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Conformation and packing of poly(diphenylphosphazene): the crystal structure of the α-form

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Abstract

The structure of the α-form of poly(diphenylphosphazene) (PDPhP) has been determined and refined from powder diffraction data, using also literature electron diffraction information. The most plausible unit cell is monoclinic, space group $P2_1/b$, with $a = 10.23$ Å, $b = 20.00$ Å, c (chain axis) $= 10.18$ Å; $\gamma = 99.8(1)°$ and contains two chains with opposite side group orientation. The chain periodicity requires four monomer units, two of them non-equivalent. The standard moderately distorted $(TCTC)_n$ conformation of polyphosphazenes is stretched by nearly 4% with respect to the usual value, mainly widening the PNP bond angle to about 150°. Because only relatively weak, diffuse intensity is present on odd layer lines of fibre patterns, and due to the limited quality of the available diffraction data at higher angle, the refinement has been carried out adopting a simplified model with chain periodicity 5.09 Å, i.e. assuming equivalence of all monomer units. Two over-short contacts are found, both intermolecular suggesting that the conformation with the 5.09 Å repeat is acceptable for the isolated chain and that the doubling of the chain periodicity arises to optimise the packing. The proposed crystal structure represents a first simplified model of the organisation of PDPhP in the α-form. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(diphenylphosphazene); Crystal structure; X-ray diffraction

1. Introduction

Polyphosphazenes [1] are a growing class of polymers in which a wide range of side groups can be attached to the inorganic backbone of P–N units, originally via a heteroatom but more recently also by direct carbon–phosphorus bonds. Halogen polyphosphazenes and specifically poly(dichlorophosphazene) (PDCP) [2] and later poly(difluorophosphazene) (PDFP) [3] were first synthesised. Chlorine atoms on PDCP can be substituted by many different organic groups, leading to polymers where side chains are bonded to phosphorous atoms through O or N links. Few symmetrical dialkyl homopolymers have been prepared by the Neilson method consisting in the thermal polymerisation of N-silylphosphoranimines [4–8] and only some have been structurally and spectroscopically characterised in the solid state so far [9–13], namely poly(dimethylphosphazene) (PDMeP), poly(diethylphosphazene) (PDEtP) and poly(dipropylphosphazene) (PDPrP). Poly(diphenylphosphazene) (PDPhP), on the other hand, cannot be prepared from the corresponding phosphoranimine because this compound is stable above 250 °C [4]. Therefore, it has been prepared from diphenylphosphinite and trimethylsilylazide [14–16] obtaining only polymers of rather low molecular weight.

The present investigation on PDPhP was meant to evaluate the influence of rigid and relatively bulky phenyl groups, bound directly to the P–N backbone, mainly on the conformation and on the solid state organisation of the polymer. Thermal and diffraction data are already available for PDPhP [15,16] and they trace a complex polymorphic behaviour, even more intricate than what is usually found in polyphosphazenes. The crystallographic unit cells proposed for various phases of PDPhP [16] appear to correlate well with those of most other polyphosphazenes, suggesting strong similarities with respect to the main chain conformation. The data present in the literature appear, however, hardly sufficient to characterise how the phenyl side groups affect the conformation of the phosphazenic main chain. This study represents the first contribution to establish reliable models of the structures and conformations accessible to PDPhP.

2. Experimental section

2.1. Synthesis

All the reactions were performed under argon

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atmosphere. All the solvents were distilled over Na–K benzophenone ketyl. Trimethylsilylazide and chlorodiphenylphosphine (Aldrich) were used as purchased. Diphenylether and triethylamine were refluxed and distilled over P_2O_5 and CaH_2, respectively. Trifluoroethanol was stored over 3 Å molecular sieves.

2.1.1. Synthesis of 2,2,2-trifluoroethyl-diphenylphosphinite ($Ph_2POCH_2CF_3$)

19.6 g (89 mmol) of Ph_2PCl and 15 ml (107 mmol) of triethylamine were dissolved in 120 ml of dry petroleum ether. The solution was cooled to 0 °C and 10.7 g (107 mmol) of 2,2,2-trifluoroethanol were added dropwise in 20 min under stirring. After 6 h at room temperature, the suspension was filtered and the solid washed twice with petroleum ether. All the collected filtrates were distilled first at atmospheric pressure to eliminate the solvent and then at reduced pressure. The product distilled as a white liquid at 80 °C (10^{-2} mbar) and the yield was 68%. The product must be kept out of the contact with air and light. ^1H NMR, $CDCl_3$, δ: 4.22 (CH_2, doublet of quartet $J_{H-F} = 8.6$ Hz); 7.45 (multiplet, C_6H_5).

2.1.2. Polymerisation

A flask connected to the argon line, containing 2.53 g of $Ph_2POCH_2CF_3$ and 1.6 g of trimethylsilyl azide (Me_3SiN_3) dissolved in 10 ml of diphenylether was placed in a thermostatic bath at 80 °C. Heat was removed as soon as the reaction started with evolution of N_2 and the reaction was continued for 1 h reapplying heat as needed to bring the reaction to completion. After cooling, the solid polymer was extracted with chlorobenzene several times to separate the soluble low molecular weight components (linear and cyclic). The residue polymer was finally washed with acetone and dried at reduced pressure. Yield 50%. ^{31}P (CD_3COOD) 9.87 (main peak). In the spectrum several other minor peaks were detectable indicating a rather low molecular weight ($M_n \approx 6000$).

2.2. Calorimetry

DSC runs were carried out using a Perkin–Elmer DSC-7 differential scanning calorimeter with a CCA7 liquid nitrogen cooling device. Polymer samples were treated in the range 25–230 °C with typical heating and cooling rates of 10 °C/min. The annealing procedures were also performed on small sample quantities using this equipment.

2.3. X-ray diffraction

X-ray diffraction measurements on PDPhP were carried out on powder and unoriented bulk samples with an Italstructure θ/θ diffractometer, using Ni-filtered Cu Kα radiation (40 kV, 30 mA). The data used in the refinement were collected with a step width of 0.02° (2θ) and a count time of 60 s per step.

3. Thermal treatment and characterisation

The most impressive feature in the thermal behaviour of PDPhP is the complex polymorphism, which is related to the annealing treatment and the molecular weight of the sample [15,16]. The native polymer is obtained with the procedure described in Section 2, and crystallised in the α-form. Only slight traces of the mesomorphic δ-phase were detected along with a substantial amorphous fraction. To increase the crystallinity, different annealing procedures, some of which based on those reported in Ref. [15], were carried out on the native sample. However, most thermal treatments were found unsuitable because non-negligible diffraction maxima, corresponding to those attributed in the literature to β-phase, developed in annealed samples (Fig. 1).

The best procedure (which also kept at a minimum the δ and β-phase content) consisted in heating the polymer to 230 °C, then cooling it to 165 °C at 10 °C/min, from 165 to 150 °C (0.5 °C/min) and finally from 150 to 25 °C (10 °C/min) in the DSC. Even with this treatment the crystallinity of PDPhP remains quite low and a substantial amorphous contribution persists when compared to that of polydialkylphosphazenes [11–13]. In diffraction patterns, below 50°(2θ), only relatively few, often rather broad and poorly defined peaks are present, while above this angle no clear peak is detectable (Fig. 2). This is not surprising, considering the bulk and rigidity of the side groups (directly connected to the main chain), which probably make crystallisation difficult. Because of the relatively poor quality of the diffractometer powder data, photographic data from a Debye–Scherrer camera were also used for the indexing

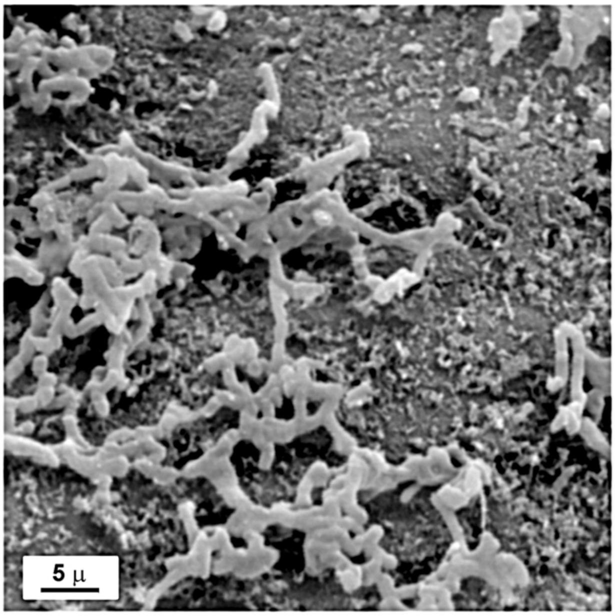

Fig. 1. X-ray diffraction pattern of an annealed sample of PDPhP, with evidence of β-phase peaks (shown by arrows).

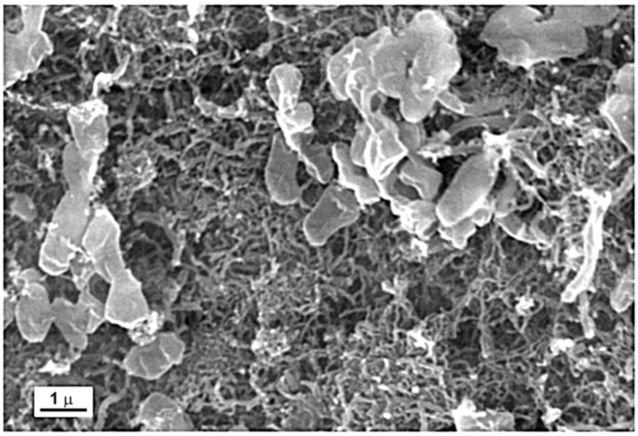

Fig. 2. X-ray diffraction pattern of PDPhP: (a) observed profile; (b) calculated profile; (c) difference curve.

procedure, since, especially at wide angle, they showed a better peak position definition.

Consistent with literature reports [16], DSC analysis performed on polydiphenylphosphazene evidenced, on heating, a quite large endothermic peak at 187 °C ($\Delta H =$ 3.9 kJ/mol) corresponding to the first order transition from the crystal to the columnar mesophase, detected in many other polyphosphazenes and usually termed T(1). Upon cooling, a sharp exothermic peak is found at 158 °C ($\Delta H = 4.9$ kJ/mol), while in successive heating runs the endothermic peak moves up to 197 °C and is associated to a perceptible increase in enthalpy values ($\Delta H = 4.4$ kJ/mol). The overall thermal and crystallisation behaviour is similar to the one reported for polymer 1 in Ref. [16] for which an M_n value of 4400 was measured by GPC: all transitions in our system appear to occur just a few degrees higher than with that sample, consistent with the slightly higher molecular weight ($M_n \approx 6000$) suggested by NMR end groups evaluation in the present case.

4. Structural determination: the model

The determination of the crystal structure of polydiphenylphosphazene (phase α) was performed from unoriented bulk spectra (Fig. 2) since we were unable to draw fibres suitable for structural analysis, due to the low molecular mass of our polymer. Available information [15,16] from oriented samples and electron diffraction was used in the lattice selection procedure.

Two proposals can be found for the unit cell of α-PDPhP in Refs. [15,16]. The first is an orthorhombic lattice [15] with $a = 9.9$, $b = 12.5$ and c (chain axis) $= 9.8$ Å, based on oriented film data. Electron diffraction data allowed successively to revise the original proposal to a monoclinic unit cell with $a = 10.1$, $b = 10.1$, c (chain axis) $= 9.95$ Å with $\gamma = 101°$. As correctly recognised and already found for various diphenoxyphosphazenes [36,37], the chain periodicity involves plausibly four monomer units in the identity period [16] and could suggest modest deviations from the standard $(cis\text{–}trans)_n$ conformation found in polyphosphazenes. As compared to the orthorhombic lattice, the monoclinic unit cell affords a calculated density of 1.29 g/cm^3, in good agreement with the experimental value of 1.25 g/cm^3 and appears clearly more reliable since it is based on two-dimensional electron diffraction data. However, also this lattice appears improbable because it implies the presence of just one chain in the unit cell. Such an occurrence was never observed in the case of refined polyphosphazene crystal structures, possibly because the two equi-probable antiparallel arrangements which the polyphosphazenic main chain can adopt have different packing requirements and are unlikely to coexist statistically at a given crystallographic position. Furthermore, the two arrangements are not likely to interconvert readily because this would require that all *cis* conformations on main chain bonds change cooperatively to *trans* and vice versa.

Another aspect requiring some consideration is that while only continuous intensity and no discrete Bragg reflection is reported on the first layer line, meridional reflections on the second, third and fourth layer line, indexed as 002, 003 and 004 were identified [16]. In essence no discrete reflections, except for 003, would thus be observed on odd layers. Strictly speaking the occurrence of the 003 reflection would require four non-equivalent chemical repeats in the chain periodicity of about 10 Å, i.e. the absence of either a glide plane or a 2_1-screw axis as intramolecular symmetry elements, normally present in other polyphosphazenes. Note that if reflections 003 is observed ([16], Table 2) we would not have any meaningful systematic absences and the most probable space group would become $P1$ since the single chain present in the cell does not admit any, except the rejected, symmetry elements. Alternatively we could interpret the data as suggesting disorder along the chain axis direction and, considering the intensity on the third layer due to continuous scattering, take space group $P2_1$ to build an approximate 2_1-helical model with two non-equivalent chemical repeats in the chain periodicity.

In the present work, we adopted the following, subsequently refined two chain unit cells: $a = 10.24(1)$ Å; $b =$ 20.02(1) Å; $c = 10.18(1)$ Å; $\gamma = 99.9(1)°$. Note that assuming space group $P2_1/b$, a space group with high packing efficiency often occurring also with polyphosphazenes, because of the $hk0$ with k odd systematic absences, the $hk0$ reciprocal lattice network practically coincides with the one of the proposed monoclinic lattice based on electron diffraction data. Because of the new indexing, the reflection previously identified as 003 can now be indexed as 013, although it could conceivably be considered also continuous scattering. Thus, the only conflict with the space group assignment is eliminated and we can assume the chain to have at least a 2_1 axis with the non-equivalent chemical repeats in the chain periodicity reducing to two.

Considering the limited quality of our diffraction data, before refining main-chain conformations containing more than one independent monomer unit in the fibre repeat, we preferred to test simplified models with the standard axial periodicity close to 4.9–5.0 Å, found in a variety of differently substituted polyphosphazenes, disregarding the observed intensity on odd layer lines.

Again space group $P2_1/b$ was adopted and confirmed by the satisfactory refinement with such a model. As already stated this simplified cell contains four equivalent monomer units belonging to two different polymeric chains. In the initial model, we assumed the molecular axis to be parallel to the monoclinic axis and coincident with the crystallographic 2_1 screw axis, i.e. on a close to tetragonal network.

5. Structural refinement

The refinement of the structure was performed with the Rietveld technique (i.e. the best fitting of the whole X-ray powder diffraction profile). We implemented all the available 'a priori' information (i.e. bond lengths and angles taken from other polymeric [11,13] and oligomeric [17,18] structures) in the program DEBVIN [19,20], which allows for constrained refinement. The final disagreement factor $R2'$ ($R2' = \sum|\mathrm{Iobs} - \mathrm{Icalc}|/\sum \mathrm{Inet}$ where $\mathrm{Inet} = \mathrm{Iobs} - \mathrm{Ibkg}$) is 0.12. In Fig. 2 the observed (a), calculated (b) and difference (c) profiles are reported. The shoulder found at 8.5° (2θ) could not be properly fitted because it is probably due to traces of the δ mesomorphic phase [15]. In Table 1, we report the refined atomic parameters of all non-hydrogen atoms and in Table 2 all the most relevant refined internal coordinates for the refined PDPhP are listed. Views of the refined molecular conformation and of the packing are shown in Fig. 3.

In the molecular model, the N–P and P–C bond lengths were set, respectively, to 1.590 and 1.800 Å, corresponding to the values determined for both cyclic [21–24] and linear [18,25] phosphazenes. Phenyl rings were inserted as rigid groups with C–C bond lengths and C–C–C bond angles fixed, respectively, to 1.39 Å and 120°, and never subsequently refined. Hydrogen atoms were located on the phenyl rings and treated as rigid body. Refined bond angles on the main chain (P–N–P: 151.7°; N–P–N: 112.0°; C–P–C: 106.6°, with estimated standard deviations between 2.0 and 3.0°) show a remarkable increase in the P–N–P value compared to PDMP [11] (135.9°), PDEP [26] (136°) and PDPrP [13] (132°): this accounts for the elongation of the main chain axial periodicity (5.092 Å) by about 4% with respect to the values found in other polyphosphazenes (4.8–4.9 Å). However, the value of the bond angle P–N–P, even if wider than the usual values reported for polyphosphazenes, is neither unfeasible, nor completely new: in many oligomeric linear phosphazenes in fact, it ranges from 120 to 150° [25,34,35] and in polydiisopropylphenoxyphosphazene [36], where bulky substituents are attached to the main chain through an oxygen atom, it is found to be around 143°. For the corresponding angles, namely the Si–O–Si angles in some polysiloxanes, similar values, ranging from 128 to 155° have been proposed [37–40].

Table 1
Refined atomic parameters of non-hydrogen atoms in PDPhP. Estimated standard deviations for fractional coordinates vary between 1.3 and 0.1. The *z* coordinates refer to the subcell with *c* equal to 5.09 Å

	X	*Y*	*Z*	*B* (Å^2)
N	−0.030	0.254	0.560	20
P	0.081	0.244	0.767	20
C1	0.130	0.163	0.709	20
C2	0.081	0.108	0.867	20
C3	0.120	0.045	0.822	20
C4	0.207	0.038	0.620	20
C5	0.257	0.094	0.462	20
C6	0.219	0.156	0.506	20
C7	0.228	0.307	0.729	20
C8	0.344	0.300	0.860	20
C9	0.457	0.349	0.830	20
C10	0.454	0.406	0.670	20
C11	0.338	0.413	0.538	20
C12	0.225	0.363	0.568	20

Table 2
Refined internal coordinates for PDPhP. Estimated standard deviations on bond angles and on torsion angles vary between 2.0 and 3.0°

Bond lengths (Å)			
N–P	1.590[a]	P–C	1.800[a]
Bond angles (°)			
N_1–P_1–N_{1A}	112.0	N–P–C	109.00°[a]
P_1–N_{1A}–P_{1A}	151.7	P–C–C	120°[a]
C_1–P_1–C_7	106.6	C–C–C	120°[a]
Torsion angles (°)			
N_1–P_1–N_{1A}–P_{1A}	− 3.6	C_7–P_1–N_{1A}–P_{1A}	120.5
P_1–N_{1A}–P_{1A}–P_2	− 175.0	C_2–C_1–P_1–N_{1A}	21.4
C_1–P_1–N_{1A}–P_{1A}	− 123.5	C_8–C_7–P_1–N_{1A}	67.5

[a] Values not refined. Values refer to all bond lengths and angles of the indicated type.

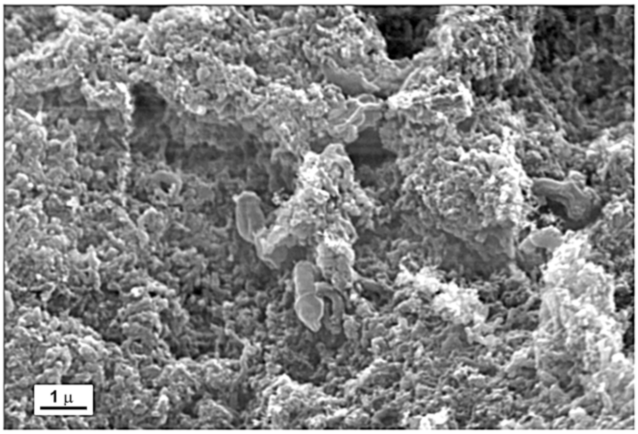

Fig. 3. Structure of PDPhP (a) and packing (b) viewed down the *c*-axis.

These literature data, together with successful refinement, suggest the reliability of the refined angle value. The remarkable flexibility of the P–N–P bond angle, together with the rigidity and bulkiness of the side groups, allow an axial periodicity higher than usual, while maintaining a *cis–trans* planar conformation on the main chain (the same established for PDMP [11], PDCP [2] and PDPrP [13]). It seems reasonable that elongation should occur because of an optimisation of the sterically unfavourable interactions between substituents, but no over-short intramolecular contacts are found in the refined structure on the same chain. The *cis* torsion angle (−3.6°) is smaller than in PDMP and PDCP (23.9 and 31°, respectively), while the *trans* torsion angle (−175.0°) is closely comparable to the one found in both PDMP and PDCP (174.1 and 175°, respectively).

The orientation of the side groups was modelled using the conformation found in the diphenylphosphazene trimer [27] as a sterically acceptable starting point and on the basis of overall pattern fitting. Similarly to what was found in the trimer [27], in our model the two rings attached to a given P atom approach orthogonality to each other, forming an angle of 73°. Each of them is in a nearly eclipsed arrangement with respect to one of the two adjacent nitrogen atoms along the main chain (see Fig. 4). Such a conformation is probably favoured by the sp^2 hybridisation of both the carbon and nitrogen atoms: an eclipsed conformation does not occur with ethyl and propyl side groups in oligomers and polymers but is found also in polystyrene [28,29], poly(*p*-methyl)styrene [30] and in some polydienes [31,32], involving, however, in the latter cases one hydrogen atom attached to the main chain. Pairs of phenyl rings on phosphorus atoms superimposing in the projection along the chain axis (see Fig. 3) are related by a *c* lattice translation (5.09 Å) and are hence parallel. Short but acceptable distances (never under 3.5 Å) between them are observed (see Fig. 3). A similar arrangement is also found in polydiphenylsiloxanes [33] where attractive non-bonding interactions between aromatic rings play a role: the highly flexible main chain is likely to adopt the conformation, which most favours these specific interactions. Intermolecular C···C distances are above 3.3 Å, with the exception of two contacts of about 3.0 Å, occurring between phenyls of chains related by one *a* lattice vector translation and having a relative orientation of about 40 °C (see Fig. 3). These contacts probably relate to two distinct causes: (i) the adoption of the simplified model with a 5.09 Å rather than a 10.18 Å axial periodicity, (ii) the stringent constraints in the model: namely the treatment of phenyl groups as rigid bodies while using for the P–C–C and N–P–C bond angles the idealised values of 120 and 109°, respectively. It should be noted that the refinement with DEBVIN is carried out only against diffraction data while high-energy non-bonding interactions can be avoided only through ad hoc weighted restraints. Given the limited quality of the diffraction data, we preferred keeping the number of variable parameters at the minimum concentrating on intramolecular rather than intermolecular interactions.

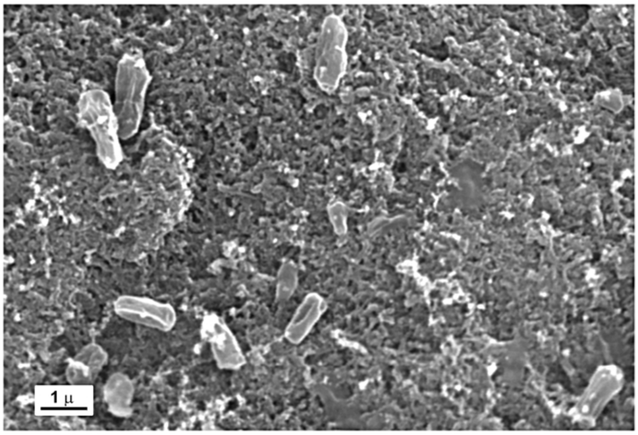

Fig. 4. Newman projection along the P–C bonds of the two phenyl rings.

It is interesting to note that using a lattice with $b = 10.01$ Å consistent with original literature proposals [16] and assuming a simplified model in space group $P2_1$ (rather than $P1$ that is implied by such interpretation of the data), the refinement yield results which are comparable to those presented above. An additional over-short C···C contact of 3.0 Å however arises between chains separated by a *b*-axis translation. Because of this and for the other reasons discussed in Section 4, we consider the larger, more symmetric unit cell with $P2_1/b$ symmetry far more reliable.

Non-structural parameters were refined as well and are listed in Table 3. A zero correction was applied to the whole diffraction pattern. Modelling of the background was difficult due to the high content of amorphous and to δ-phase traces. Since two distinct maxima were found in the background (around 9 and 20° (2θ), respectively), we treated the background as a segmented line defined by 13 points refined on the intensity scale with one superimposed bell-shaped curve for which we refined three parameters corresponding to integrated intensity, width and 2θ position. A Cauchy function was used to fit peak shapes; peak asymmetry was considered and described using two half-peak functions with different half-height widths. Refinement of U, V and W parameters in the Caglioti and Cox equation [41] led to values of crystallite dimensions (60, 56 and 37 Å) which are consistent with the hypothesis of a chain running parallel to *c*-axis, considering the very small crystal size in that direction.

6. Concluding remarks

The determination and refinement of the structure of the α-form of PDPhP indicates that the standard $(TCTC)_n$ conformation of polyphosphazenes can be effectively deformed, mainly at the PNP bond angle, increasing the

Table 3
Refined non-structural parameters

Zero correction (2θ) (°)	−0.122
Profile function parameters[a]	
U	62.8731
V	−7.3939
W	0.6870
A[b]	1.104
Preferred orientation parameter[c]	
G	0.009
Background parameters	
Segmented line points location (2θ°)	Intensity (counts 10^{-3})
5	0.064
7	0.071
10	0.068
13	0.045
15	0.061
17	0.096
20	0.139
22	0.156
25	0.116
27	0.087
30	0.059
40	0.053
52	0.037
Bell-shaped curve parameters	
Position (2θ°)	8.94
Width	3.32
Intensity (counts 10^{-3})	0.237

[a] Peak shapes are calculated analitically through a Cauchy function: $f(z) = (C/H_k)[1 + 4z^2]^{-1}$; with $z = (2\theta_i - 2\theta_k)/H_k$ and $H_k^2 = U \tan^2 \theta_k + V \tan \theta + W$.

[b] Peak asymmetry is accounted for by splitting a peak into two halves with different FWHM, so that $H'_k - H''_k = 2(A/(2\theta)^2)$, where *A* is a refinable parameter.

[c] Preferred orientation parameter is $\mathrm{PO} = \exp(-G\alpha_k^2)$ where α_k is the angle between the scattering vector of the kth reflection and the scattering vector of a fixed (the preferred) reflection of indices $h'k'l'$ given in input file, in this case 010.

chain periodicity by 4% from the usual 4.8–4.9 Å value to 5.09 Å.

The fact that the only slight $(\mathrm{TCTC})_n$ conformation of relatively flexible polyphosphazenes is favoured by so widely differing polymers suggests that it may well be stabilised also by efficient packing. Indeed, it is quite likely to occur also in the γ-phase of PDPhP, for which in Ref. [15] an orthorhombic lattice with $a = 19.9$, $b = 10.5$, $c = 9.95$ Å is reported which is a two chain unit cell metrically very close to the α-phase, except for the γ angle. It should be noted that the interchain chain packing in the α-form is close to tetragonal and chains of opposite chirality occur in the unit cell. The strong 110 reflection in the γ-phase of PDPhP is on the other hand consistent with chains located, respectively, at the origin and at the centre of the unit cell with a quasi-hexagonal chain packing. This seems broadly consistent with general trends for polymer crystallisation recently proposed by some of us [42]. The 12.5 Å value reported for the fibre repeat distance of the β-phase of PDPhP in Ref. [15] suggest that other conformations beyond the $(\mathrm{TCTC})_n$ can also be accessible to this polymer.

Even if the diffraction data used in this study were of modest quality, it was possible to reproduce the diffraction patterns using simple ordered molecular models, although with a high temperature factor. As already discussed the two over-short intermolecular distances in our model are plausibly a consequence of the simplifications adopted to keep the number of refined parameters at a minimum. Our structure could be either an 'averaged' configuration describing a disordered structure where over-short intermolecular contacts are obviously avoided. Alternatively, the packing of an ordered α-form PDPhP should take account of the non-equivalence of successive monomeric units implied by the 10.2 Å axial periodicity which was disregarded in the present refinement. Such doubling of the axial repeat and of the number of refined structural parameters seems to arise in order to optimise the intermolecular packing of the side groups, while the 5.1 Å periodicity used in our refinement already affords acceptable intrachain contacts. Better quality diffraction data would be needed to attempt developing more detailed models of the packing of the PDPhP α-form, but we are confident that the structural model we propose is a very good approximation to the structure of this phase.

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