spirals did become visible after initiation of the polymerization reaction. This did not happen often, and, when it did, the area of the crystal in the vicinity of the spiral was poorly situated for observation.
3. No evidence of polymer growth along an as-grown edge of a crystal was observed. In almost all cases, the crystal edges were noticeably free of polymer.

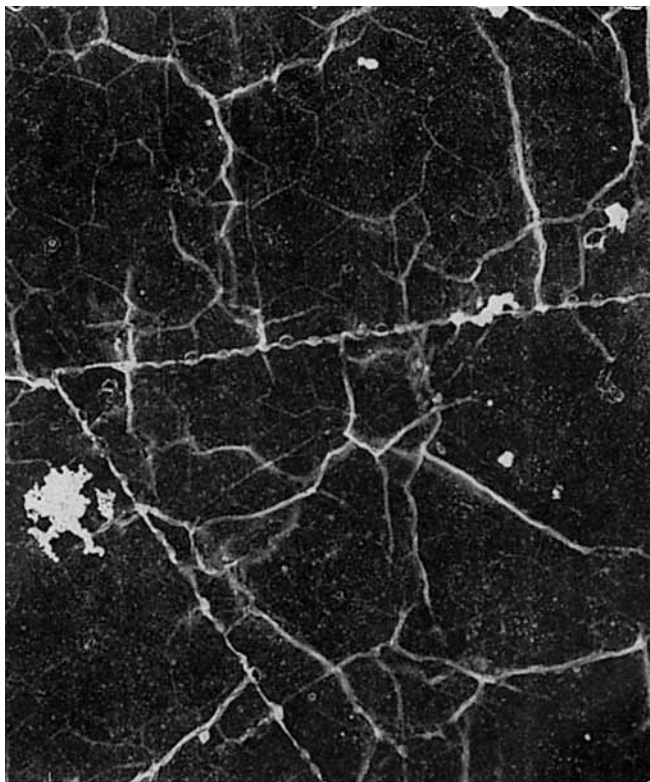
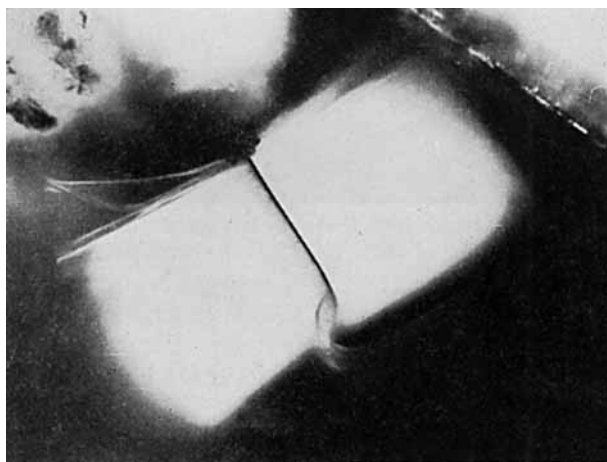


Fig. 10. Electron photomicrograph obtained after only a small amount of polymer had formed. 3550x.



(a)



(b)

Fig. 11. Polymer growth as seen from the edge of a crystal: (a) polymerization for 52 hr.; (b) polymerization for 75 hr. Optical photomicrographs. 350x.

This last result can be seen by observing a crystal from the edge. After polymer growth on a large crystal had begun, a small crystal quite often appeared on top of the large crystal being observed. The small crystals were apparently at one time either a part of or adhered to the large crystal. When these small crystals stood on edge, they provided an excellent view of polymer growth. Figure 11 is a typical view of such a crystal. This one was contacted with triethylaluminum solution for 22.5 hr before the addition of ethylene. A similar view of a somewhat larger crystal is presented in Figure 12. Note the clarity of the catalyst edge in all three of these photomicrographs. This was always the case when crystals were viewed

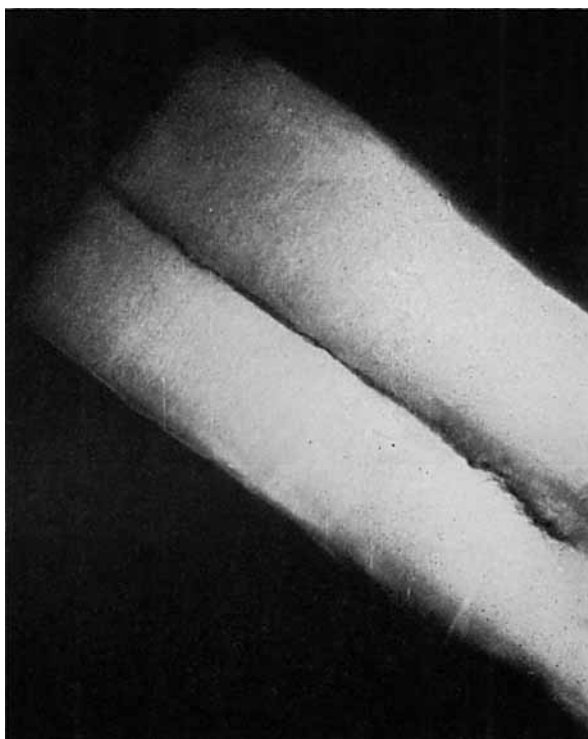


Fig. 12. Polymer growth as seen from the edge of a crystal. Activation time of 22.5 hr. Polymerization time of 49.25 hr. Optical photomicrograph. 350x.

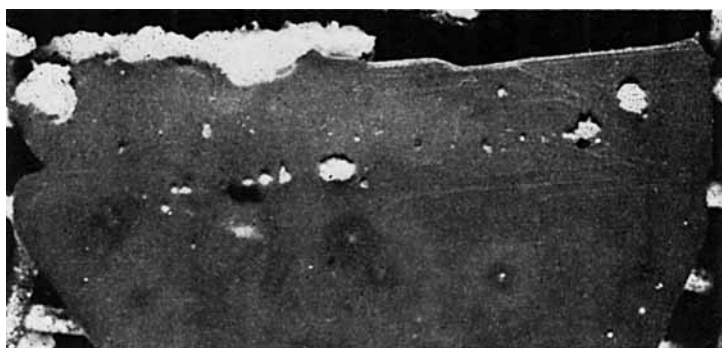
from the side. When viewed from above the crystals had well defined edges.

Most observations thus far have supported the hypothesis that exposed titanium ions are necessary for active site formation. Polymer forms on basal surfaces only where cracks are present, and polymer forms directly on steps. But polymer growth was never detected on as-grown edges. Since titanium ions are exposed on all lateral surfaces, including as-grown edges, some reason for the lack of polymer on these edges is needed. Observations described in the next section are helpful in resolving this issue.

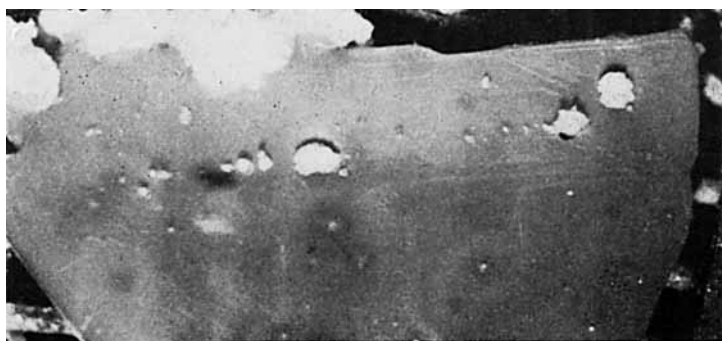
Polymer Growth on Cleaved Edges

Figures 11 and 12 show very clearly the general appearance of polyethylene as it grows on a smooth crystal surface. Note the fibrous appearance of the polymer, the crystalline appearance of the polymer, and the constant thickness of the polymer mass. All of these features were generally observed on ordinary crystal surfaces. Exceptions were noted at cleaved edges and on damaged areas.

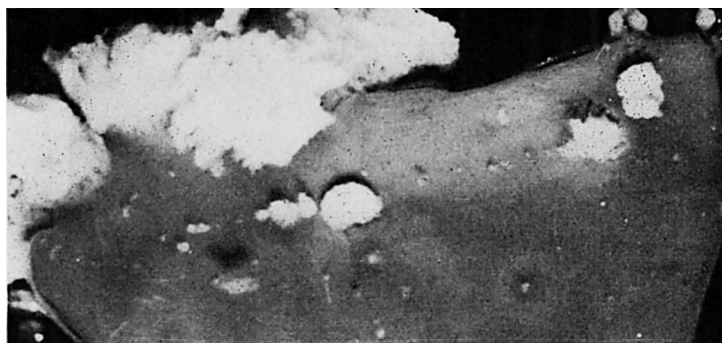
Cleaved edges also served as the exception to the observation that polymer did not form at an edge. Great amounts of polymer were always seen to form along such an edge. Figure 13 is a low magnification photomicro-



(a)



(b)



(c)

Fig. 13. Polymer growth along a cleaved edge: (a) 31 hr after addition of monomer; (b) 51 hr after addition of monomer; (c) 119 hr after addition of monomer. Optical photomicrographs. 24x.

graph of a titanium trichloride crystal. Ethylene was added after 117 hr of activation. The left half of the upper edge was originally attached to another crystal. The two were separated by cleavage. Other edges were not treated in any manner. In all three photographs shown, most of the basal surfaces are covered by a thin covering of the fibrous-looking polymer which appears light grey in the figure.

Additional views of polymer growing along cleaved edges are presented in Figure 14. Again, the center portion of part 14a is covered by the fibrous polymer.

The low-power photomicrographs shown in Figures 13 and 14 were taken through the Bausch & Lomb microscope. Viewing cleaved edges at higher magnifications was difficult because of the roughness of the edge. Near the bottom of Figure 14a is a crystal on edge such as those seen in Figures 11 and 12.

Note that the polymer growing along a cleaved edge does not have the fibrous appearance of the polymer growing on a flat surface. Its appearance could best be described as a nodule or blob. Also, it always occurred in large quantities relative to adjacent areas of the catalyst particle. Thus, it is obviously produced at a highly active area of the catalyst.

Further, polymer growing on a cleaved edge contained a lot of pink and purple color. In particular, there were usually many purple specks scattered throughout it. These appear as dark spots in Figure 14. Berger and Grievesson¹ made a similar observation and attributed it to catalyst particles

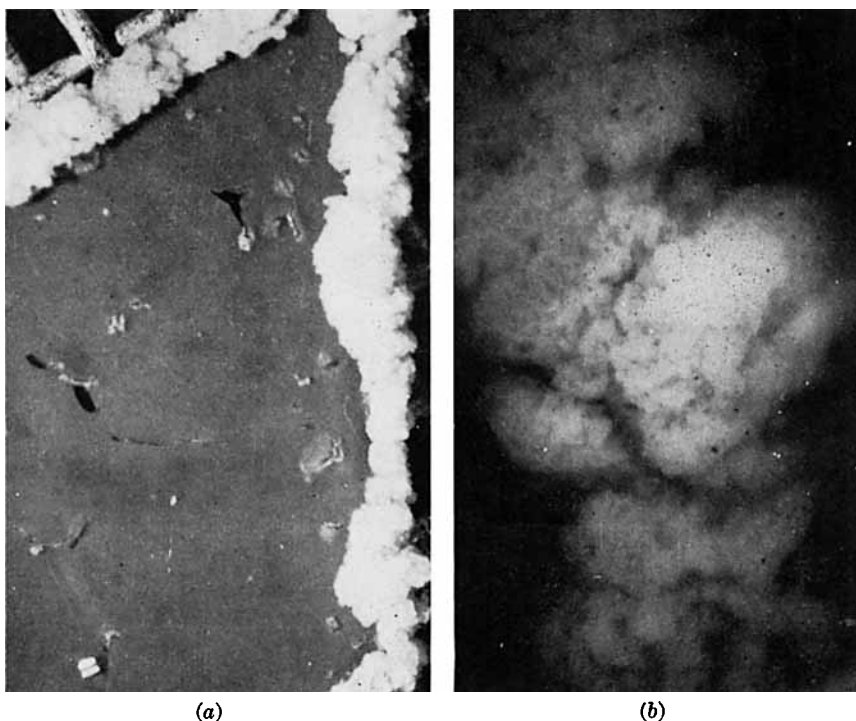


Fig. 14. Optical photomicrographs of polymer growth along a cleaved edge: (a) After 117 hr of activation, monomer was added. Photomicrograph taken 51 hr after monomer addition. All edges of this crystal had been cleaved. 24x. (b) Monomer added after 334 hr of activation. Photomicrograph taken 76 hr after monomer addition. 350x.

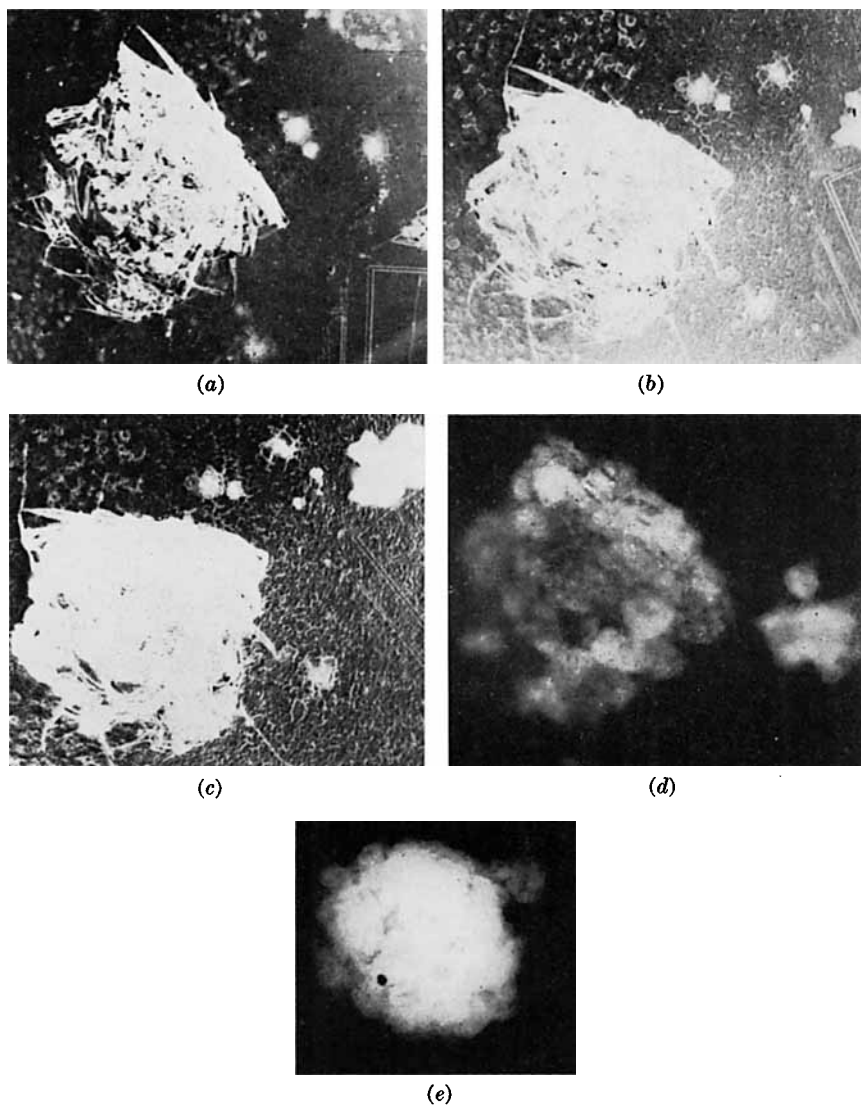


Fig. 15. Optical photomicrographs showing polymer growth on a damaged area.

entrained by the polymer. This explanation seems to apply here, and the presence of small catalyst particles along the cleaved edge would certainly be understandable.

Since cleaved edges were produced immediately prior to activation and subsequent polymerization, these edges can logically be called "fresh" relative to as-grown edges. It might be hypothesized that the as-grown edges were also highly active but lost activity during the period between growth and activation. Of course, one cannot overlook the fact that cleaved surfaces are much more defective than the edge produced during

growth of the crystal. It is these defective edges that are certainly the common ones in industrial processes. In fact, the as-grown edges produced by the sublimation process may be unique and are certainly more perfect.

Combining these observations with those of the previous section, we are led to conclude that active sites form directly on lateral surfaces and that such sites are highly active. Probably because of their high activity, these sites are quite susceptible to poisoning. We cannot rule out the hypothesis that defects greatly enhance active site formation on lateral surfaces.

Polymer Growth on Crushed Areas

Nodular growths of polymer appeared in places other than a cleaved edge, most notably on a damaged area. Like cleaved edges, damaged areas appeared to be much more active than other areas. The mounds of polymer seen on the crystal in Figure 13, for example, look like formations growing on damaged areas. The sequence of photomicrographs presented in Figure 15 records the growth of polymer on an area damaged by tapping the catalyst crystal at the spot shown with a stirring rod. In part 15a, the area is shown after 21.25 hr of activation by TEA solution. Monomer was added after a total activation time of 22.5 hr. Photomicrograph 15b was obtained 17 min after ethylene addition, 15c was obtained 85 min after ethylene addition, 15d was obtained 7 hr and 17 min after ethylene addition, and 15e was obtained 49 hr and 35 min after ethylene addition.

Note the slight change in orientation of the catalyst particle in the various photographs. The smaller damaged area which appears at the extreme right of part 15a can be used as a direction reference. In the last photograph shown, note that the polymer formations above the two damaged areas have grown together. Note also the change in magnification in part 15e. When photographs 15d and 15e were obtained, the surrounding area of the catalyst particle was covered by the fibrous polymer. The "blob" of polymer over the damaged area, however, towered high above the fibrous formations.

A GENERAL VIEW AND SUMMARY

The low-magnification view of a catalyst crystal presented in Figure 16 shows in one picture many of the various types of formations previously discussed. The crystal was tapped rather severely with the end of a glass rod before being placed in the reactor and contacted with triethylaluminum. After removal from the dry box, the crystal was observed with the Zeiss microscope. As was often the case, the "crystal" was seen to be not a single crystal but rather a stack of several leaflets. The results of the pretreatment were apparent. The catalyst was badly scarred and crushed.

Ethylene was added after an activation period of 14 days. After seven days of polymerization, a part of the crystal appeared as shown in Figure 16. This photograph shows many of the previously described polymer



Fig. 16. General view of a catalyst crystal. Optical photomicrograph. 9x.

formations much as they appear to the naked eye after long polymerization times.

When this photograph was taken, most of the catalyst surface was covered by the fibrous polymer. Its depth, however, was not as uniform as usually observed on a more carefully handled crystal. Note the dark, curved line across the center of the figure. This is an edge of one of the catalyst leaflets. An even covering of the fibrous polymer can be seen on both sides of this leaflet. Several other dark lines which are edges of catalyst leaflets can also be seen. Other areas of the photomicrograph which appear smooth are also covered by a uniform thickness of the fibrous polymer.

A large number of nodular blobs of polymer can also be seen in the photomicrograph. Notice the large one at the upper center of the figure. This type formation usually grew above a crushed area of the catalyst. Several similar, but smaller, formations are also present.

The large formations at the bottom of the figure are of the type seen along a cleaved edge. Note the morphology of the polymer and also the dark specks of entrained catalyst. Polymer forming on the usually rather roughly treated catalyst particle must be quite complex in morphology. Although this study used large crystals, the observations have some relation to what might occur on small commercial-size catalyst particles. It is clear that polymer forms on activation cracks, cleaved edges, and crushed spots. Activation cracks appear to be the major source of polymer growth on basal surfaces which interestingly produce polymer of a fibrous appear-

ance, with all fibers of equal length. By contrast, polymer on the highly active crushed and cleaved areas does not have this fibrous and ordered character. One wonders if these two types of formations might have different molecular weight distributions and may, in part, explain the kinds of molecular weight distributions seen with Ziegler catalysts. These and other such possibilities can only be suggested by the photographic insights which have been presented. Further studies would be needed on commercial systems to test the relevant hypotheses that can be formulated.

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