with a Vibromixer stirrer, oxygen inlet tube and a thermometer in a bath at 85° was added 100 ml of *o*-dichlorobenzene. Oxygen was passed through (500 ml/min) the vigorously stirred solution and over a 1 hr period there was added dropwise a solution consisting of 30 g (0.12 mol) of 2,6-diphenylphenol, 0.28 g (0.002 mol) of copper(I) bromide and 0.23 g (0.002 mol) of TMEDA dissolved in 40 ml of *o*-dichlorobenzene (under N_2). After a further 100 min the reaction mixture was very viscous. The polymer was isolated by adding the reaction mixture dropwise to 500 ml of methanol, to which was added 5 ml of concentrated hydrochloric acid and 5 ml of hypophosphorous acid, and removed by filtration. The precipitate was dissolved in 250 ml of chloroform filtered through Celite, and reprecipitated by dropwise addition of 750 ml of methanol. The almost colorless polymer was removed by filtration and dried *in vacuo* (15 mm) at 100° for 6 hr. There was obtained 28.3 g (0.116 mol, 93% yield) of polymer with $[\eta] = 0.58$; $\bar{M}_n = 150{,}000$, $\bar{M}_w = 296{,}000$.

Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.62, 88.31; H, 4.85, 5.01.

The polymer has a glass transition at 230° and above the glass transition temperature it rapidly crystallized and then melts at approximately 480°. Thermogravimetric analysis (300°/hr) indicates the polymer is thermally stable up to 520°; in nitrogen and in air it begins to lose weight at 430°.

Further details will be published in a subsequent paper.

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Spontaneous Catalyst Fracture and Its Influence on Nascent Polyethylene Morphology

Previously, we have described a way to produce nascent polyethylene films from vanadium based Ziegler-Natta polymerization catalyst anchored on various substrates which were immersed in nonsolvent media for polyethylene.[1] The mechanical properties and consequently the inherent morphology of these films vary widely depending upon the polymerization conditions and catalyst deposition. A direct electron microscopic observation of these films reveals that their texture is constituted of a great number of small polyps in the range of 1000 Å diameter, bonded together by a network of ribbons. According to the polymerization conditions, the texture can be described in some cases as essentially "polyplike" leading to almost no mechanical strength while in other cases a significant network of ribbons has developed during the polymerization, linking polyps together and imparting an increased tensile and tear strength to the film. Figure 1 is a combination of these two cases and illustrates a texture showing various size ribbons emerging from a matrix of polyps. The relationship between these observations and those reported by other authors also studying the structure of nascent polyolefins does not appear straightforward on first examination but they are probably reconcilable. In the case of polypropylene grown on large crystals of α-$TiCl_3$, the initial structure of the nascent polymer is essentially polyplike[2] even though recent evidence[3] tends to favor a "whiskerlike" structure in later phases of polymerization. In other cases, and particularly with polyethylene,[4,5] the structure of the nascent polymer is described as fibrillar, which probably can be related to the ribbons that are observed on Figure 1.

In order to understand why such a variety of structures are found, a number of experiments were performed wherein nascent polyethylene films were prepared under a variety of conditions, with rate of polymerization varying several hundredfold. In all cases the catalyst was support-anchored crystalline VCl_3, while the cocatalyst was $AlEt_3$. Polyps were found even after a few seconds of polymerization and originated from polymer coating of catalyst crystals or fragments thereof. This phenomenon is shown by observing the support side of a thin nascent polyethylene film grown on glass-supported VCl_3 and having essentially a polyplike texture at its upper surface; after polymerization and subsequent washing with methanol, one finds the exact casting of the catalyst crystals with dimensions comparable with those of the polyps, as illustrated in Figure 2. This proves not only the one-to-one relation between catalyst crystal and polyp but also that in this case the catalyst has not moved from the substrate surface where it stayed firmly anchored throughout the polymerization. In the majority of cases, however, observations on the substrate side of the nascent polymer do not show any trace of the catalyst crystals although polyps, or polymer encapsulated catalyst fragments, are found throughout the thickness of the polymer films. In this case the polyethylene skin hampers contact between the inorganic nucleus of the polyp and external chemical agents. Even after thorough washing and exposure to ambient atmosphere, electron diffraction patterns of catalyst crystal can still be recorded and the purplish color of VCl_3 is apparent. Significantly, after several days this tint becomes greenish, a color associated with hydrolyzed VCl_3.

If polyps were the only morphological features of the nascent polymer films, polymerization would not go very far since the active sites would be rapidly encapsulated and as a consequence deactivated toward further polymerization. This is in fact the case for films such as the one shown in Figure 2 which remained relatively thin even after prolonged time of polymerization. Fortunately, the movement of growing polymer at the active sites on the surface of the catalyst

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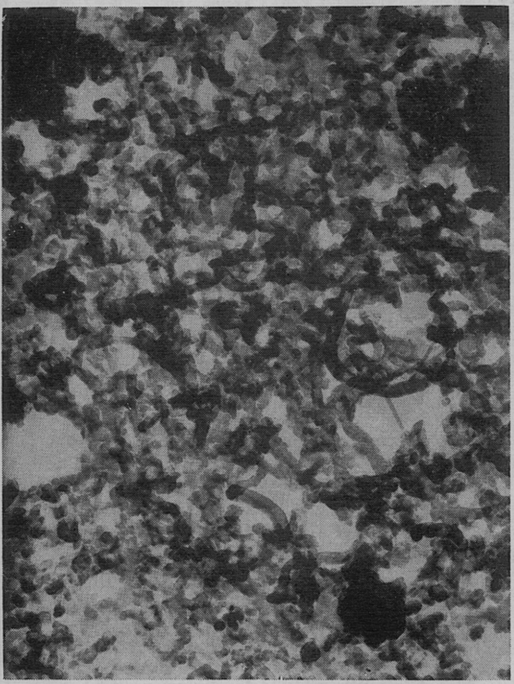

Figure 1. Direct electron micrograph of a thin membrane of polyethylene grown on glass and germanium shadowed on the free side of the membrane and showing both polyps and ribbons, shadow angle 30°.

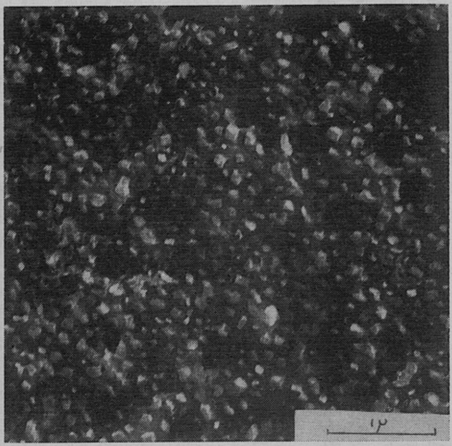

Figure 2. Direct electron micrograph of a thin membrane of polyethylene grown on glass and germanium shadowed on the support side of the membrane, shadow angle 30°.

crystals is able to provoke fracture and breakdown of these crystals.[6,7]

In order to observe the influence of catalyst breakage on nascent morphology, a series of experiments were performed where the splitting of the catalyst crystals was deliberately encouraged. For instance, polymerization was carried out in an ultrasonic field or chemical etching by electron donors was used to "prefacture" the catalyst crystals before the start of polymerization. In each case, polymer films with superior mechanical properties resulted and their inner structure revealed a proliferation of ribbons whose interlacing is most likely responsible for the observed toughness. In another series of experiments, VCl_3 catalyst crystals were slowly grown on a glass substrate at room temperature from a VCl_3 mother solution. In such a case, it may take several days to obtain suitable size crystals and usually their perfection and hence their resistance to breakage is quite good. When such crystals were used to produce nascent polyethylene films, polymerization was very slow and the texture was only polyplike. From these data, we conclude that the ribbons which are observed in the nascent polyethylene films are generated by fracture and movement of the catalyst crystals whereby flakes containing multiple adjacent active sites are generated and put into motion while they are producing polymer. Caught in the dynamics of bulk polymer generation at its surface, the catalyst moves away from the polymerization front leaving a ribbonlike trail or shattering further to polyp-generating fragments, an observation which agrees with that of other authors.[8,9]

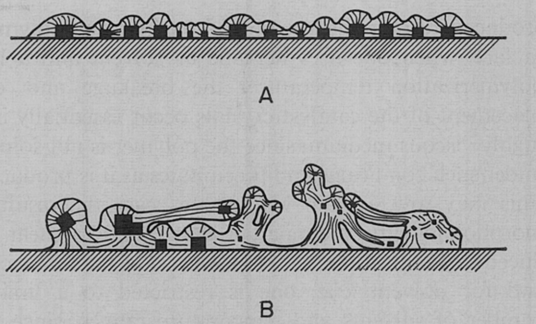

Figure 3. Schematic representation of a nascent polyethylene film grown on glass: A, polyplike structure obtained when the catalyst has not migrated or broken during polymerization; B, polyp- and ribbonlike structure obtained when the catalyst has fractured and moved extensively [■, catalyst crystal; ≈, polymer; /////, glass support].

To summarize our way of thinking, two schematic diagrams have been drawn explaining how coherent films of nascent polyethylene are produced (Figures 3A and B). Figure 3A is the case where breakage does not occur; polyethylene grows rapidly at first, encapsulates the catalyst crystals, and produces essentially a polyplike texture. Figure 2 corresponds to this situation as evidenced by the appearance of the substrate side of the film, after removal of catalyst. In Figure 3B, the forces of polymerization, together with a more fragile crystalline structure of the catalyst, lead to fracture and breakage. During this mechanical action, polyp splitting occurs and fragments of catalyst are pushed away by the growing polymer. This movement is able to generate the ribbons seen in Figure 1. Thus a freshly cleaved surface of catalyst can be compared to a spinneret where adjacent catalytic sites are the spinning holes with the difference however that the ribbons or filament produced are stationary, while the generating part is moving.

On a different level, this mechanism has the advantage of showing how considerable shear can be

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produced during the growth of the nascent polymer. In fact, when one uses heptane as solvent and a low polymerization temperature, the breakage and displacement of the catalyst crystals occur essentially in a highly viscous medium, since the polymer is not soluble under such conditions and precipitates as it is produced. This may well explain why in this case the resulting morphology can be similar to that found in shear induced crystallization.[10-12] However, in the latter case and for polyethylene, one is restricted to a limited number of solvents and temperature ranges, since the polymer must be put in solution prior to crystallization. In the case of polymerization with crystallization to produce nascent polyethylene, a much wider range of conditions is offered: for instance, temperatures ranging from −80 to above 140° and a variety of solvents and nonsolvents, including heterogeneous gas phase polymerization. Such a variety of conditions may explain why extensive differences in degree of order and morphology can be found in samples produced by different authors.

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E. P. Otocka and T. K. Kewi: Properties of Ethylene–Acrylic Acid Copolymers.

Page 245. The copolymer compositions given in the fourth column of Table I are incorrect. The correct values of COOH:100 CH_2 are: polymer A, 0; polymer B, 0.66; polymer C, 1.57; polymer D, 2.78; polymer E, 3.40.—T. K. KWEI AND E. P. OTOCKA

E. P. Otocka and T. K. Kwei: Properties of Ethylene–Metal Acrylate Copolymers

Page 402. The copolymer compositions given in the third column of Table I are incorrect. The correct values of $COO^-/100\ CH_2$ are: Na-B, 0.66; Na-C, 1.57; Na-D, 2.78; Na-E, 3.40; Mg-B, 0.66; Mg-C, 1.57.—T. K. KWEI AND E. P. OTOCKA.