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# Polydipropylsiloxane Single Crystals

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# Polydipropylsiloxane Single Crystals

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## SUMMARY

Polydipropylsiloxane single crystals, grown from a dilute n-butylacetate solution, were characterized by electron microscopy and by selected-area electron-beam diffraction techniques. The electron diffraction study shows that the growth face was parallel to the {100} plane. Fracture of single crystals parallel to the fold plane takes place during the electron diffraction examination to give ribbonlike lamellae about 300 Å wide and 80 Å thick. Fracture normal to the fold plane was also observed.

## INTRODUCTION

Although polymer single crystals have been reported for a number of organic polymers [1], the preparation of polymer single crystals of $(R_2SiO)_x$ type polysiloxanes, where R is alkyl or aryl substituent, has not been demonstrated. The preparation of a single crystal of polydimethylsiloxane and polydiethylsiloxane is rather difficult due to the low melting temperature of the polymers. These two polymers are liquids or noncrystalline gums at room temperature. Single crystals of polydipropylsiloxane (PDPS) can be prepared rather easily since the crystals can be handled at room temperature due to a higher melting temperature of the polymer. (Note: The melting point of PDPS is 74°C at infinite molecular weight [2]). A typical electron micrograph of PDPS single crystals obtained in this laboratory has been reported elsewhere [3]. In this paper the characteristics of the PDPS single crystals are described in more detail;

and the postulated fold-chain packing, leading to flat or pyramidal PDPS single crystals, is presented.

## EXPERIMENTAL

### Material

The PDPS sample employed in this work is a fractionated material. The fractionation procedure has been described elsewhere [4]. The number-average molecular weight of the fractionated sample was 67,000 and the melting point determined by differential scanning calorimetry was 70°C. The sample is a fluffy powder but forms a brittle waxy solid after melting followed by cooling.



### Preparation of Single Crystals

The single crystals were grown from a 0.05% solution of PDPS in n-butylacetate at 5°C for 3 days. The crystals suspended in the solution were stored at this temperature until they were needed. The crystals in suspension were transferred onto a carbon film on a copper grid for electron diffraction and direct transmission electron microscopy. The replica was prepared as a chromium-shadowed carbon replica at 15° shadowing angle.

## RESULTS AND DISCUSSION

### Electron Micrographs

A typical electron micrograph of PDPS single crystals has been given elsewhere [3]. The polymer single crystals consist of thin lamella about 80 Å thick. Both spirals and a stepped pyramid of complete lamellae were observed to have grown on a basal lamella. The spiral growth, however, has been observed more frequently than the pyramid type growth.

The PDPS single crystals were found to be brittle and subject to fracture during the crystal preparation. Figure 1A shows the primary fracture of crystals in the direction parallel to the growth face. The width of each lamella is on the order of 0.3 to 0.5 $\mu$. The factor which causes the primary fracture of the crystal is unknown at the present time. We did observe, however, that a secondary fracture took place, when the crystals

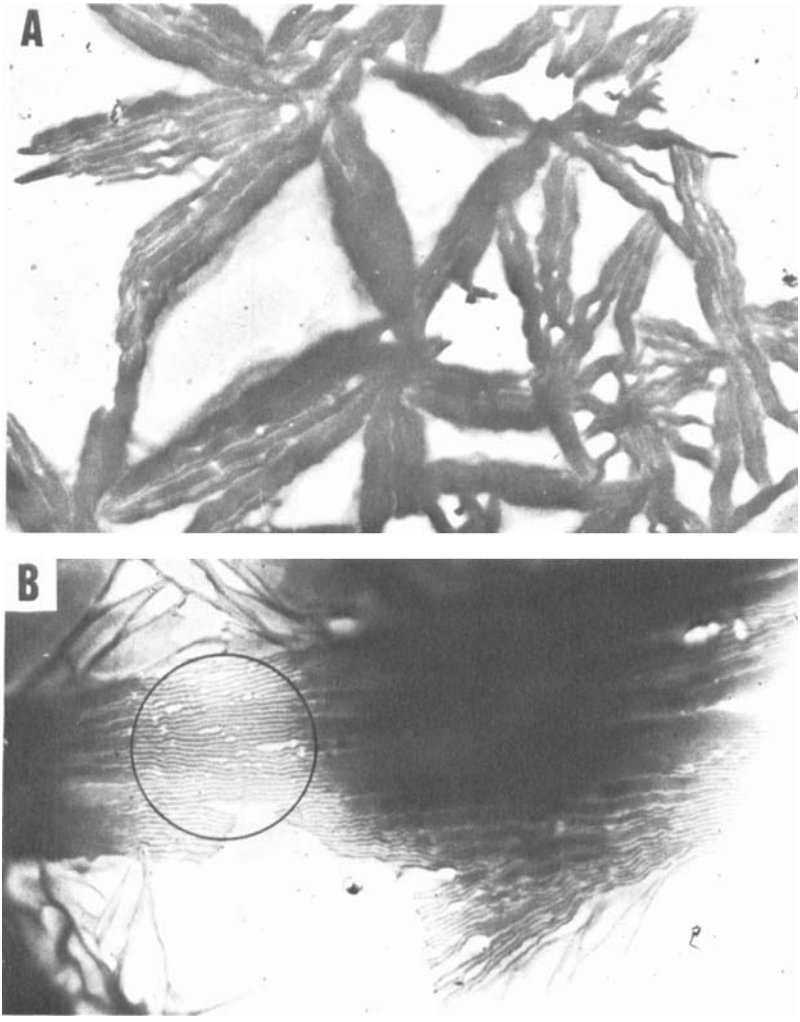


**Fig. 1.** Ribbonlike lamellae due to (A) primary fracture and (B) secondary fracture.

were exposed to the electron beam during the electron diffraction examination, to give ribbonlike lamellae. Figure 1B illustrates the appearance of the lamellae formed by the secondary fracture during the electron diffraction experiment. The direction of the fracture, again, is parallel to the growth face. The width of the ribbonlike lamella, about 300 Å , was

found to be fairly uniform. The electron diffraction pattern of these ribbonlike lamellae shows that the c-axis of the crystal lattice is still perpendicular to the plane of the flat face of the lamella and the chain molecules are folded within the lamella.

## Fold Packing Model

It has been reported that the orientation of the PDPS molecules is normal to the lamellae, and molecules are folded back and forth on themselves in the lamellae [3]. The question arises as to whether the molecules are folded in the {110}plane or in the {100}plane. Since the crystal lattice is tetragonal [3] and the shape of the single crystal is square, both directions of fold are possible.

Selected-area electron diffraction was carried out in an effort to resolve this question. Figure 2 shows the electron diffraction pattern superimposed onto the electron micrograph of a stepped pyramid of complete lamellae. These results suggest that the growth face is in the {100}plane rather than in the {110}plane. Thus the "fold plane," defined as the plane in which a molecule folds presumably parallel to a growth face [5], is therefore in the {100} plane. A postulated fold packing which leads to flat PDPS crystals (projected onto {001} plane is also shown in Fig. 2. The dotted lines are fold-domain boundaries. Figure 3 is a photograph of the Fisher-Hirschfelder-Taylor model, taken in the direction parallel to the c-axis, to show the upper fold surface and also the shape of the cross section of a singlefold PDPS molecule. The scale is 1 cm to 1 Å. The molecular model indicates that although the polymer molecule of PDPS is fairly stiff and the rotation of bonds about the Si–O bond is limited due to the bulkiness of the propyl group [4], the chain molecule can be folded easily. Only four siloxane units are involved in the folding as illustrated by the model.

No attempt was made in this work to determine the indices of the fold surface involved in the spiral growth nor the origin of the spiral growth.

## Fracture of Single Crystal

According to the model postulated above, the primary and the secondary fracture of single crystals mentioned previously take place along the {100} plane. Since the ribbonlike lamellae obtained after the secondary fracture are about 300 Å wide and 80 Å thick, one ribbonlike lamella therefore consists of 30 rows of folded-chain molecules running along the {100} plane. A close examination of Fig. 1 reveals that there are a number of discontinuities in the ribbonlike lamella. This is shown more clearly in Fig. 4.

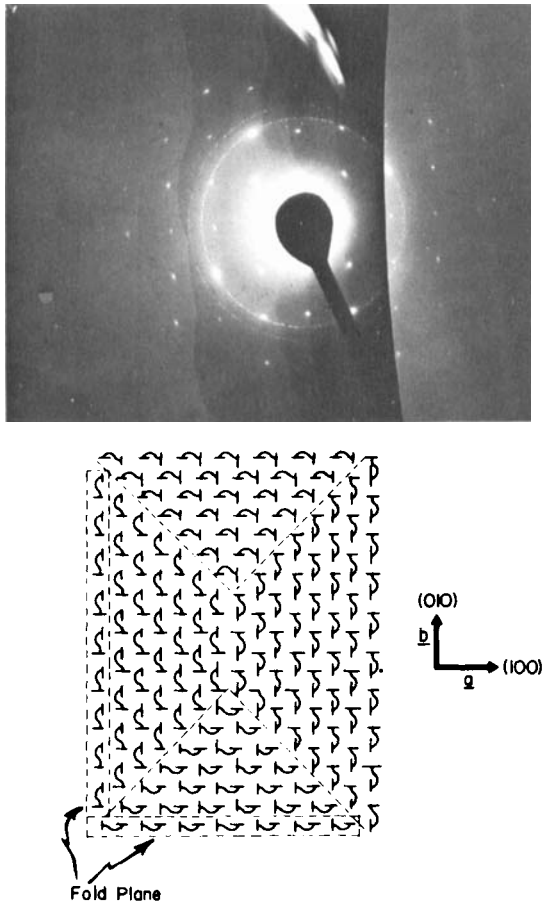


**Fig. 2.** Top: Superposition of diffraction pattern on electron micrograph of PDPS single crystals. Bottom: Postulated fold packing leading to flat single crystals.

Two types of discontinuity, namely Type A and Type B, were observed. Type A represents the end of a single ribbonlike lamella which may be present in the original state, whereas Type B represents the fracture normal to the fold plane due probably to the mechanical rupture of the ribbonlike lamella. Type B rupture could arise from an improper fold, e.g., a long molecule crystallizes with its ends in two adjacent fold planes. These improper folds bridge adjacent fold planes and may cause brittle fracture normal to the fold plane [1].

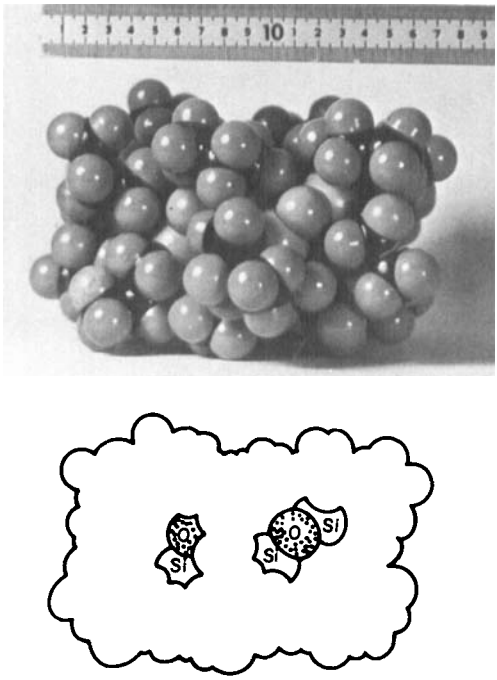


**Fig. 3.** Fisher-Hirschfelder-Taylor model showing the upper surface of fold, {001} plane.

The cohesion between adjacent planes containing the fold molecules would be expected to be small. The fact that the primary fracture occurs readily, requiring no external forces, implies therefore that the interfold-plane cohesion in PDPS single crystal is much weaker than that of other organic polymer single crystals. This is probably due to the weak intermolecular force arising from the presence of the large Si–O internal dipole acting to lower the external fields of substituent groups, thus decreasing the interaction between the force field of the hydrocarbon portion of the siloxane [6, 7]. This is supported further by the fact that PDPS has a very low value of heat of fusion, $\Delta H_u$. The $\Delta H_u$ obtained by the calorimetric studies [2] is only 362 cal/deg/mole of chain atoms, which is considerably lower than those of other organic polymers (600 to 1000 cal/deg/mole of chain atoms). It has been shown that $\Delta H_u$ is contributed mostly by the cohesive energy density (CED), a measure of the intermolecular force, according to the following empirical equation:

$$\Delta H_u = \Delta H' + k(CED)$$

where $\Delta H'$ and k are constant [8, 9]. The low $\Delta H_u$ value, therefore, implies a low cohesive energy density or weak interfold-plane cohesion (between adjacent planes), which might be responsible for the occurrence of unusual fractures in PDPS.

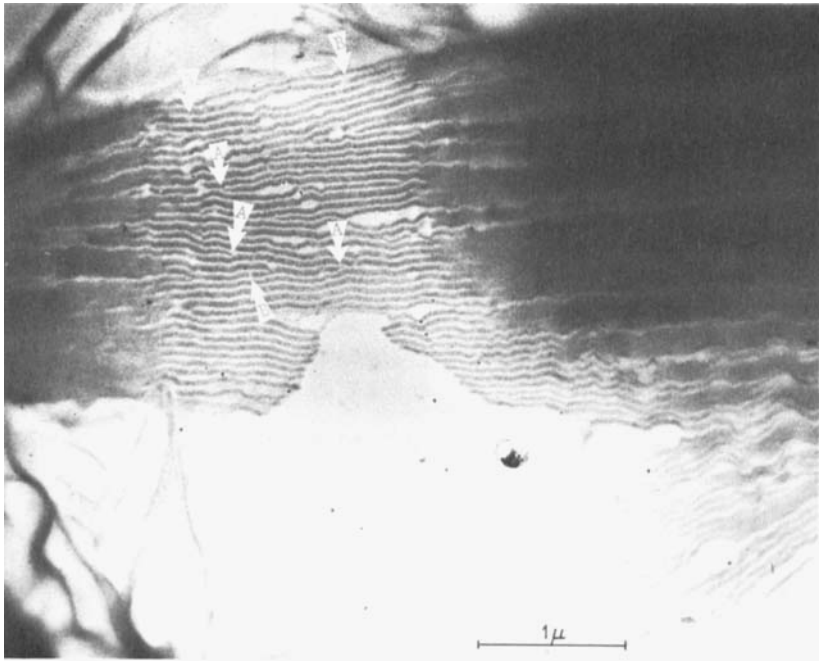


**Fig. 4.** Discontinuities in ribbonlike lamellae of PDPS.



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