Crystals of Polymers Derived from Divinyl Compounds by Photoradiation in the Solid State

We have reported that 2,5-distyrylpyrazine (DSP) (I) polymerizes by photoirradiation in the solid state, resulting in a linear polymer (II) containing a cyclobutane ring in the main chain.[1] This reaction has been attempted with various divinyl compounds, and *trans,trans*-1,4-bis[β-pyridyl-(2)-vinyl]benzene (P2VB) (III) has been found to give a polymer (IV) just the same as that obtained with *trans,trans*-DSP; the details of the polymerization will be described elsewhere.

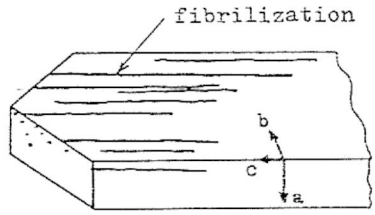


Fig. 1. Sketch of a fibrilar striation observed in the course of polymerization. Arrows indicate the crystallographic axes of the monomer crystal (Orthorhombic; $a = 20.9$, $b = 9.6$, $c = 7.3$ A.).

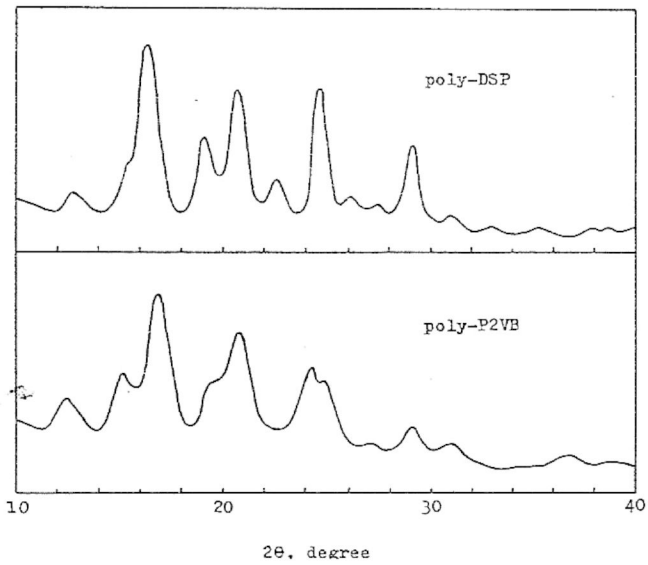
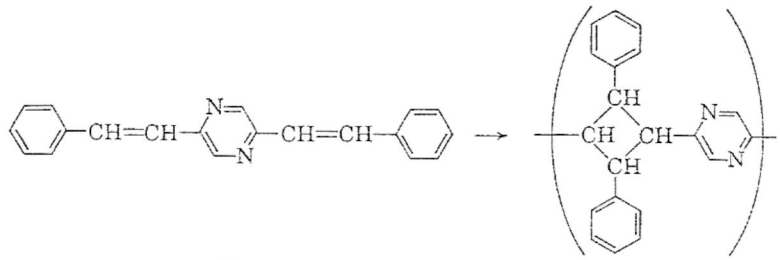


Fig. 2. X-ray diffraction diagrams of fibrilar poly-DSP and poly-P2VB as polymerized. Powder diagram.

Some crystallographic studies have also been carried out for both the polymers of DSP and P2VB. An observation of the crystal in the course of polymerization shows a fibrilar striation of the polymerized fraction aligned in a direction of the mother crystal as shown schematically in Figure 1 in the case of swordlike crystals obtained by sublimation. As the polymerization proceeds, the polymer tends to separate into a needle-

like material, 1–5 mm. in length, which shows a clear birefringence under a polarizing microscope. Formation of the needlelike substance is quite common in the above two



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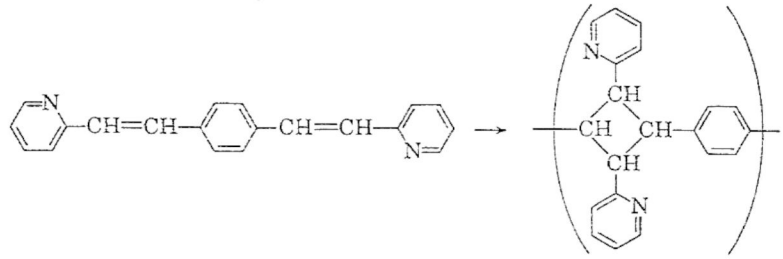
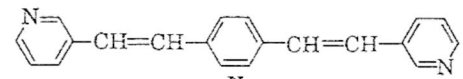


III IV

monomer crystals (DSP and P2VB) and does not depend on the conditions of preparation of the monomer crystals, i.e., a scalelike crystal of the monomer obtained from a solution shows the same fibrillation.

The x-ray diffraction of the two polymers as polymerized is indicative of quite a high crystallinity, as seen in Figure 2, in contrast with the amorphous nature of the film when cast from a solution of polymer in trifluoroacetic acid followed by an extraction with triethylamine. In Figure 2 it is also seen that the main peaks of the two curves are at the same angles for poly-DSP and poly-P2VB, although they differ in their intensities. This suggests that crystals of the two polymers have the same unit cell and symmetry.

In order to investigate the mechanisms of polymerization, x-ray analysis has also been carried out on the two monomers and similar divinyl compounds. The powder diagrams of DSP and P2VB are nearly identical in both of their diffraction angles and intensities. They are, however, different from the curves of 1,4-bis[β-pyridyl-(3)vinyl]benzene (P3VB) (V) and 1,4-bis[β-pyridyl-(4)-vinyl]benzene (P4VB) (VI) which do not polymerize under the same radiation conditions (Fig. 3).



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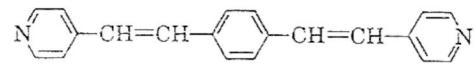

VI

Thus it may be assumed that the molecules of DSP and P2VB are favorably arranged for polymerization in the crystalline state and differ from those which do not polymerize. The unit cell of P2VB is orthorhombic with $a = 20.9$, $b = 9.6$ and $c = 7.3$ A., with the axes oriented as indicated in Figure 1 by arrows. The details of the arrangement of the

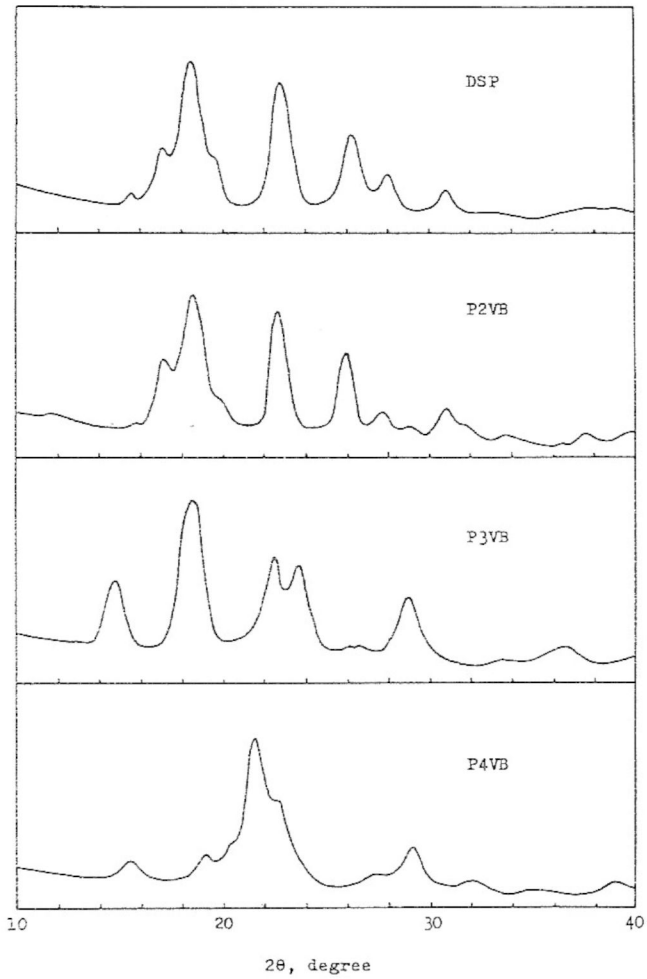

Fig. 3. X-ray diffraction diagrams of monomeric DSP and P2VB and similar divinyl compounds. Powder diagram.

molecules in the unit cell will be discussed elsewhere, but the direction of the polymer axis is nearly parallel with the *c* axis of the monomer, which may give rise to a specific growth of polymer into an extended-chain crystal with an extremely high crystallinity.

Reference

1. M. Hasegawa and Y. Suzuki, *J. Polymer Sci. B*, **5**, 813 (1967).

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