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Crystal Structure of Acrylonitrile

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Structure analysis of acrylonitrile, which is a low-melting-point (189.5 K) material, was performed using an imaging-plate-Weissenberg-camera-type-diffractometer at 153 K. The crystal was grown on the diffractometer. The molecule is almost planar and the molecular planes are stacked at regular distances along the *a* axis. The molecule takes a disordered structure since the N atom and the approximate center of the C=C double bond lie on the crystallographic mirror plane. This causes the C=C bond to be aligned to be in parallel or perpendicular arrangements to the neighboring ones along the stacking. If the solid state polymerization induced by radiation is carried out, the isotactic structure may be obtained for the parallel stacking and the syndiotactic structure may be obtained for the perpendicular stacking. Since the crystal structure is disordered, either structure or a structure with the two structures mixed (atactic structure) should be formed in the solid state polymerization.

Acrylonitrile is used as the raw material of acrylic fiber, which is one of the synthetic fibers, nylon and polyester, ABS resin, NBR rubber, etc. Solid state polymerization of acrylonitrile on exposure to vacuum ultraviolet rays,1) γ-rays,2) and electron beam3) forms poly(acrylonitrile). Its stereoregularity has been investigated by spectroscopic analyses,4) but the tacticity observed has been different in different reports. The tacticity of the polymer prepared in the solid state seems to depend on the crystal structure of the monomer. Since the melting point of acrylonitrile is 189.5 K and the single crystal formation and analysis below room temperature were very difficult, its crystal structure has not been obtained yet.

Recently, we analyzed 1,2-dimethoxyethane,5) which has long been a subject of interest for conformational studies as a monomer of poly(oxyethylene), using a new type of diffractometer with two cylindrical imaging plates as detectors (IP-Weissenberg type diffractometer) and a new type of low temperature equipment.6) The crystal structure of acrylonitrile was analyzed in the same method as that applied for 1,2-dimethoxyethane. In this paper the tacticity of poly(acrylonitrile) obtained by solid state polymerization will be discussed from the viewpoint of the crystal structure of acrylonitrile.

Experimental

Crystal Structure Analysis. Acrylonitrile was purchased from Tokyo Kasei Kogyo Co., Ltd. and was crystallized by a method similar to that reported previously.5) From the oscillation photographs at 153 K the cell dimensions and the orientation matrix were determined. The crystal data and the experimental details are summarized in Table 1. The structure was solved by the direct method with the program SHELXS-86,7) and refined by the full-matrix least-squares with the program SHELXL-93.8) Non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located on a difference Fourier map and refined isotropically. The atomic scattering factors were taken from the International Table for Crystallography.9) The final atomic parameters and the equivalent isotropic temperature factors are given in Table 2. Lists of the anisotropic temperature factors for non-hydrogen atoms and the observed and calculated structure factors are deposited as Document No. 71009 in the Office of the Editor of Bull. Chem. Soc. Jpn.

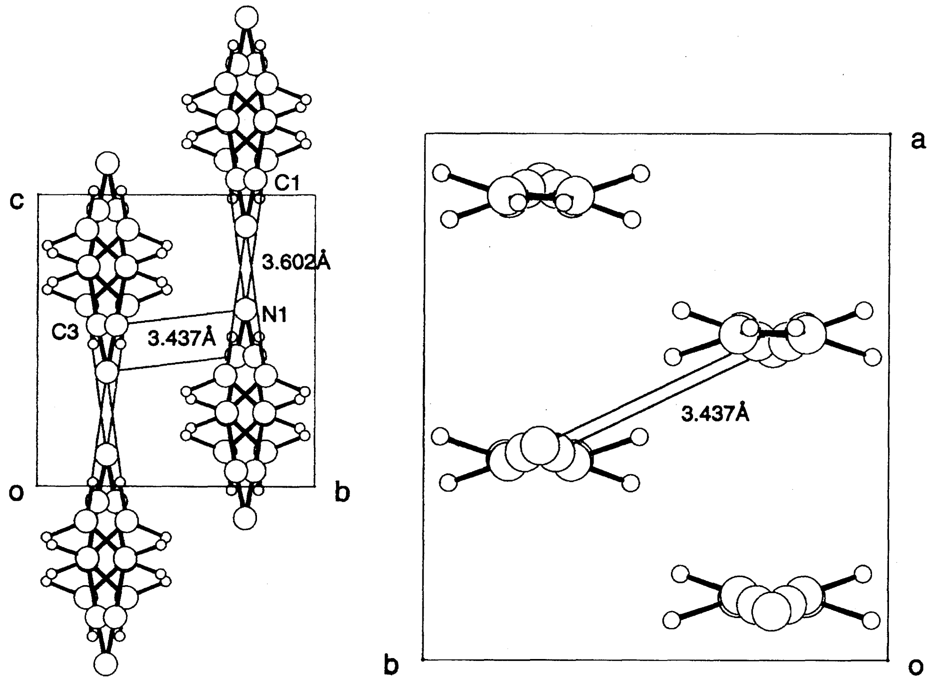
Molecular Mechanics and Molecular Orbital Calculations. Molecular mechanics calculations were carried out with the Cerius2 program10) in order to calculate the packing energy. Universal force field and Dreiding force field were used. The molecular structure obtained from the X-ray analysis was used and the molecule was treated as a rigid body when minimizing the energy.

Molecular orbital calculations were carried out with the GAUSSIAN 94 program.11) The geometry of acrylonitrile was optimized with MP2/6-31G* level.

Results and Discussion

The crystal structures viewed along the *a* axis and *c* axis and the ORTEP drawing12) of the molecular structure with the atomic numbering are shown in Figs. 1 and 2, respectively. The molecule is almost planar, within 0.005(1) Å. The molecule takes a disordered structure, since the N atom and the center of the C=C double bond lie exactly and approximately, respectively, on the crystallographic mirror plane at $y=0.25$ or 0.75 and the molecular plane is almost parallel to the *bc* plane (the angle between the planes: 6.5°). The molecules are aligned as a ribbon along the *a* axis at regular distances. The CN groups of the two molecules in the neighboring ribbons are antiparallel to each other and the intermolecular N1···C3 distance is 3.437(3) Å. This is brought about by the strong dipole–dipole interaction. In addition, the CN group directs toward C1 of the molecule in the neighboring ribbon and the intermolecular N1···C1 distance is 3.602(3) Å. These interactions play important roles in the packing of the molecules.

Bond distances and angles are also given in Fig. 2. These



(i) (ii)

Fig. 1. Crystal structure viewed along (i) *a* axis and (ii) *c* axis.

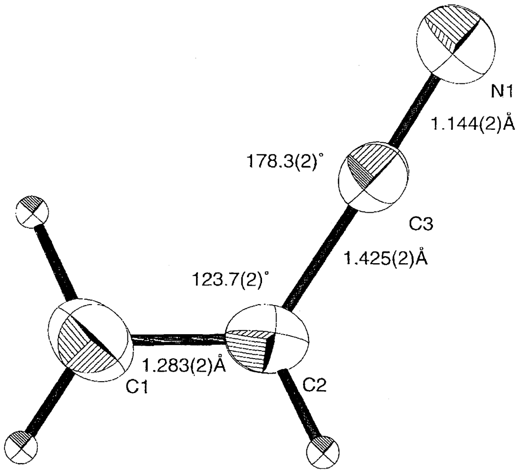
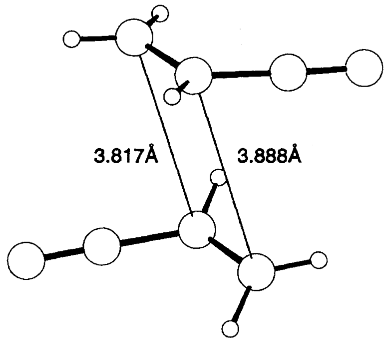


Fig. 2. ORTEP drawing with the numbering of the atoms. Thermal ellipsoids scaled to enclose 30% probability.



(i) parallel packing

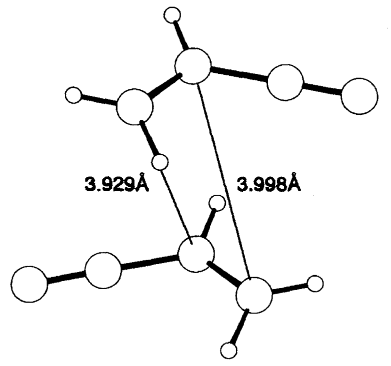


Fig. 3. The possible packing of acrylonitrile molecules (i) parallel packing, (ii) perpendicular packing.

values are consistent with the corresponding ones of the related molecules expect the $C{=}C$ distances, which is significantly different from those obtained by molecular orbital calculation, 1.342 Å, and by electron diffraction and microwave spectroscopy, 1.343 Å.[13] Since the $C{=}C$ bond lies across the mirror plane and takes a disordered arrangement, the errors in the refinement may be concentrated on the bond.

The packing pattern of the molecules in one ribbon are divided into two from the viewpoint of the relative arrangement of the $C{=}C$ double bonds. As shown in Fig. 3; one is the stacking to make the double bonds parallel and the other is perpendicular stacking. In the case of the parallel stacking in the ribbon the distances between the intermolecular carbon atoms at the end of the double bonds are 3.817(3) and 3.888(3) Å, and in the case of the perpendicular stacking in the ribbon the distances are 3.929(3) and 3.998(3) Å. These distances are less than the threshold value for polymerization, 4.2 Å.[14]

If the disordered structure is composed of the ordered do-

Table 1. Crystal Data and Experimental Details

Crystal data	
Chemical formula	C_3H_3N
Chemical formula weight	53.06
Crystal system	Orthorhombic
Space group	*Pnma*
a/Å	7.474(3)
b/Å	6.592(2)
c/Å	6.965(2)
V/Å^3	343.1(2)
Z	4
D_x/Mg m^{-3}	1.027
F(000)	112
Radiation type	Mo $K\alpha$
Wavelength/Å	0.71069
μ/mm^{-1}	0.065
Temperature/K	153
Crystal form	Cylindrical
Crystal size/mm	$0.7\phi \times 5$
Crystal color	Transparent
Data collection	
Diffractometer	Rigaku R-AXIS-II-CS
Monochromator	Graphite
Data collection method	Weissenberg
Absorption collection	None
No. of measured reflections	2649
No. of independent reflections	401
No. of reflections observed	319
Criterion for observed reflections	$I > 2\sigma(I)$
$\theta_{\max}$/°	27.49
Range of h,k,l	$-9 \to 9$ $-8 \to 8$ $-8 \to 7$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0296
$wR(F^2)$	0.0798
No. of reflections used in refinement	2649
No. of parameters	43
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.0089P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	−0.013
$\Delta\rho_{\max}$/eÅ^{-3}	0.068
$\Delta\rho_{\min}$/eÅ^{-3}	−0.057
Extinction correction	none

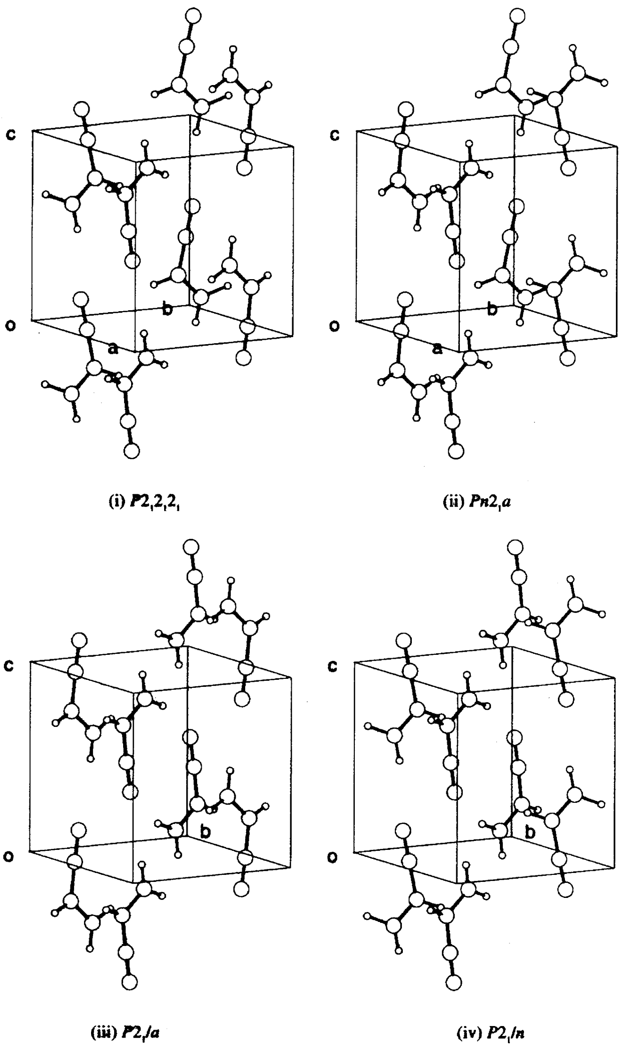
main structures, four types of crystal packing are considered, as shown in Fig. 4. The space groups are $P2_12_12_1$, $P2_1/a$, $P2_1/n$, and $Pn2_1a$, which are the maximal subgroups of *Pnma* and have no crystallographic mirror plane, causing the disordered structure. In two of four packings ($P2_12_12_1$ and $P2_1/n$) the double bonds are parallel to each other and in the other two ($P2_1/a$ and $Pn2_1a$) they are perpendicular in the neighboring molecular planes.

If the solid state polymerization induced by radiation is carried out on these four types of packing, the bonds should be formed between the intermolecular carbon atoms of the double bonds. Because the acrylonitrile in the crystal structure reacts with the radiation-induced polymerization, the concerned frontier orbitals are (1) the HOMO' of the molecules in their excited states (π) and the HOMO of the molecules in their ground states (π) or (2) the LUMO' of the

Table 2. Positional and Isotropic Thermal Parameters for Atoms
The equivalent isotropic thermal parameter is shown for non-hydrogen atoms.

Atom	x	y	z	U or U_{eq}
N1	0.5927(1)	0.2500	0.3922(1)	0.0728
C1	0.6183(2)	0.3232(3)	0.8804(3)	0.0716
C2	0.6232(2)	0.1819(2)	0.7538(3)	0.0601
C3	0.6054(2)	0.2170(4)	0.5529(2)	0.0516
H1A	0.631(2)	0.299(3)	1.013(3)	0.086
H1B	0.576(3)	0.464(3)	0.825(3)	0.086
H2	0.644(2)	0.054(3)	0.799(3)	0.072

$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.



(i) $P2_12_12_1$ (ii) $Pn2_1a$

(iii) $P2_1/a$ (iv) $P2_1/n$

Fig. 4. Four possible packing of acrylonitrile molecules (i) $P2_12_12_1$, (ii) $Pn2_1a$, (iii) $P2_1/a$, (iv) $P2_1/n$.

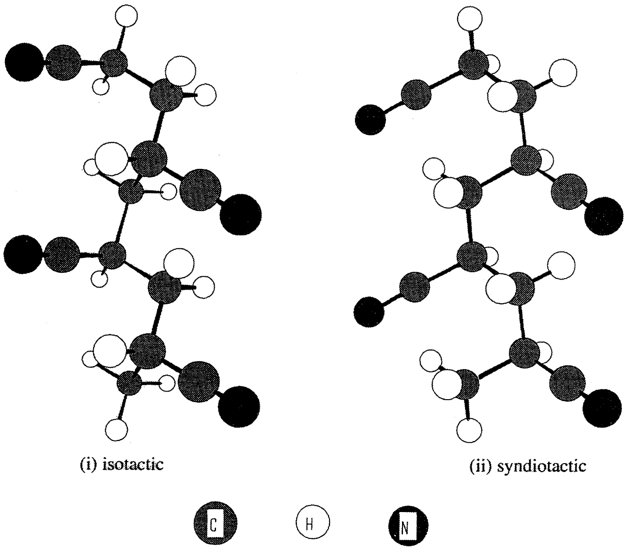

(i) isotactic (ii) syndiotactic

Fig. 5. (i) isotactic and (ii) syndiotactic structure of the polymerized acrylonitrile.

Table 3. Packing Energy of Four Non-disordered Structures (E/kJ mol^{-1})

	Dreiding force field	Universal force field
$P2_12_12_1$	−41.03	−47.79
$Pn2_1a$	−40.48	−47.22
$P2_1/a$	−39.73	−46.46
$P2_1/n$	−39.26	−46.10

molecules in their excited states (π^*) and the LUMO of the molecules in their ground states (π^*). The phase of π and π^* orbitals on the double bonded carbon atoms are in-phase and inverted at the center of C=C double bond, respectively. For both cases (1) and (2) the orbitals of two neighboring molecules in the ribbon can be in-phase between the C1 atom in one molecule and the C2 atom in another molecule and the bond can be formed between them in the crystal structure. In addition, since the bond should be formed at the shorter C1···C2 distance, the polymerization may proceed more easily than the dimerization. The shorter distances are 3.817(3) Å for the parallel stacking and 3.929(3) Å for the perpendicular one. This causes the isotactic structure for the parallel stacking and the syndiotactic structure for the perpendicular stacking. For the parallel stacking, the isotactic structure is constructed as shown in Fig. 5(i). The central part of Fig. 5(i) corresponds to Fig. 3(i) and the C···C (3.817(3) Å) interaction is indicated as bond in Fig. 5(i). For the parallel stacking, the syndiotactic structure is constructed as shown in Fig. 5(ii).

In order to investigate which structure is formed more easily than the others in view of the stability of the crystal structure of the monomer, the packing energies of four ordered crystal structures were calculated. As shown in Table 3, the packing energies of four structures are insignificantly different from each other, even if the isotactic or syndiotactic structure is formed. This result is independent on the force fields used. Therefore, either structure or the structure mixed with two structures (atactic structure) should be formed in the solid state polymerization, which well explains the results obtained form the spectroscopic analyses.[4)]

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