Molecular and crystal structure of a polycyanoarylether: poly[oxy-1,3-(2-cyanophenylene)-oxy-1,3-phenylene]

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The crystal structure of poly[oxy-1,3-(2-cyanophenylene)-oxy-1,3-phenylene] was determined by X-ray diffraction. The structure belongs to the monoclinic system with the space group $P2_1/a$, and has unit cell constants of $a=8.62$ Å, $b=13.07$ Å, c (chain axis) $=9.03$ Å and $\beta=99.0°$ (second setting). There are four monomer units (i.e. four chains) in the unit cell. The molecules in the crystal are constricted by 0.5 Å per monomeric unit from the fully extended conformation, and the planes of the adjacent benzene rings lie at an angle of ~90° to each other. The longitudinal elastic modulus of the crystalline component was estimated to be 44 GPa from the X-ray diffraction measurements. Because the polymer is not fully extended, this elastic modulus is not very high.

(Keywords: polycyanoarylether; X-ray diffraction; crystal/molecular structure)

INTRODUCTION

Poly(*p*-phenylene oxide) and poly(*p*-phenylene sulfide) are both well known engineering plastics and their crystal structures have previously been reported by Boon and coworkers[1,2]. A series of polycyanoarylethers, represented by the general chemical formula shown in *Figure 1a*, are related aromatic polyether compounds where Ar represents different kinds of aromatic groups. They have previously been synthesized by using dinitrobenzonitrile and alkali metal salts of aromatic diatomic alcohols in solution. In the case when the aromatic diatomic alcohol is resorcinol, no high polymer had been obtained. Recently, however, a new polymerization method has been developed by the Idemitsu Kosan Co. Ltd.[3] and crystalline polymers were obtained by this method which had good thermal resistance as well as high chemical resistance. In practice, the polycyanoarylether represented by the formula shown in *Figure 1b* was found to be useful as an engineering plastic. In the following, use of the term 'polycyanoarylether' implies this polymer.

This paper presents the crystal structure of this polycyanoarylether, as determined by X-ray diffraction. The so-called 'tilting phenomenon' in the stretched sample, as has been found for several other polymers[4–7], was also investigated. In addition, the longitudinal elastic modulus of the crystalline part which is an important property of an engineering plastic, was also measured by the X-ray method.

EXPERIMENTAL

Material

The reduced viscosity of the polycyanoarylether sample was more than 1.2 dl g^{-1} for a *p*-chlorophenol solution (0.2 g dl^{-1}) at 60°C. No further purification was carried out on this original polymer. Uniaxially oriented specimens were prepared by hot-drawing a hot-pressed amorphous sample to approximately five times its original length, at 230°C, with the crystallinity being improved by annealing under tension at 330°C for about 6 h.

X-ray measurements

Nickel-filtered CuKα radiation was used throughout this study. One of the fibre photographs of the uniaxially oriented specimens is shown in *Figure 2*. The *d*-spacings of the reflections were measured with a cylindrical camera of diameter 100 mm, and they were corrected with those of NaCl powder. The reflection intensities were obtained by the multiple-film method and measured visually with a standard intensity scale. The observed intensities were corrected by the use of a Lorentz-polarization factor.

The elastic modulus of the crystal was measured in the direction of the fibre axis. The measurement method was essentially the same as that developed in the Sakurada Laboratory of Kyoto University[8–10]. In this the profile of the 004 reflection was measured with a position-sensitive proportional counter (PSPC) system equipped with a curved probe of radius 200 mm, using a varying load with values up to 3.5 kg along the fibre axis. The peak-position of the reflection profile was estimated by assuming that the intensity curve could be expressed in

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terms of a second order function, as the dependence of the peak-shift (in 2θ) on the load was very small. The strain was expressed in terms of the increase in the d-spacing (as a percentage), while the stress was estimated from the load and the cross-sectional area of the specimen. In the data processing, any decrease in the cross-section of the specimen as a result of the elongation was neglected. This analysis is based on the 'series model', in which both crystalline and amorphous regions suffer the same stress in the presence of an external load.

Density measurements

The densities of two samples (with one being the uniaxially oriented sample used in the X-ray diffraction measurements, and the other a quenched, amorphous specimen) were determined by a flotation method, with the density of the liquid media (carbon tetrachloride/toluene) measured using a pycnometer.

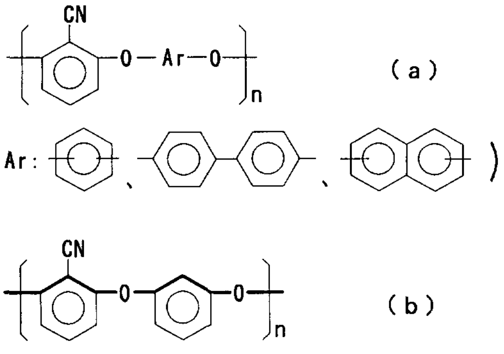

Figure 1 Chemical formulae of the polycyanoarylether series: (a) general formula and; (b) poly[oxy-1,3-(2-cyanophenylene)-oxy-1,3-phenylene]

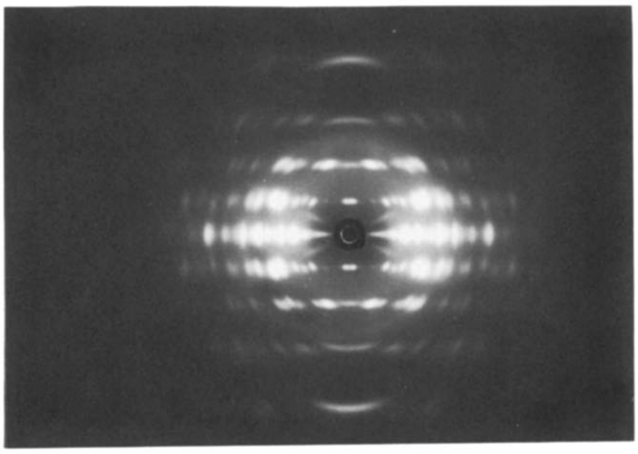

Figure 2 X-ray fibre photograph of polycyanoarylether

Thermal measurements

A Rigaku Denki differential scanning calorimeter was employed in this analysis. A hot-pressed amorphous sample was scanned from room temperature to 355°C, at a heating rate of $10^\circ C\,min^{-1}$. After the first run, the sample was cooled to room temperature (at a rate of $10^\circ C\,min^{-1}$) and a second scan was carried out in the same way. After this run, the sample was then quenched to 0°C and a third scan was then taken under the same conditions.

STRUCTURE ANALYSIS

Unit cell and space group

The X-ray fibre photograph showed 46 independent reflections from the equator up to the fourth layer line. All the reflections were indexed in terms of a monoclinic cell with cell dimensions of $a = 8.62$ Å, $b = 13.07$ Å, c (fibre axis) $= 9.03$ Å, and $\beta = 99.0^\circ$ (b-unique). The space group was not determined unequivocally from the systematic absences of the reflections alone, because, by chance, several reflections overlapped with one another. The number of monomeric units per unit cell was determined to be four by comparing the observed density of the uniaxially oriented specimen ($\rho_{obs} = 1.32\,g\,cm^{-3}$) with the calculated density of the crystalline part ($\rho_{cal} = 1.38\,g\,cm^{-3}$). Therefore, space groups $P2_1/m$, $P2/m$, $P2_1/a$, and $P2/a$, providing four general equivalent positions, were taken into account in the crystal structure analysis. The degree of crystallinity was estimated to be approximately 35% from the relationship between ρ_{obs}, ρ_{cal}, and the observed density of the quenched amorphous sample, ρ_{amor} ($= 1.29\,g\,cm^{-3}$).

Molecular structure

The observed fibre period of 9.03 Å was ~0.5 Å shorter than would be expected for a fully extended chain, where the bond lengths and bond angles used were compared to those of poly(p-phenylene oxide)[2]. Their values are shown in *Figure 3*. To calculate values for the internal rotation angles, i.e. τ_1, τ_2, τ_3 and τ_4, which satisfy the observed fibre period, apparent glide symmetry was assumed only for the backbone chain conformation, i.e.

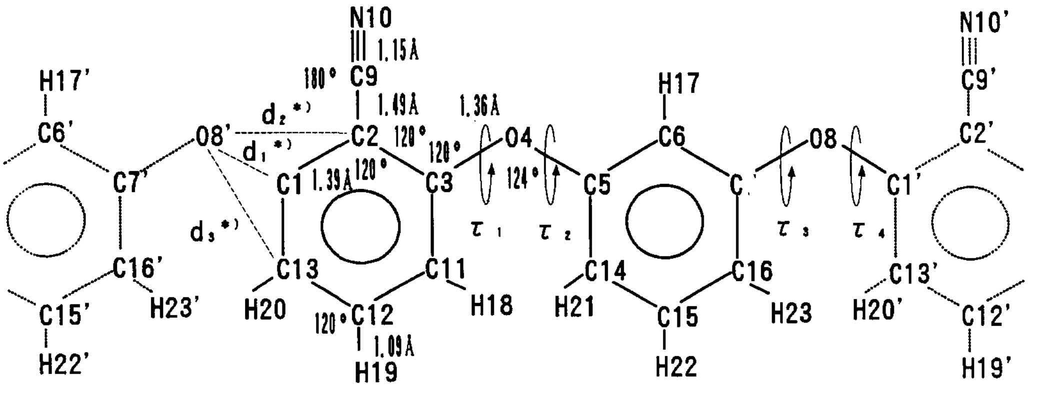

Figure 3 Parameters and constraining conditions used for refinement of the structure of polycyanoarylether: d_1^*, d_2^* and d_3^* indicate the constraining conditions used and have values of 1.36, 2.38 and 2.38 Å, respectively

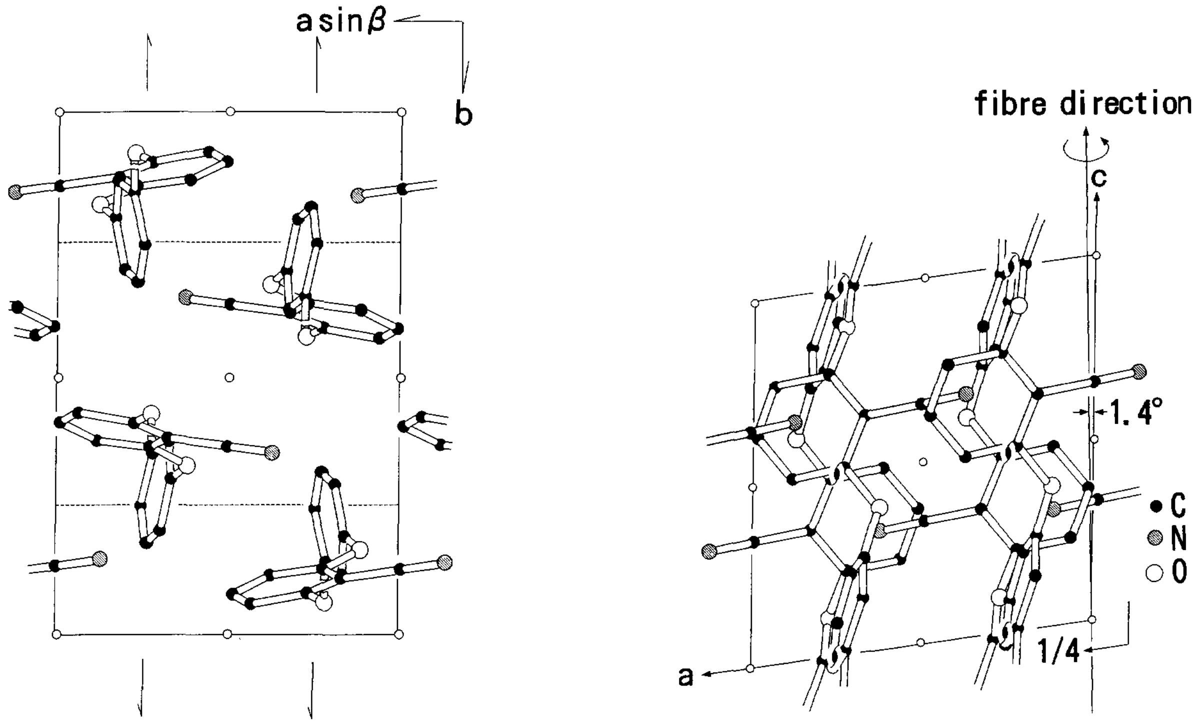

Figure 4 Crystal structure of polycyanoarylether. The left and right diagrams represent c and b projections, respectively. Hydrogen atoms are omitted

$\tau_1=-\tau_3$ and $\tau_2=-\tau_4$. Here, the backbone structure was defined by the thick lines indicated in *Figure 1b*. Accordingly, for the fully extended chain, all the internal rotation angles are 180° (*trans*-conformation). This approximation reduced the degrees of freedom for the internal rotation angles from four to one[11]. The calculated values are therefore as follows; $\tau_1=175.5°$, $\tau_2=87.0°$, $\tau_3=-\tau_1=-175.5°$, and $\tau_4=-\tau_2=-87.0°$.

Crystal structure

The crystal structure analysis has been undertaken for all of the four space groups mentioned above by using the molecular model as previously described. The translational position and orientation of the molecular model around the chain axis was examined for each space group by taking into account both the steric factor and the X-ray structure factor, using a trial-and-error procedure. For example, both of the space groups $P2_1/m$ and P2/m have mirror planes at every interval of 1/2*b*, so that the minimum size of the cross-section of the chain in the *b*-direction must be within 1/2*b*. However, it is bigger than 1/2*b* for the polycyanoarylether, so these space groups were rejected on account of steric considerations. After space group P2/a was rejected due to mismatch between the observed and calculated structure factors, only the space group $P2_1/a$ remained.

Figure 4 shows the crystal structure obtained for polycyanoarylether with the space group $P2_1/a$; the *R*-factor ($R=\sum|I_0^{1/2}-I_c^{1/2}|/\sum I_0^{1/2}$) for the observed reflections at this stage was 0.19. The model was refined by the constrained least-squares method[12,13], with the three constraining conditions which are shown in *Figure 3* being used. These constrain the bond length and angles between the ether oxygen and the aromatic ring. The adjustable parameters used in this refinement are as follows: four internal rotation angles τ_1, τ_2, τ_3 and τ_4 and two bond angles between the aromatic rings and the ether oxygens, i.e. C3–O4–C5 and C7–O8–C1′, plus the scale factor and overall temperature factor *B*.

Table 1 Fractional atomic coordinates

Atom	*x*	*y*	*z*
C(1)	0.716	0.091	0.223
C(2)	0.819	0.119	0.351
C(3)	0.762	0.141	0.483
O(4)	0.862	0.169	0.608
C(5)	0.819	0.193	0.742
C(6)	0.818	0.118	0.851
C(7)	0.773	0.142	0.988
O(8)	0.773	0.069	1.095
C(9)	0.991	0.126	0.346
N(10)	1.123	0.133	0.342
C(11)	0.618	0.134	0.488
C(12)	0.499	0.105	0.360
C(13)	0.556	0.084	0.228
C(14)	0.775	0.292	0.771
C(15)	0.731	0.317	0.908
C(16)	0.730	0.242	1.017
H(17)	0.852	0.040	0.829
H(18)	0.557	0.151	0.591
H(19)	0.374	0.100	0.364
H(20)	0.476	0.061	0.128
H(21)	0.776	0.351	0.685
H(22)	0.696	0.395	0.930
H(23)	0.695	0.261	1.124

The final atomic coordinates are listed in *Table 1*, with values for the observed and calculated structure factors given in *Table 2*. The final *R*-factor is 0.17 for all of the observed reflections, where the seven adjustable parameters are as follows: $\tau_1=179.2°$, $\tau_2=93.0°$, $\tau_3=-174.4°$, $\tau_4=-95.6°$, C3–O4–C5 = 124.9°, C7–O8–C1′ = 119.9°, and $B=9.7$ Å^2.

Table 2 Observed (F_0) and calculated (F_c) structure factors

hkl	F_0	F_c
020	53	48
120	166	157
200	98	109
130	34	48
220	51	58
040	109	120
230, 140	39	34
310	60	65
320, 240	28	22
330	38	47
400, 410, 340, 160	60	65
430, 350, 260	29	27
001	12	7
011	12	3
−111	40	20
111	31	26
−121	41	27
031	103	93
201	85	88
041	52	53
141	35	45
311, 051	30	24
321, 241, 151	33	33
−401, −411, −341, 061	38	40
401, 411	32	27
431, 351, 071	47	36
511, 521, 451	33	20
012	41	38
−112	29	23
112	25	24
−202	37	29
122	26	35
−132, 032	39	40
−312, 142	34	11
−322 232, −242	27	32
−332, −152, 052	36	39
023	26	17
113	22	22
−223, −133, 033	31	27
203, 213, 133, 043	23	26
−243	36	18
−403, −413, −343, −253	28	24
−224	13	13
−234	23	14
−314, 214, −324, 134, −144, 044	22	35
234, −154, 054	18	13

RESULTS AND DISCUSSION

Molecular and crystal structures

The internal rotation angles of the polycyanoarylether ($\tau_1 = 179.2°$, $\tau_2 = 93.0°$, $\tau_3 = -174.4°$, $\tau_4 = -95.6°$) and of poly(*p*-phenylene oxide) (*trans*-conformation; virtual bonds) are very different. As is seen in *Figure 4*, the adjacent benzene rings are at an angle of approximately 90° to each other, and the rotations of these groups reduce the chain repeat length in the case of *meta*-substitution, but they do not for a *para*-substituted species. The polycyanoarylether has CN groups which have a large dipole moment, and the antiparallel alignments of the CN groups at $z = 0.34$ and 0.66 negate the dipole moments in the crystal.

Figure 5 shows the differential scanning calorimetry (d.s.c.) traces of polycyanoarylether. Curve (a) was obtained for the amorphous starting material, while curve (b) was produced for a sample that had been slowly cooled from the melt (at a rate of 10°C min^{-1}) after the first run. Curve (c) is the scan obtained for a sample that had been rapidly quenched from the melt. It can be seen that curves (a) and (c) are essentially the same. Curve (a) shows a glass transition at 145°C, which is followed by a crystallization exotherm, and a melting endotherm at 340°C. The melting temperature is considerably higher than that of poly(*p*-phenylene oxide) (i.e. 290°C), because the CN groups may affect the intermolecular interactions. In curve (a), in addition to the crystallization exotherm at 230°C, a very small exothermic peak at 280°C is observed. After the slow-cooling process from the melt this peak is, however, clearly detectable, although this heating curve does not show either the glass transition or the original crystallization exotherm. This sample (curve (b)) is fairly well crystallized as a result of the slow cooling process. The characteristic features of curve (b) are the double-melting peaks. However, X-ray investigations of many different samples of this polymer revealed that the material does not exhibit any polymorphism. Therefore, the double-melting peaks may be attributed either to the existence of crystallites having two different sizes and/or crystal perfection, or to crystal reorganization on heating.

Elastic modulus of crystal

The elastic modulus of the crystal in the direction of the fibre axis was calculated to be 44 GPa from the slope of the stress–strain curve shown in *Figure 6*. This value was not corrected for the angle of inclination between

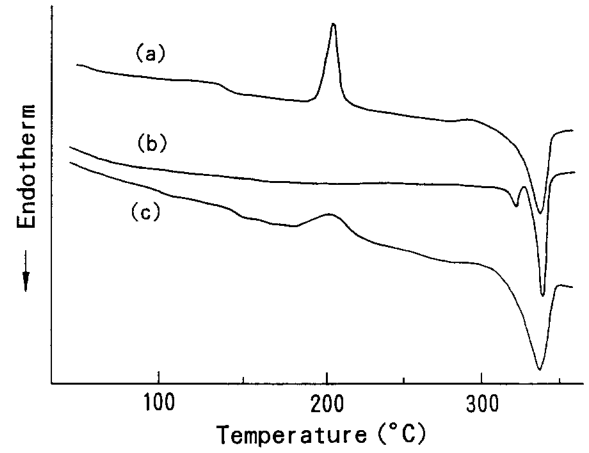

Figure 5 D.s.c. traces of polycyanoarylether, obtained for: (a) the amorphous starting material; (b) a sample that had been slowly cooled from the melt and; (c) a sample that had been rapidly quenched from the melt

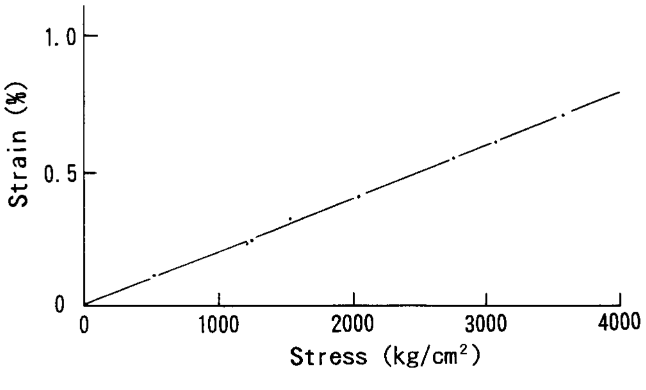

Figure 6 The stress–strain curve for polycyanoarylether obtained from the 004 reflection from X-ray diffraction measurements

the fibre axis and the normal of the (004) plane (~10°). The elastic modulus obtained is comparatively small.

In general, *para*-substituted aromatic polymers exhibit higher elastic moduli than those of *meta*-substituted ones; for example, the value for the elastic modulus of poly(*p*-phenylene terephthalamide) (Kevlar) of 153 GPa is higher than that of poly(*m*-phenylene isophthalamide) (Nomex), which has a value of 88 GPa[14]. The *para*-substituted polymer adopts an all-*trans* conformation at the virtual bonds, while the *meta*-substituted material has a molecular conformation which is shorter than the fully extended chain[15]. This feature brings about a decrease in the elastic modulus and this is also the case for the polycyanoarylether.

'Tilting phenomenon'

In principle, the chain axis in a uniaxially oriented sample coincides with the direction of drawing, but for polycyanoarylether this is not the case. As can be seen in the X-ray fibre photograph (*Figure 2*) the reflections on each layer do not make a straight line. Such a phenomenon (known as 'tilting') was first discovered and examined in poly(ethylene terephthalate) by Bunn and co-workers[4]. The origin of the tilting, however, remains uncertain. According to a quantitative analysis, the tilting in polycyanoarylether was characterized by a rotation of the chain axis (*c*-axis) around the *b*-axis by a tilting angle of 1.4°, which is defined as the angle between the chain axis and the direction of drawing (see *Figure 4*). It seems difficult, however, to find a relationship between the actual crystal structure and the tilting phenomenon. It is probable that the morphology (or the morphological change on drawing) of the crystallites (including the folded chains on the crystalline surfaces) affects this phenomenon.

CONCLUSIONS

The crystal structure of poly[oxy-1,3-(2-cyanophenylene)-oxy-1,3-phenylene] was determined, and it was found that the polymer chains in the crystal are shortened by ~0.5 Å from the fully extended form. The small longitudinal elastic modulus of 44 GPa is attributed to the chain conformation. This polymer exhibits the same 'tilting phenomenon' as is observed in poly(ethylene terephthalate): in this present case the chain axis tilts by an angle of 1.4° to the direction of drawing.

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