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Structural Studies of Poly(phosphazenes). 1. Molecular and Crystal Structures of Poly(dichlorophosphazene)

Yozo Chatani* and Koh Yatsuyanagi

Department of Material Systems Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan. *Received August 20, 1986*

ABSTRACT: The molecules of crystalline poly(dichlorophosphazene) have a glide conformation $(\text{-T}'\text{-C}'\text{-}\bar{\text{T}}'\text{-}\bar{\text{C}}'\text{-})_n$ rather than a 2/1 helix conformation as proposed previously. The internal rotation angles of the main chain are 175° (T′) and 31° (C′). The crystals belong to the monoclinic system of space group $P2_1/c$. The cell constants are a = 5.98 Å, b = 12.99 Å, c (chain axis) = 4.92 Å, and β = 111.7°. The volume of the unit cell is half that reported previously, and it contains four monomeric units (two chains). The final crystal structure was obtained by a diagonal least-squares refinement and the discrepancy factor R was 9.7%. No consideration of disorder in molecular arrangement was necessary.

Introduction

Poly(dichlorophosphazene) (PDCP, $\text{—PCl}_2\text{=N—}$) is a well-known rubbery inorganic elastomer,[1] from which a variety of poly(organophosphazenes) can be derived by substituting the chlorine atoms by alkoxy, aryloxy, or amino groups.[2] PDCP crystallizes at room temperature under tension like natural rubber and poly(isobutylene). Structural X-ray work on PDCP commenced in 1936. But probably because of the sensitivity of PDCP to atmospheric moisture, the crystal structure is still uncertain despite its simple chemical composition.

Meyer et al.[3] reported that PDCP crystallized in the orthorhombic system with cell constants of a = 11.07 Å, b (chain axis) = 4.92 Å, and c = 12.72 Å, and that the polymer chains might have a 2/1 helix conformation. In 1962 Giglio et al.[4] proposed another 2/1 helix, which was a slightly distorted cis–trans planar chain. However, this model was subjected only to examination of the molecular transform instead of calculation of the structure factor of each reflection. In the most recent X-ray work, Allcock et al.[5,6] reported many reflections. However, they could not decide the final structure among several plausible models and concluded that disorder among the setting angles of adjacent chains and, in a directional sense (up and down), of each chain might make it difficult to determine the crystal structure definitely.

Most poly(organophosphazenes) derived from PDCP have a phase transition between crystal and mesophase prior to melting. Structural investigations[7-15] on these polymers have been concentrated exclusively on the morphology, crystal modification, and the phase transition, and hence little is known about their molecular and crystal structures.[16,17] In order to establish a base line for examining the crystal structures of poly(organophosphazenes), we have reexamined the crystal structure of PDCP.

Experimental Section

Since it is well-known that atmospheric moisture induces cross-linking or degradation in PDCP, we used polymer freshly synthesized from hexachlorocyclotriphosphazene.[18] Bulk polymerization of the trimer was carried out in vacuo at 240 °C for 10 h, and the resulting polymer was purified by reprecipitation from a benzene solution with n-heptane. Specimens for X-ray diffraction measurements were prepared by casting films from benzene solution followed by stretching the film to about 8 times the original length. Specimens about 0.15 mm thick and 0.2 mm wide were fixed on a metal holder under tension and stored in a vacuum desiccator.

X-ray Diffraction. X-ray fiber photographs of the stretched specimen were taken at 10 °C in a dry nitrogen stream. Nickel-filtered copper Kα radiation was used (Figure 1). Spacings of the reflection planes were measured with a cylindrical camera of 100-mm diameter and were corrected with those of NaCl powder. Reflection intensities were obtained by using the same camera with the multiple-film method and were visually estimated with a standard intensity scale. The Lorentz polarization factor and spot shapes were corrected for the observed intensities. The total number of observed reflections was 66 on the zeroth-, first-, and second-layer lines. This number is larger than the 48 of Allcock et al. (Table I in ref 6), probably because of our better resolution of reflections.

Crystal Structure Analysis. Structure of the *ab* Projection. The equatorial $hk0$ reflections are explained in terms of an orthogonal cell with cell constants of a = 5.56 Å and b = 12.99 Å. This ab cross section is half that proposed earlier.[3,4,6] However, this cell is essentially identical with the previously reported ones, for example, when the a (=12.99 Å) and b (=11.11 Å) axes of the Allcock cell are exchanged and the a dimension is halved. Actually in the Allcock cell a systematic absence of reflections for $hk0$ when k is odd is fully allowable (Table I in ref 6). Therefore the cell constants of the ab projection are consistent with each other. It appears from the earlier studies that the observed fiber period of 4.92 Å comprises two monomeric units. Therefore the cell contains four monomeric units (two chains); the calculated and observed densities are 2.17 and 2.00 g cm^{-3}, respectively.

An absence of reflections ($0k0$ when k is odd) suggests that the plane group of the ab plane is $p2gm$, which has four general equivalent points (no. 7 of plane group in ref 19). Assumption of the plane group $p2gm$ enabled us to select two types of molecular models with one monomeric unit being the asymmetric unit.

With the 2/1 helix model, the chain axis should coincide with the twofold rotation axis perpendicular to the ab plane sited at x = 0 and y = 0. The crystal structure variable in this model is therefore only rotation of the chain around the chain axis, ignoring the detailed chain conformation.

With the glide model, the glide plane of the chain should coincide with the mirror plane perpendicular to the ab plane at $y = {}^1/_4$. The crystal structure variable in the glide model is the transition of the chain along the a axis. The cis–trans planar chain model is allowable in both cases. Although the reported P–N and P–Cl bond lengths and the P–N–P and N–P–N bond angles in several chlorocyclophosphazenes $[(\text{—PCl}_2\text{=N—})_x$, x = 3–5] are widely scattered,[20-23] plausible steric models of a 2/1 helix and of a glide that satisfy the observed fiber period can be defined.

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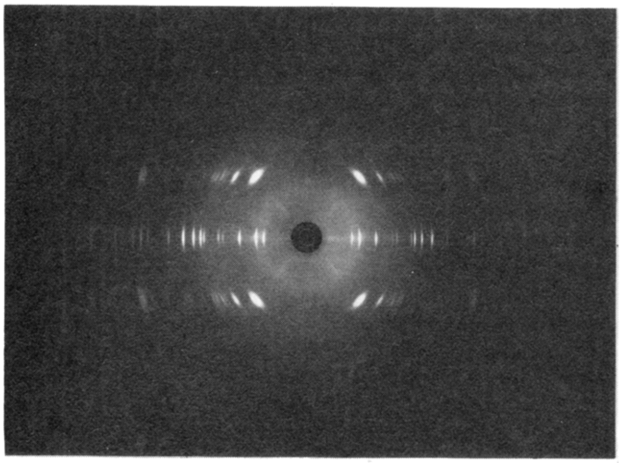

Figure 1. X-ray fiber photograph of PDCP.

Strong intensities of 100, 120, and 220 reflections together with the nonobserved 110 reflection can be explained only in terms of the glide model. The glide model was refined by a diagonal least-squares method in which a quantity $\sum(I_o^{1/2} - I_c^{1/2})^2$ was minimized by using 21 independently observed equatorial reflections, where $I_c^{1/2} = (\sum mF_c^2)^{1/2}$, where F_c is the calculated structure factor, m is the multiplicity of a reflection plane, and the sum in the parentheses is extended over all superimposed $hk0$ reflections. The discrepancy factor R $(=\sum|I_o^{1/2} - I_c^{1/2}|/\sum I_o^{1/2})$ dropped from 19% for the initial trial-and-error model to 7% after eight cycles of refinement. The very small R value encouraged us to proceed to a three-dimensional analysis of the glide model.

Three-Dimensional Structure Analysis. In the X-ray fiber photographs of a uniaxially oriented polymer sample, reflections with different *hkl* indices are frequently superimposed by chance, making it difficult to determine the unit cell and the space group without ambiguity. Allcock et al.[6] proposed several unit cells and a variety of space groups by assuming plausible systematic absences of reflections. The best unit cell they proposed is an orthorhombic cell with cell constants of a = 12.99 Å, b = 11.11 Å, and c (chain axis) = 4.92 Å, with eight monomeric units (four chains) in the unit cell. This orthogonal cell represents a transformation of our cell by doubling its a dimension and exchanging the a and b axes. The reflections of layer lines in our X-ray photographs can be roughly but not exactly explained by the Allcock cell; they are well indexed only by a monoclinic cell of the space group $P2_1/c$ with cell constants of a = 5.98 Å, b = 12.99 Å, c (chain axis) = 4.92 Å, and β = 111.7°, with four monomeric units (two chains) in the unit cell. The a dimension used in the analysis of the ab plane is therefore $a \sin \beta$ = 5.56 Å. The reciprocal lattice grid for each layer is shown in Figure 2, in which the radii of circles represent the observed ξ values of reflections.

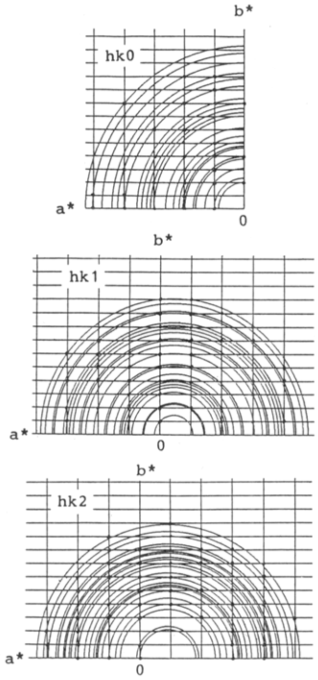

Figure 2. Reciprocal lattice grid for each layer. The radii of circles represent the observed ξ values of reflections.

Table I
Atomic Coordinates and Isotropic Thermal Parameters[a]

atom	x	y	z	B/Å^2
Cl(1)	0.195 (4)	0.077 (1)	0.358 (6)	8.3 (5)
Cl(2)	−0.333 (4)	0.140 (2)	0.088 (6)	9.0 (6)
P	0.003 (4)	0.196 (2)	0.154 (7)	7.9 (6)
N	0.041 (9)	0.214 (4)	−0.163 (15)	6.4 (16)

[a] Values in parentheses are estimated standard deviations.

Since the x and y coordinates of the atoms were determined with relatively high accuracy by examination of the $hk0$ reflections, the disposition of the chain along the c axis was found to be such that the chlorine atoms of nearest-neighbor chains are separated by about half the fiber period. This model was then refined by the least-squares method, and the R factor for all observed reflections from l = 0–2 dropped to 9.7%. Structure factors were also calculated for nonobserved reflections with the final atomic coordinates, and these reflections had small F values without abnormality. Because of the small R value, no consideration was given to any disorder in molecular arrangement as proposed by Allcock et al.[6] Table I shows the atomic coordinates and isotropic thermal parameters. Observed and calculated structure factors are listed in Table II.

Results and Discussion

Molecular Conformation. The conformation of PDCP has been shown to be a glide type. Such a glide conformation has not been reported for poly(dichlorophosphazene) or for poly(organophosphazenes). Poly(difluorophosphazene),[24] poly[bis(*p*-chlorophenoxy)phosphazene],[16] and poly[bis(3,3′-dimethylphenoxy)phosphazene][17] have 2/1 helix conformations.

We did not undertake a conformational energy calculation for PDCP because the result is strongly affected by the bond lengths and bond angles assumed in the calculation. A glide conformation, however, is not improbable, having been shown to exist in poly(vinylidene fluoride) form II[25] and poly(vinylidene chloride).[26] Table III lists the molecular dimensions obtained in the present study for PDCP together with those for the chlorocyclophosphazenes. Figure 3 shows the bond lengths, bond angles, and internal rotation angles in PDCP. It would not be expected that the small standard deviations in atomic positions found for the cyclic oligomers would also be found for PDCP. Nevertheless, the P–N–P bond angle (131°) is obviously larger than that of N–P–N (115°), and such a feature is commonly found in the cyclic oligomers.[28] The small bond angle of Cl–P–Cl (99°) is again common for these oligomers. The lengths of the two P–N bonds in PDCP, 1.67 and 1.44 Å, are appreciably different, while the P–N bond lengths of the four cyclic oligomers are between 1.492 and 1.581 Å, and a significant difference in

Table II
Comparison between Observed ($I_o^{1/2}$) and Calculated ($I_c^{1/2}$) Structure Factors

hkl	$I_o^{1/2}$	$I_c^{1/2}$
020	45	39
100	75	64
120	61	56
130	28	28
040	38	37
140, 200	41	44
210	70	64
220	69	68
150, 230	75	77
240	38	34
300	36	29
320	46	48
260, 330	29	31
080, 340	20	17
180	31	34
190, 280, 360, 400, 410	43	44
430	23	24
1,10,0	15	19
2,10,0	13	14
470, 500, 510	12	13
480	9	10
011	6	10
021	61	71
-121	62	69
031	53	58
111	22	25
211	41	43
121	32	34
041, -221, -141	37	33
131	23	24
051	28	27
141, -151	20	21
221, 151, 061, -311	37	41
-331	28	23
161	24	23
241, -261, 071	46	41
-171, -341	47	45
251	17	18
-271	23	21
311, 081, -181	26	24
321, 261, -411	26	18
341, 271, 091, -191	23	22
-371, -441	13	11
-291, -451	15	14
361, 0,10,1, -1,10,1, -381	15	15
002	9	7
012	18	19
032	16	18
-142, -232	28	25
102, 042	19	19
122, -312, -302, -152	37	40
-322	16	17
052, 132	35	38
-252	18	20
142, -162	12	17
062, -342	16	15
202, 212	13	11
222, -172, -352	16	17
072, -412, -402	13	14
232, 162, -272, -422	24	20
-432	10	10
-182	11	5
-442, 082, 172	16	13
252, -282, -372	13	11
262, -192	12	13
312, 182	13	12
-462, -382, -292, 322	20	21
-1,10,2, 192, -472, -532	16	15

Table III
Bond Lengths (Å) and Bond Angles (deg) of PDCP and Cyclic Chlorophosphazenes[a]

	P–N	P–Cl	Cl–P–Cl	N–P–N	P–N–P
PDCP	1.44, 1.67	2.04, 1.97	99	115	131
$(PCl_2N)_3$	1.581	1.993	101.4	118.4	121.4
$(PCl_2N)_4$ K form	1.570	1.989	102.8	121.2	131.3
$(PCl_2N)_4$ T form	1.559	1.992	103.1	120.5	135.6
$(PCl_2N)_5$	1.521	1.961	102.2	118.4	148.6

[a] For the cyclic oligomers averaged values are shown if there are more than two nonequivalent values.

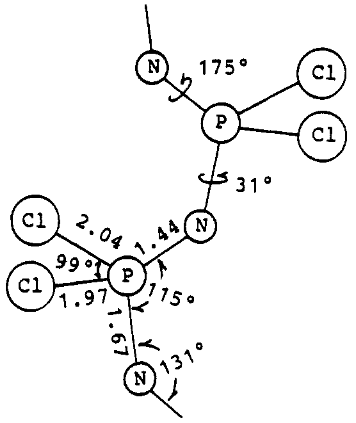

Figure 3. Bond lengths (Å), bond angles (deg), and internal rotation angles (deg) of PDCP.

P–N bond lengths was not found in any of the oligomers. The standard deviations of the P–N bond lengths in PDCP are 0.08 Å for the 1.67-Å bond and 0.05 Å for the 1.44-Å bond; accordingly, we do not discuss the bond character in detail. It is of interest to note, however, that in a dielectric study of poly(phenoxyphosphazene) in dilute solutions,[27] a large dipole moment along the chain was attributed to nonequivalent P–N bonds. The glide conformation of PDCP is expressed as $(\text{-}T'\text{-}C'\text{-}\bar{T}'\text{-}\bar{C}'\text{-})_n$, where the internal rotation angles are 175° (T′) and 31° (C′).

Molecular Arrangement. The molecular arrangement in the crystal is shown in Figure 4. No consideration of disorder in molecular arrangement was necessary to eliminate the discrepancies between observed and calculated structure factors.

The glide-type PDCP chain has directional qualities in the plane perpendicular to the chain axis as well as along the chain axis. The molecules that align along the *a* axis have the same directional qualities in both senses, and in the neighboring alignment the senses are opposite; thus the dipole moments of the molecules are cancelled as a whole in the crystal. PDCP is therefore rather similar to poly(vinylidene fluoride) form II in molecular arrangement as well as in molecular conformation.

The direct intermolecular contacts occur between chlorine atoms. The intermolecular Cl- -Cl distances, 3.61, 3.72, 3.79, and 3.84 Å, are in the range of usually accepted values.

Comparison with Earlier Studies. We comment on differences between our conclusions and those of earlier studies of PDCP.

The Giglio study[4] was concerned with molecular conformation and made no detailed examination of the unit cell and the space group. The diffraction data were shown only diagrammatically (Figure 2 in ref 4). The positions and relative intensities of reflections in the figure, however, seem to be essentially in accordance with ours. Accordingly it appears that both studies were done on the same crystal phase.

We are not sure why the data of the layer lines of Allcock (Table I and Figure 8 in ref 6) and ours are appreciably different despite the similarity on the equator. The reason

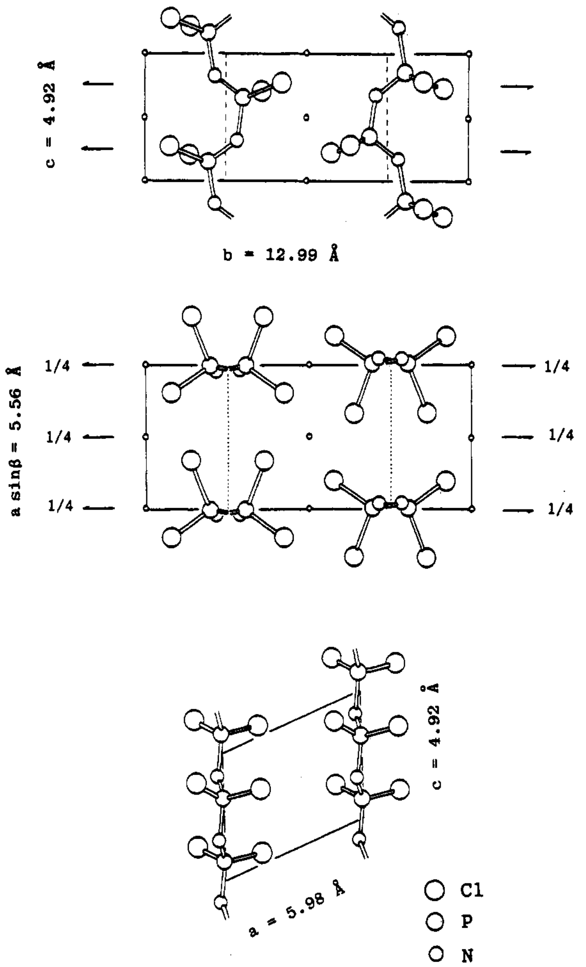

Figure 4. Crystal structure of PDCP.

could be a difference in resolution of reflections. Another possiblity is a crystal modification or a crystal phase transition, because our X-ray photographs were taken at 10 °C while the Allcock data were determined at 20 °C.

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Registry No. PDCP, 26085-02-9; $(PCl_2N)_3$, 940-71-6; $(PCl_2N)_4$, 2950-45-0; $(PCl_2N)_5$, 13596-41-3; $(PCl_2N)_3$ (homopolymer), 25231-98-5.

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