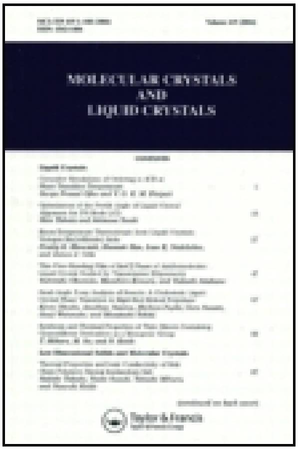

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Direct Imaging of The Lattice In Poly(Phthalocyaninato-Germoxane) Single Crystals

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DIRECT IMAGING OF THE LATTICE IN POLY(PHTHALOCYANINATO-GERMOXANE) SINGLE CRYSTALS

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Abstract Poly(phthalocyaninatogermoxane, $[Ge(Pc)O]_n$, was prepared from single crystals of the monomer phthalocyaninatogermanium dihydroxide, $Ge(Pc)(OH)_2$, by thermal condensation polymerization in solid state. Direct imaging of (100) lattice planes containing the extended molecular chains in the polymer single crystals was achieved using transmission electron microscopy. A mosaic block structure and many lattice imperfections were recorded.

INTRODUCTION

In 1956 Menter (1) first succeeded in recording the direct images of copper and platinum phthalocyanine crystal lattices and their imperfections by transmission electron microscopy (TEM). Menter (2) and Allpress & Sanders (3) have also discussed the details about the direct imaging of lattices. This kind of investigation on polymer crystals started in 1968 (4), but up to now, only a few polymers, viz., poly(p-xylene) (4,5,6), poly(p-phenylene terephthamide) Kevlar(R) (7,8), poly[1,6-di-(N-carbazolyl)-2,4-hexadiyne] (9) and poly(p-phenylene benzobisthiazole) (10), have been studied by direct imaging of their lattices. These polymers, in particular, contain a high proportion of aromatic rings and are, therefore, relatively less sensitive than typical polymers to electron beam damage.

There is also a considerable aromaticity in the phthalocyanine subunits of the cofacially arrayed metallomacrocyclic polymer, poly(phthalocyaninatogermoxane), $[Ge(Pc)O]_n$. Using electron microscopy and selected area electron diffraction, it was found that as-polymerized $[Ge(Pc)O]_n$ exists as collections of lath-like crystals whose _b_ direction is perpendicular to, and the _a_ and the _c_ directions are parallel to, the large surface of the lath (11,12). In addition, the spacing of (100) lattice planes is 13.27 Å, while that of (001) is 3.53 Å. It is, thus, reasonable to expect to obtain direct imaging of (100) lattice planes with TEM in two beam condition by means of excluding the 001 diffracted beam with an objective aperture of suitable diameter.

EXPERIMENTAL

The $[Ge(Pc)O]_n$ samples were polymerized from single crystals of the monomer, $Ge(Pc)(OH)_2$, in solid state at 440°C and 10^{-3} torr dynamic vacuum. The resulting polymer crystals were separated into very thin lath-like single crystals using very mild mechanical action. They were then carefully transferred onto 300 mesh grids with a carbon supporting film. A JEOL-100B TEM, with spherical aberration coefficient of 5.1 mm and chromatic aberration coefficient of 2.3 mm, was used here and operated at an accelerating potential of 100 KV. A 60 μm objective aperture was chosen to admit only the incident, 100, and $\bar{1}00$ beams, thereby causing a (100) lattice planes image to form.

RESULTS AND DISCUSSION

We had found earlier (12) that the molecular chains in most cases lay along the length dimension of the lath. We report here in Figure 1 the direct image of the lattice planes which contain these molecular chains. This figure shows that $[Ge(Pc)O]_n$ molecular chains are roughly parallel to the crystal long edge, and that the lattice is not as orderly as that in Pt(Pc) crystals (1). In Figure 2, it is quite obvious that there does not exist a strict long-range order throughout the crystal.

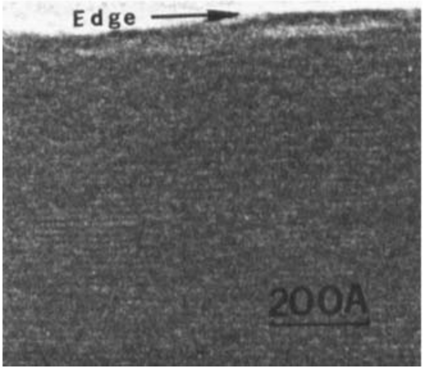

FIGURE 1 Direct imaging of (100) lattice planes in the $[Ge(Pc)O]_n$ single crystal. The molecular chains are parallel to the long edge of the lath-like crystal.

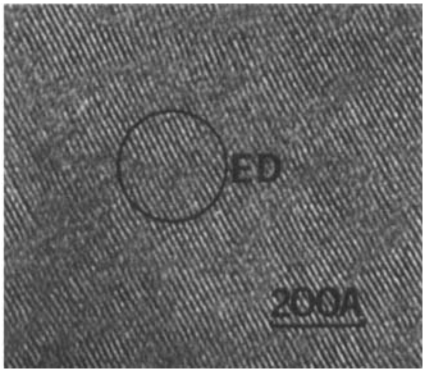

FIGURE 2 Direct imaging of (100) lattice planes in the $[Ge(Pc)O]_n$ single crystal. The mosaic structure is very clear. Edge dislocation can be seen within the circle labelled ED.

Based on the selected area electron diffraction patterns, we had earlier proposed (12) that there are mosaic blocks in the $[Ge(Pc)O]_n$ crystals, but we did not, at that time, have information on the actual character of lattice order/disorder. Now, the mosaic structures of 200-400 Å size are vividly shown in the direct image. On account of these resolved lattice images, we suggest that the mosaic structures in $[Ge(Pc)O]_n$ crystals result from the topotactic polymerization process (13-15) itself. Edge dislocations, such as can be seen within the circle labelled ED of Figure 2, are also numerous. That the temperature dependence of the charge transport in doped phases of $[Ge(Pc)O]_n$ could be fit to a model involving fluctuation-induced carrier tunneling through insulating potential barriers would appear to be in accord with such a microstructure.

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