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AN X-RAY STUDY OF CRYSTALLINE-STATE PHOTO-POLYMERIZATION OF 1,4-BIS-[β-PYRIDYL-(2)-VINYL]-BENZENE

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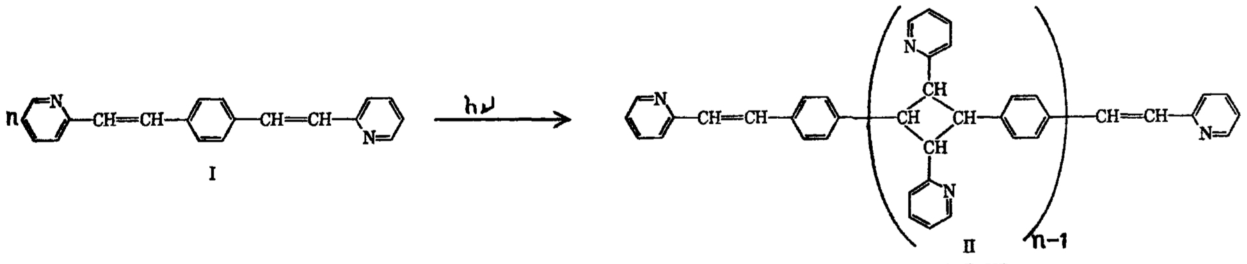
The crystal and molecular structure of 1,4-bis-[β-pyridyl-(2)-vinyl]-benzene [$C_{20}H_{16}N_2$] was determined. Change of crystal structure on polymerization was investigated by X-ray diffraction method. The polymer obtained is three-dimensionally oriented and the molecular arrangement in the original crystal is preserved in the resultant crystal.

As a part of studies on the crystalline-state photo-polymerization of diolefinic compounds, we have previously reported the crystal structures of 2,5-distyrylpyrazine (DSP)1) and poly-DSP.2) The molecular arrangement in the monomer crystal was found to be approximately duplicated in the polymer crystal, and the polymerization mechanism was discussed on the basis of these crystal structures.2)

1,4-Bis-[β-pyridyl-(2)-vinyl]-benzene (P2VB) (I) is also photo-polymerized in the crystalline-state,3) as



but the rate of polymerization is considerably less than that for DSP.4) Therefore, it may be interesting to investigate the crystal structures of P2VB and poly-P2VB.

The crystals of P2VB are orthorhombic,5) and the space group is Pbca. The crystallographic data are listed in Table 1, together with those of DSP. Intensity data were collected on the Hilger & Watt linear diffractometer, and non-zero structure factors for 1033 independent reflexions were derived by correcting Lorentz-polarization factors. Since the unit cell dimensions, the space group , and the intensity distribution of the present crystal are similar to those of DSP, the approximate structure was set using the atomic coordinates in the DSP crystal, which gave the

R of 0.489. The least-squares refinement reduced the R to 0.084, when the contribution from hydrogen atoms were included and the anisotropic temperature factors for non-hydrogen atoms were applied.

The molecular structure of P2VB is shown in Fig. 1. All bond lengths and angles are reasonable. Benzene, pyridine and C(2)-C(3)-C(4)-C(5) groups are planar. The benzene ring rotates by 1.87° about the bond C(2)-C(3) from the ethylenic plane, and the pyridine ring rotates by 11.77° about C(4)-C(5) in the same direction. Thus, the mean planes of these two rings make an angle of 10.57°. It should be noted that in both of P2VB and DSP crystals the rotation of the pyridine or pyrazine ring is larger than that of the benzene ring.

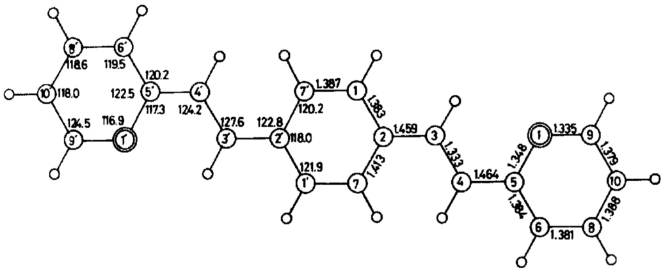


Fig. 1. Bond lengths (Å) and angles (degrees).

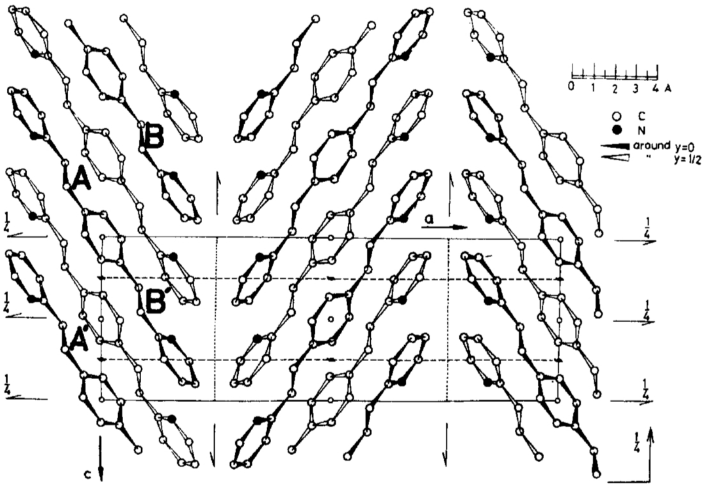


Fig. 2. The crystal structure viewed along the b-axis.

The crystal structure of P2VB is similar to that of DSP. The molecular arrangement viewed along the b-axis is shown in Fig. 2. The shortest distance between reactive double bonds (A and B) is found to be 3.910 Å, which are related by the center of symmetry. The second shortest is greater than 5 Å. Therefore, it is most probable that the double bonds mentioned above react to form a cyclobutane ring and consequently polymer chains should grow in the direction of the c-axis.

A single crystal of P2VB mounted on the goniometer head of Weissenberg camera, whose c-axis was parallel to the rotation axis of the camera, was irradiated with 100W high pressure Hg lamp, and then the rotation and Weissenberg photographs were taken. Very sharp diffraction patterns on these photographs indicate that the polymer crystal is three-dimensionally oriented; the degree of orientation along the c-axis is quite high while there is some disorder in (001) plane, as was found in the case of poly-DSP.2) From the rotation and Weissenberg photographs of partially polymerized crystal, it was revealed that the three axes of poly-P2VB coincide to those of the monomer crystal. Unit cell dimensions obtained are listed in Table 1. From the systematic

Table 1. Crystallographic data

		a	b	c	z	$\rho_{calc.}$	space group
P2VB	monomer	21.060	9.567	7.311	4	1.281	Pbca
	polymer	18.9	10.5	7.53	4	1.26	Pbca
DSP	monomer	20.639	9.599	7.655	4	1.244	Pbca
	polymer	18.4	10.9	7.52	4	1.26	Pbca

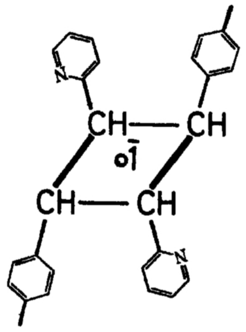


Fig. 3. The steric configuration of poly-P2VB.

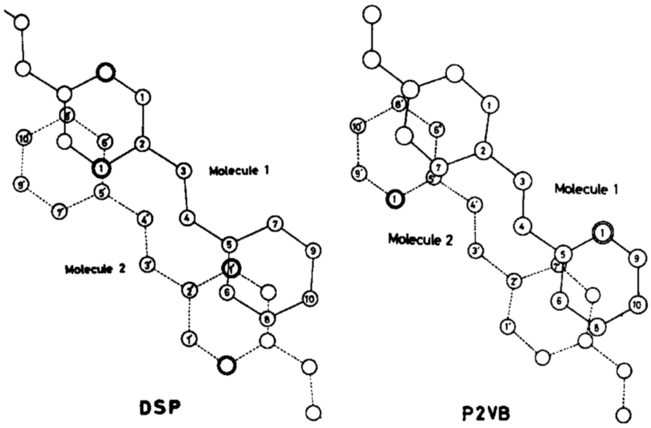


Fig. 4. The overlapping of the reactive molecules viewed along the normal of average plane of the molecules.

extinction in hk0 and hkl Weissenberg photographs, the space group is determined to be Pbca. Since the space group Pbca requires the center of symmetry at the center of the cyclobutane ring, the steric configuration of poly-P2VB is concluded to be 1,3-trans with respect to the planar cyclobutane ring, as shown in Fig. 3. This configuration is compatible with that presumed from the crystal structure of monomer.

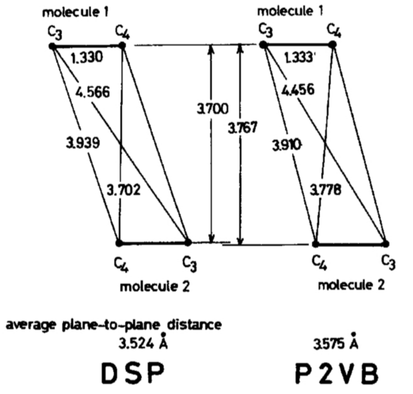


Fig. 5. Interatomic distance between reactive double bonds.

As a result of polymerization of P2VB, the c-axis, (the direction of chain growth) is elongated by 2.7 % and the density decreases about 1.6 %. In the case of DSP, the c-axis is contracted by 1.5 % and the density increases 1.3 %. The change of the a- and b-axial lengths on polymerization are similar to those of DSP. It should be pointed out that the unit cell dimensions of poly-P2VB are very close to those of poly-DSP. Since the steric configurations of both polymers are also identical to each other, it can be concluded that the general structure of poly-P2VB is similar to that of poly-DSP.

The quantum yield of P2VB is 0.04, 30 times smaller than that of DSP (1.20), at the initial stage of the crystalline-state photo-polymerization,[4] while nearly equal reactivity was found for the photo-cycloaddition oligomerization of P2VB and DSP in solution.[6] Accordingly, the great difference can not be ascribed to the isolated molecules. Although the crystal structures of P2VB and DSP are similar to each other as described above, there are some slight but definite differences as follows: (1) The overlapping of the reactive molecules viewed along the normal of the average plane of the molecules is shown in Fig. 4. The overlap of the nitrogen atom and the benzene ring is completely different in both crystals. The average plane-to-plane distance of 3.58 Å in P2VB crystal is somewhat longer than that in DSP crystal (3.52 Å). (2) Intermolecular contacts between the reactive double bonds are shown in Fig. 5. The distance (3.910 Å) between the atoms which should form a σ-bond in P2VB crystal is shorter than that in DSP crystal (3.939 Å).

It is also remarkable that the axial length in the chain growth direction slightly increases in polymerization of P2VB, while it decreases in DSP. Elongation of the c-axis on chain growth may result in some strain against neighbouring molecules.

At the present stage, it can not be concluded whether any of these subtle differences might directly correlate to the polymerization behaviours. But a molecular orbital treatment on the basis of the present crystal structures has well explained the observed difference in quantum yield.[7]

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