# Fold-Plane Epitaxial Crystallization of Poly(oxymethylene) on Mica

**C. M. Balik and A. J. Hopfinger***

*Department of Macromolecular Science, Case Institute of Technology, Case Western Reserve University, Cleveland, Ohio 44106.* *Received December 12, 1979*

ABSTRACT: Epitaxial crystallization of poly(oxyethylene) from concentrated (1.0 wt %) iodobenzene solutions onto the (001) cleavage face of mica yields two distinct morphologies. In one structure, the polymer forms epitaxial rodlike lamellae which exhibit preferential orientation in three directions spaced 60° apart. These lamellae are nearly identical with the epitaxial crystallites of POM grown on (001) alkali halide substrate surfaces where the polymer chain axis is known to be parallel to the substrate surface. In the other morphological arrangement, POM takes on a flat platelet morphology in which the platelets resemble incomplete hexagonal single crystals of POM, like those grown from dilute solution. The straight edges of the platelets also exhibit orientation in three directions on the surface. Selected area electron diffraction from the platelets indicates that the *ab* plane of POM is parallel to the substrate surface. There are very favorable lattice matching interactions (less than 0.7% mismatch) between POM fold planes and the (001) mica surface, according to reported crystal structures. Possible reasons for the nucleation of POM fold planes at the polymer–mica interface are discussed, as well as implications fold-plane epitaxy might have concerning the issue of adjacent/nonadjacent reentry polymer chain folding.

## Introduction and Background

Epitaxial crystallization of polymers onto inorganic substrates is now a well-recognized phenomenon.[1-8] The most frequently reported systems are semicrystalline polymer/alkali halide substrates.[1-6] In virtually all cases reported to date, the polymer chain axis is oriented parallel to the substrate surface, and the closest packed polymer crystallographic plane is preferentially nucleated at the surface. Occasionally, favorable lattice matching between certain polymer and substrate crystallographic dimensions can induce limited growth of high-energy crystal forms for several nanometers above the surface.[4,5]

The (001) face of mica has been rarely used as a substrate for polymer epitaxy.[9] However, in view of past results relating the possible effects of lattice matching and substrate geometry on polymer morphology and crystal structure,[3-5] the hexagonal structure of (001) mica offers interesting possibilities for the nucleation of hexagonally packed polymer crystals such as poly(oxymethylene) (POM). The epitaxial crystallization of a polymer in which the chain axis is oriented perpendicular to the substrate surface is not often observed. Kobayashi and Takahashi[9] have observed surface-oriented deposition of a polymer phase with the chain axis normal to the substrate surface for poly(ethylene oxide) on mica and KBr, POM on NaCl, and polyethylene on POM single crystals. The method of producing the oriented overgrowth in ref 9 was to slowly cool a polymer solution containing an immersed substrate. This nonisothermal technique might allow the single crystals of polymer to form in solution and subsequently deposit on the substrate. In this case, the chain axis would be expected to be perpendicular to the substrate. Thus, the substrate's only function would be to induce final alignment of the deposited single crystals to yield a regular orientation over the surface. In this article, we report some isothermal crystallization experiments in which the substrate appears to play a more prominent role in controlling the fold-plane epitaxial growth of the polymer, as evidenced by the unique morphology obtained.

## Experimental Section

Commercial POM (Delrin D-900) was used in all experiments. Dilute (0.1 wt %) and concentrated (1.0 wt %) POM solutions in iodobenzene were prepared by dissolving at 180 °C. Mica was obtained as large sheets of natural muscovite from the Cleveland Mica Co. The polymer solutions were initially heated to 180 °C and subsequently cooled to 150 ± 0.5 °C for crystallization in thermostated silicone oil baths. Small sections of mica were air-cleaved and preheated in pure solvent at 150 °C immediately prior to each crystallization experiment. The mica was subsequently transferred to the POM solution for a crystallization time of 10 min. The substrate was then rinsed in pure solvent at 150 °C to remove the unadsorbed polymer. The POM film and replica were stripped from the substrate with collodion after Pt/C replication. The samples were studied with a JEM-100B electron microscope after extracting the collodion through EM grids into filter paper soaked with amyl acetate.

## Results and Discussion

Initial experiments were conducted with dilute (0.1 wt %) POM solutions. Very sparse nucleation on mica occurs under these conditions, with large areas of the surface relatively bare. The morphology of the adsorbed polymer appears as large, seemingly unordered patches of material, ranging in size up to several microns. Occasionally, rodlike lamellae are observed which are roughly oriented in three directions spaced 60° apart on the surface. This morphology is to be expected from substrate symmetry for the epitaxial crystallization of a polymer onto a hexagonal surface. It has been noted for polyethylene on graphite.[8] In contrast, POM forms a very thick, interwoven epitaxial network in the [110] and [1$\bar{1}$0] directions on the (100) surface of KCl under identical conditions. Nearly the entire KCl surface is uniformly covered by this epitaxial growth.

The adsorption of POM onto mica is more substantial at higher polymer concentrations (1.0%). Two distinct morphologies are observed, as shown in Figures 1 and 2. In Figure 1, epitaxial rodlike lamellae, similar to those observed on alkali halides, are distinctly oriented in three directions spaced 60° apart. The lamellae have a rather uniform width of 28 nm and lengths broadly varying from 0.1 to 3 $\mu$m. These lamellae are assumed to contain chain-folded molecules in which the chain axes are perpendicular to the long axis of the resulting lamella and parallel to the substrate surface. This postulate is consistent with all previous studies of polymer epitaxial crystallites on various substrates which are morphologically congeneric to Figure 1.[1-6] Electron diffraction can provide a definitive answer to our assumed geometry. Unfortunately, electron diffraction intensities obtained to date from areas such as Figure 1 have been too weak and short-lived to record on film.

The platelet morphology, shown in Figures 2 and 3, is of considerably more interest to us than the rodlike

0024-9297/80/2213-0999$01.00/0

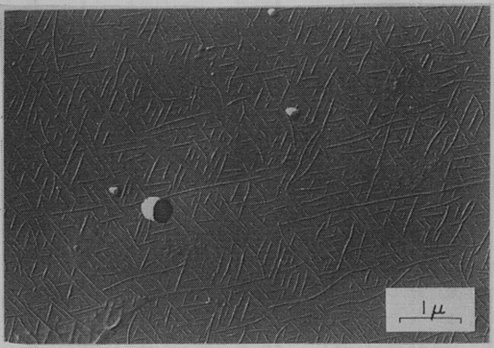

**Figure 1.** Epitaxial crystallization of POM from 1.0% iodobenzene onto (001) mica for 10 min at 150 °C. The chain axis is most likely oriented parallel to the surface. Pt/C shadowing at 45°.

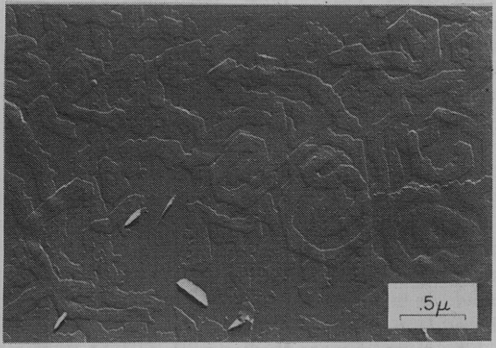

**Figure 2.** Fold-plane epitaxial crystallization of POM onto (001) mica. (Same experimental conditions as Figure 1.) Preferred orientation in three directions spaced 60° apart can still be observed for the straight edges of the platelets. Note the similarity to solution-grown single crystals of hexagonal POM. Pt/C shadowing at 45°.

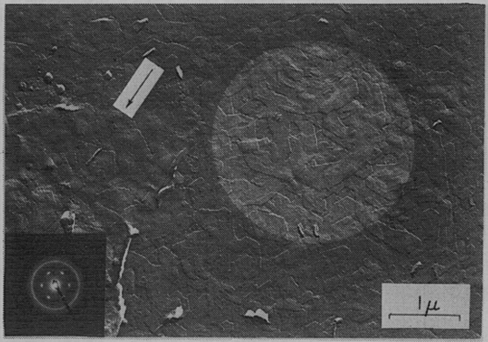

**Figure 3.** Selected area electron diffraction from the fold-plane epitaxial crystals, proving that the POM fold plane is parallel to the surface. The {100}, {110}, and {200} sets of reflections are visible. The arrow points to a group of spiral screw dislocations characteristically similar to those observed on solution-grown POM single crystals. Pt/C shadowing at 45°.

morphology. The selected area electron diffraction pattern (Figure 3) indexes as the (*hk*0) plane of hexagonal POM ($a$ = 0.446 nm). The {100} set of reflections is clearly visible, while the {110} and {200} sets are somewhat less distinct, being superimposed on the platinum rings. This is strong evidence that the fold planes of these POM crystals are parallel to the substrate surface. Also, the straight edges of the platelets are uniformly aligned in one of three directions spaced 60° apart on the mica surface. This indicates that an epitaxial growth relationship has been established between polymer and substrate. The alignment and regular orientation of these platelets, as well as their unique appearance, suggest that they have grown on the surface and not in solution. The thickness of the fold-plane epitaxial film is about 10 nm, also comparable to the thickness of POM single crystals grown from dilute solution. Spiral screw dislocations are observed (arrow, Figure 3) which again are identical with those of solution-grown single crystals. Interestingly, completed hexagons appear most often to have grown from the outside to the inside. The outside edges are usually regular while the inside edges appear diffuse.

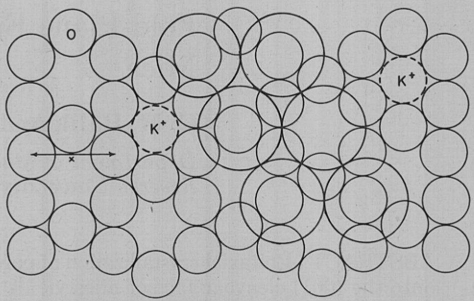

**Figure 4.** Schematic illustration of the arrangement of oxygen atoms in the mica (001) cleavage surface (small circles). If any potassium ions remain on the surface after cleavage, they would randomly occupy the positions shown, coordinating with six oxygens. The large circles represent a possible orientation of the *ab* plane of hexagonal POM on the mica surface. The lattice mismatch is less than 0.7% in three directions.

These preliminary data lead to the conclusion that the mica (001) surface is promoting and controlling the growth of the fold plane of hexagonal POM. An investigation of the crystallographic relationships at the polymer–substrate interface reveals that very favorable lattice matching interactions can occur. Figure 4 shows the structure of the (001) mica surface. The perpendicular distance between contiguous rows of oxygens ($x$) is 0.449 nm.[12] The "$a$" spacing of hexagonal POM is 0.446 nm,[13] a difference of only 0.67%. In this interfacial alignment, the (110) POM lattice planes parallel the contiguous rows of oxygens in the mica surface. The hexagonal interfacial symmetry allows the growing polymer to experience the same high degree of lattice matching in all directions on the surface. A schematic representation of the superposition of the *ab* plane of POM aligned as described above on (001) mica is also shown in Figure 4. We stress that at this time we have no experimental proof that this indeed is the epitaxial relationship that exists. However, this proposed interfacial structure is stereochemically quite reasonable and is also consistent with the preferred three-directional orientation morphology shown in Figures 2 and 3.

Several factors may be involved in the formation of fold-plane epitaxial crystals on mica. The results of the dilute-solution experiments suggest that POM has a lower thermodynamic preference for the mica surface than it does for KCl. This may be a result of the difference in surface energies between KCl and mica. Crystallization of the fold plane of POM next to mica would minimize the polymer–substrate contacts, in accordance with this low thermodynamic preference. The occurrence of edge-on lamellae (Figure 1) with the chain axis parallel to the surface might be due to preferential nucleation at step defects, as are known to exist on mica cleavage surfaces.[11] The polymer solution concentration used (1.0%) to grow fold-plane epitaxial crystals of POM is probably sufficient to allow nucleation to occur in solution in the absence of a substrate. Adsorption of these nuclei (with the chain axis normal to the surface), followed by growth directed by the surface, could result in the morphology shown in Figures 2 and 3. Indeed, Koutsky et al.,[10] using an experimental technique similar to ours, have observed what appeared to be nuclei of poly(propylene oxide) on KI surfaces that produced ordered diffraction patterns showing the chain axis to be perpendicular to the substrate surface. Unfortunately, it is not possible to be more definitive at this time. Future experiments will be directed toward explaining these observations.

Finally, one cannot ignore that the polymer–substrate interfacial fold plane in fold-plane epitaxy may be an example of an adjacent reentry chain fold. Thus, our work may be relevant to the issue of adjacent vs. nonadjacent reentry of chain-folded polymer single crystals.[14-17] Conceptually, the very nature of epitaxial crystallization, requiring that a crystalline polymer plane interact with a crystalline surface to produce the observed regular orientations, would lead one to envision a highly ordered, if not crystalline interfacial fold-plane surface for fold-plane epitaxial crystals. This intuitive feeling is further supported by the potential lattice matching between the substrate surface and the *ab* plane of the polymer crystal. A crystalline interfacial fold plane seems to be a quite probable state. However, nonadjacent reentry chain segments, which run parallel to the substrate surface along the directions observed for POM in Figure 1 and which likely have lengths which are integral multiples of the fold-plane separation distances, before reentering the polymer crystal, are also possible. Clearly, however, tie chains, fold loops of arbitrary size, and random chain reentry into the same polymer crystal, with respect to a frame of reference at the interface, are quite unlikely for the interfacial layer of polymer.

These preliminary investigations cannot resolve, nor were they originally intended to resolve, the question of adjacent vs. nonadjacent reentry. However, fold-plane epitaxial studies may be helpful in the investigation of this issue. We have shown, through morphological observations and electron diffraction, that fold-plane epitaxial crystallization of POM does occur from concentrated solutions onto (001) cleavage planes of mica. Ongoing and future experiments will deal with the mechanism of fold-plane epitaxial growth, as well as with extensions to other polymers and substrates.

**Acknowledgment.** We gratefully acknowledge the support of this work by the National Science Foundation (Grant No. ENG 78-24007).

### References and Notes

(1) J. Willems, *Discuss. Faraday Soc.*, **25**, 204 (1957).
(2) E. W. Fischer, *Kolloid-Z.*, **159**, 108 (1958).
(3) J. A. Koutsky, A. G. Walton, and E. Baer, *J. Polym. Sci., Part A-2*, **4**, 611 (1966).
(4) S. Wellinghoff, F. Rybnikar, and E. Baer, *J. Macromol. Sci., Polym. Phys. Ed.*, **B10**, 1 (1974).
(5) S. E. Rickert and E. Baer, *J. Appl. Phys.*, **47**, 4304 (1976).
(6) C. M. Balik, R. Farmer, and E. Baer, *J. Mater. Sci.*, **14**, 1511 (1979).
(7) C. M. Balik and A. J. Hopfinger, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1897 (1978).
(8) F. Tuinstra and E. Baer, *J. Polym. Sci., Polym. Lett. Ed.*, **8**, 861 (1970).
(9) K. Kobayashi and T. Takahashi, *Kagaku (Tokyo)*, **34**, 325 (1964).
(10) J. A. Koutsky, A. Walton, and E. Baer, *J. Polym. Sci., Polym. Lett. Ed.*, **B5**, 177 (1967).
(11) E. Suito and M. Nakahira in "Electron-Optical Investigations of Clays", J. A. Gard, Ed., Alden Press, Oxford, 1971, p 231.
(12) L. Bragg, G. F. Claringbull, and W. H. Taylor in "Crystal Structures of Minerals", Cornell University Press, Ithaca, NY, 1965.
(13) G. A. Carazzolo, *J. Polym. Sci., Part A*, 1, 1573 (1963).
(14) J. I. Lauritzen, Jr., and J. D. Hoffman, *J. Res. Natl. Bur. Stand., Sect. A*, **64A**, 73 (1960).
(15) P. H. Geil in "Polymer Single Crystals", Robert E. Krieger Publishing Co., Huntington, NY, 1963.
(16) P. J. Flory, *J. Am. Chem. Soc.*, 84, 2857 (1962).
(17) P. J. Flory and D. Y. Yoon, *Nature (London)*, **272**, 226 (1978).

---

# Elastic Properties of Well-Characterized Ethylene–Propylene Copolymer Networks

**Dale S. Pearson***,† **and William W. Graessley***

*Materials Science and Engineering Department, Northwestern University,*
*Evanston, Illinois 60201.* *Received January 25, 1980*

ABSTRACT: A series of networks were prepared by cross-linking well-characterized ethylene–propylene copolymers with high-energy electron radiation. The cross-link density and other structural features of the networks were determined by analyzing the rate of increase of gel content with radiation dose. Stress–strain measurements revealed that the elastic modulus was considerably greater than that predicted by the classical theories of rubber elasticity. The initial modulus, however, could be calculated by assuming it to be the sum of two parts, one a chemical contribution proportional to the number of strands in the network and the other a topological contribution from entanglements trapped in the network by the cross-linking process. The value obtained for $G_e^{max}$, the maximum entanglement contribution to the equilibrium modulus, was equal within experimental error to $G_N^0$, the plateau modulus obtained from dynamic measurements on the un-cross-linked polymer.

Rubber elasticity is one of the classical problems of polymer physics. The essential goal is to develop a theory for relating the mechanical properties of rubber networks to their molecular structure. Early attempts in this direction assumed that the force required to deform the rubber arises entirely within the strands which connect the junctions in the network. Interactions between neighboring strands were ignored insofar as the strain-dependent properties were concerned. The principal result of this approach was the prediction that the shear modulus is approximately equal to the number density of strands in the network multiplied by $kT$[1] (eq 1).

$$G \simeq \nu kT \tag{1}$$

When rubber networks are formed from concentrated solutions or melts, the domains occupied by neighboring strands will overlap to a considerable extent.[2] Since the strands cannot pass through each other, molecular rearrangements which occur upon deformation may be influ-

---

† Present address: Bell Laboratories, Murray Hill, NJ 07974.

0024-9297/80/2213-1001$01.00/0 © 1980 American Chemical Society