ELSEVIER

Polymer 40 (1999) 4473–4481

polymer

Structure and polymorphic behavior of poly(dipropylphosphazene)

E. Corradi[a], A. Farina[a], M.C. Gallazzi[b], S. Brückner[c], S.V. Meille[a,*]

[a]*Dipartimento di Chimica, Politecnico di Milano, Via Mancinelli 7, 20131 Milan, Italy*
[b]*Dipartimento di Chimica Industriale, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy*
[c]*Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Via del Cotonificio 108, 33100, Udine, Italy*

Received 14 July 1998; accepted 10 September 1998

Abstract

X-ray diffraction and DSC investigations indicate that poly(dipropylphosphazene) is characterized by one ordered crystalline modification and a thermotropic mesophase, which is formed at temperatures higher than 248°C and appears to maintain a 2D order. The structure of the crystalline phase has been determined: the unit cell is monoclinic, space group $P2_1/c$, and the cell parameters are: $a = 9.10(5)$ Å, $b = 4.88(4)$ Å, $c = 19.05(10)$ Å, $\beta = 92.43(1)°$. The refinement indicates a twofold helical conformation with a nearly planar $(CT)_2$ backbone. The cyclic trimer was studied by DSC and single crystal X-ray diffraction: the unit cell is monoclinic, space group P2/c, cell parameters are $a = 10.0131(5)$ Å, $b = 7.8342(4)$ Å, $c = 15.1782(11)$ Å, $\beta = 95.844(7)°$. The conformations of the side chains in the polymer and the trimer are closely related, as already found in polydiethylphosphazene. In the polymer, however, the side chains probably show some disorder yet to be characterized.

Keywords: Poly(dipropylphosphazene); Synthesis; Crystal structure

1. Introduction

Polyphosphazenes [1] are a growing class of polymers in which the side groups may be attached to the P–N backbone via a hetero atom or via direct carbon–phosphorus bonds. Among the first polyphosphazenes to be synthesized were halogen phosphazenes: poly(dichlorophosphazene) (PDCP) [2] and poly(difluorophosphazene) (PDFP) [3]. Substitution of chlorine atoms with a great variety of organic groups on PDCP leads to polymers where side chains are bonded to phosphorus through O or N links. The few symmetrical dialkyl homopolymers prepared so far are the well characterized [4–7] poly(dimethylphosphazene) (PDMP) and poly(diethylphosphazene) (PDEP); they were prepared by a different route, namely the Neilson method, which comprises the thermolysis of *N*-silyldialkylphosphoranimine [8,9].

The thermal behavior of substituted polyphosphazenes often shows, between the glass and the melting transition, a first order transition which corresponds to the change from a highly crystalline phase to a mesophase. While the former displays 3D order, the latter is characterized by a highly disordered molecular structure and considerable chain mobility; the X-ray diffraction patterns of these mesophases generally show a single family of equatorial peaks related to distances between the molecular axes with a hexagonal arrangement.

Poly(halogenophosphazenes) previously studied (i.e. PDFP and PDCP) are highly crystalline and do not present such a mesophase, in analogy with poly(dimethyl) and poly(diethylphosphazene), which exhibit a melting transition at 146°C and 230°C, respectively.

The present investigation on poly(dipropylphosphazene) (PDPrP), aside from establishing the crystal structure of this polymer, is meant to highlight the fact that the thermal behavior of poly(dialkylphosphazenes) correlates well with that of other polyphosphazenes. The dimensions and properties of the side chains, as well as the molecular weight of the polymer, can be of great importance in determining the possible existence and stability of the mesophase.

A parallel study was conducted on the cyclic trimer (TDPrP): it displays clear similarities with the polymer concerning mainly the conformations of the propyl chains.

2. Experimental

2.1. Monomer synthesis

The monomer was prepared following the three step synthesis reported for the dimethyl derivative. Boiling

* Corresponding author. Tel.: + 39-2-23993021; fax: + 39-2-23993080.

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00688-0

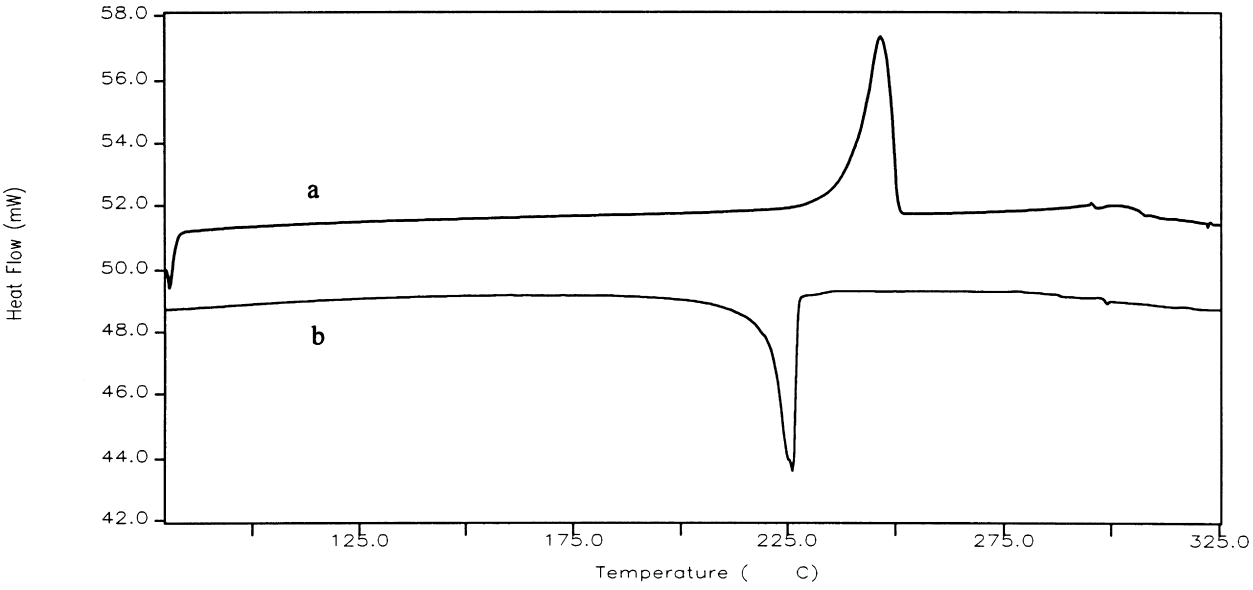

Fig. 1. DSC curve for PDPrP: (a) heating curve (10°C/min); (b) cooling curve (10°C/min).

points and NMR characterization of the phosphine, the bromide and the trifluoroethoxy monomer are reported below together with the relative yields.

P,P-dipropyl-N,N-bis(trimetylsilyl)phosphinous amide ($(Me_3Si)_2N–P(C_3H_7)_2$): boiling point: 74°C (7.2×10^{-2} bar); $^{31}P(CDCl_3)$ (H_3PO_4 external standard) δ: 49.08. Yield 68%.

P,P-dimethyl-N-(trimethylsilyl)phosphorimide bromide ($Me_3Si–N=PBr(C_3H_7)_2$): boiling point: 85°C (6×10^{-2} bar); $^{31}P(CDCl_3)$ δ: 27.1; ^{1}H ($CDCl_3$) δ: 0 (Me_3Si); 1.02 (CH_3, d, $J_{H\text{-}P} = 1.5$, $J_{H\text{-}H} = 7.25$); 1.6 (CH_2, m); 2.0 (CH_2-P, m); ^{13}C ($CDCl_3$) δ: 3.42 (Me_3Si, d, $J_{C\text{-}P} = 5.21$); 15.73 (CH_3, d, $J_{C\text{-}P} = 18.99$); 17.43 (CH_2, d, $J_{C\text{-}P} = 4.99$); 42.21 (CH_2, d, $J_{C\text{-}P} = 73.46$). Yield 82%.

2,2,2-trifluoroethyl-P,P-dipropyl-N-(trimethylsilyl)-phosphorimidate ($Me_3Si–N=POCH_2CF_3(C_3H_7)_2$): boiling point: 63.5°C (0.6 bar); $^{31}P(CDCl_3)$ δ: 39.3; ^{1}H ($CDCl_3$) δ: 0 (Me_3Si); 0.96 (CH_3, m); 1.52 (CH_2, m); 4.10 (O–CH_2, dq, $J_{H\text{-}P} = 8.8$, $J_{H\text{-}F} = 8.6$); ^{13}C ($CDCl_3$) δ: 4.16 (Me_3Si, $J_{C\text{-}P} = 2.2$); 16.08 (CH_3, d, $J_{C\text{-}P} = 16.9$); 16.69 (CH_2, s); 33.58 (CH_2–P, d, $J_{C\text{-}P} = 89.5$); 59.95 (CH_2–O, dq, $J_{C\text{-}P} = 5.2$, $J_{C\text{-}F} = 36.6$); 124.4 (CF_3, dq, $J_{C\text{-}P} = 7.5$, $J_{C\text{-}F} = 277$). Yield 60%.

2.2. Cyclic trimer synthesis

The cyclic trimer was obtained heating the bromide *($Me_3Si–N=PBr(C_3H_7)_2$)* in a glass vial sealed under vacuum at 170°C for 48 hrs. The raw product which contains 6–7% of tetramer, was purified by sublimation at reduced pressure at 100°C and crystallized from hexane. ^{31}P (external H_3PO_4) δ: 32; ^{1}H (TMS) δ: 1.01 (CH_3); 1.6 (CH_2 + CH_2–P); ^{13}C δ: 16.37 (CH_3); 16.43 (CH_2, $J_{C\text{-}P} = 17.5$); 37.32 (CH_2P, $J_{C\text{-}P} = 92.6$).

2.3. Poly(dipropylphosphazene) synthesis

2.3.1. PDPrP-30

The polymerization was performed by heating the monomer (10 ml) in a glass vial sealed in vacuum in an oven at a temperature of 190°C for 8 days. The vial was then opened in a glove box in argon and connected to a vacuum line for the elimination of $(CH_3)_3SiOCH_2CF_3$ and traces of unreacted monomer. The resulting solid was washed with methanol and methylene chloride and dried under reduced pressure. The yield was 70%.

2.3.2. PDPrP-6

The polymerization was performed at 150°C in bulk in the presence of an initiator (TBAF-tetrabuthylammonium-fluoride-) (TBAF/mon = 1/100). The yield was 89%.

Molecular weights respectively of 30 000 and 6000 were estimated according to Ref. [10]. The polymer is completely insoluble in organic solvents but can be protonated in acids and NMR data were therefore determined in deuterated acetic acid, ^{31}P (H_3PO_4 external standard) δ: 27.42; ^{1}H δ: 2.1 (t CH_3); 2.70 (m CH_3); 3.04 (m CH_2P); ^{13}C (HCOOH) δ: 15.70 (CH_3, d, $J_{C\text{-}P} = 19$); 16.69 (CH_2, s); 33.91 (CH_2P,d, $J_{C\text{-}P} = 81.2$).

2.4. Calorimetry

DSC runs were carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a CCA-7 liquid nitrogen cooling device. Polymer samples were studied in the range 40–300°C, while trimer samples were analyzed between 25°C and 170°C, both with typical heating and cooling rates of 10°C/min.

Table 1
Melting temperatures and enthalpies for alkyl substituted polyphosphazenes

	$T(1)$ (°C)	H (kJ/mol)	T_m (°C)	ΔH (kJ/mol)
PDPrP-30	248	6.6	292	1.6
PDPrP-6			205	6.8
PDEP			230	7.0
PDMP			143	5.5

2.5. X-ray diffraction

X-ray analysis of the polymer was carried out on powder samples with an Italstructure θ/θ diffractometer equipped with a thermostatic control system, using Ni-filtered Cu-$K\alpha$ 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. Single crystals of the cyclic trimer (TDPrP) were obtained crystallizing from hexane. Data were collected on a Siemens P4 diffractometer with graphite monochromated Cu-$K\alpha$ radiation at ambient conditions.

3. Results and Discussion

3.1. Thermal behavior

Heating runs of the higher molecular weight sample (PDPrP-30), show a sharp endothermic peak at 248°C and a broad one at 292°C, the enthalpies being much higher for the first transition (Fig. 1). This agrees quite well with the hypothesis of a mesophase stable in the temperature range from 248°C to about 300°C. As a matter of fact, X-ray diffraction patterns collected at 270°C show a rather sharp peak at about 9.1° (2θ), corresponding to intermolecular distances ($d = 9.7$ Å) in a hexagonal packing. In addition, residual birefringence observed by optical microscopy using polarized light, definitely confirms the presence of a certain degree of order between 248 and 300°C, while at higher temperatures birefringence totally disappears, clearly implying isotropization.

DSC runs performed on the lower molecular weight samples (PDPrP-6) do not evidence any crystalline to mesophase transition: only the melting transition is observed at about 205°C, the small polidispersity of the sample probably being the reason for the sharpness of this peak. In the second heating cycle the melting endotherm peak splits into two peaks, at 201°C and 209°C, respectively. These features may result from two distinct populations of crystal sizes. The total enthalpy value (6.4 J/mol) is quite close to that measured in the first run (6.8 J/mol), suggesting a modest change in the degree of crystallinity. X-ray diffraction data are in good agreement with all these assumptions: in fact, irrespective of the crystallization procedure used, up to 200°C, the same patterns were obtained with many well resolved sharp peaks. Patterns collected at 220°C were, no

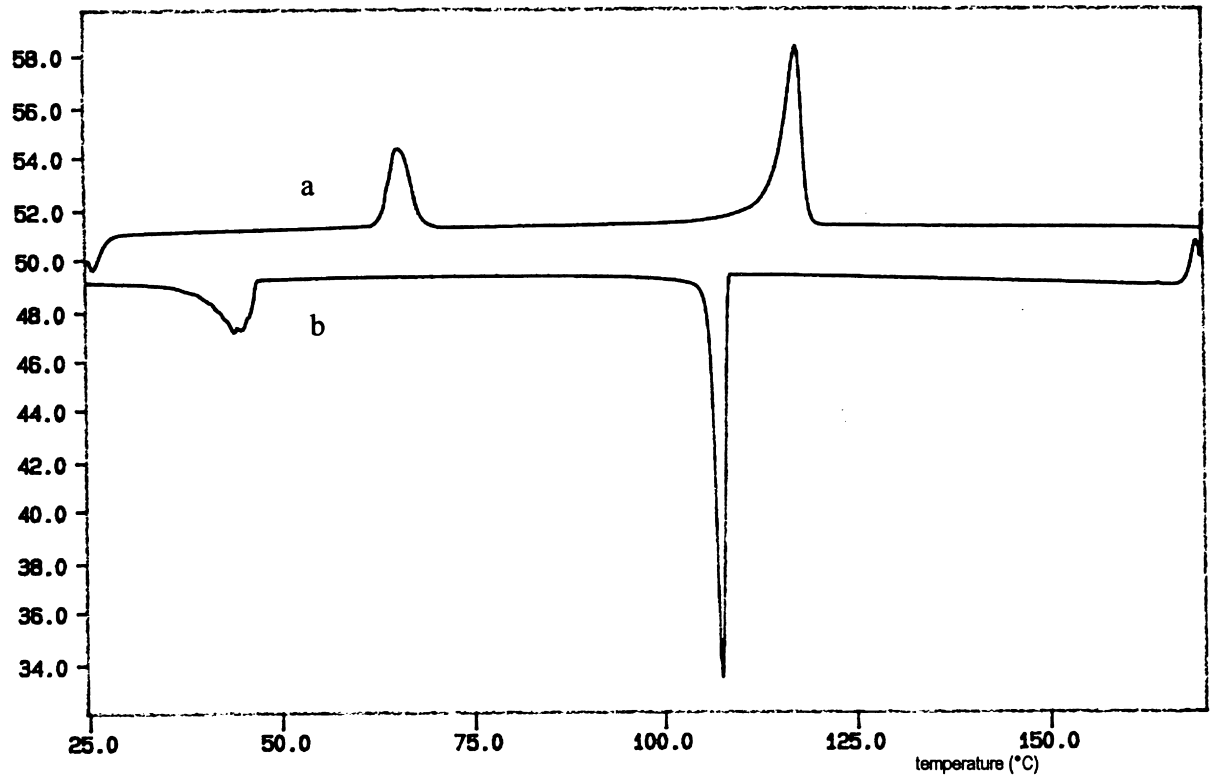

Fig. 2. DSC curve for the cyclic trimer: (a) heating curve (10°C/min); (b) cooling curve (10°C/min).

Table 2
Atomic coordinates of non-hydrogen atoms for TDPrP

Atom	X	Y	Z
P(1)	0.0000	0.8567(1)	0.2500
P(2)	0.0570(1)	1.1679(1)	0.1695(1)
N(1)	0.0400(2)	0.9646(2)	0.1666(1)
N(2)	0.0000	1.2659(3)	0.2500
C(1)	− 0.1339(2)	0.7129(3)	0.2122(2)
C(2)	− 0.2689(3)	0.7949(4)	0.1905(2)
C(3)	− 0.3785(3)	0.6711(4)	0.1575(2)
C(4)	0.2326(2)	1.2231(3)	0.1698(2)
C(5)	0.3058(3)	1.1456(4)	0.0974(2)
C(6)	0.4543(3)	1.1858(5)	0.1056(3)
C(7)	− 0.0211(2)	1.2569(3)	0.0675(2)
C(8)	− 0.1728(2)	1.2456(4)	0.0573(2)
C(9)	− 0.2357(3)	1.3376(4)	− 0.0247(2)

doubt, due to an amorphous phase. $T(1)$ and T_m transition temperatures and corresponding enthalpies of PDPrP and other substituted polyphosphazenes are reported for comparison in Table 1.

We were unable to locate the glass transition by DSC, both for the low and the high molecular weight polymers. These difficulties are consistent with the high crystallinity of the samples, estimated at about 85% from the X-ray diffraction patterns.

DSC runs were also performed on the cyclic trimer (Fig. 2); two reversible endotherms were detected at 63°C and at 117°C. The heat involved in the low temperature endotherm (4.2 kJ/mol monomer unit) is much lower than that involved in the high temperature one (10.2 kJ/mol monomer unit). In this case the first endotherm is a transition between two different crystalline modifications of the compound while the second is the melting endotherm.

3.2. Structural determination

3.2.1. Cyclic trimer

The room temperature crystal structure of the cyclic trimer (TDPrP) was determined by single crystal X-ray diffraction. Crystal data are the following: $N_3P_3C_{18}H_{42}$, $M_w = 786.91$, monoclinic, space group P2/c, $a = 10.0131(5)$ Å; $b = 7.8342(4)$ Å; $c = 15.1728(11)$ Å, $\beta = 95.844(7)°$; $V = 1184.04(12)$ Å^3; $Z = 2$; $d_c = 1.104$ g/cm^3; $F(000) = 432$; $\mu = 2.332$ mm^{-1}. Cu-$K\alpha$ radiation was used and three standard reflections were measured every 100 reflections in order to check the crystal stability: no significant variation was detected. 1613 independent reflections were collected, with $4.4° \leq \theta \leq 57.3°$ ($\pm h,k,l$; $\pm h, -k, -l$), 252 with $I < 2\sigma(I)$. Lorentz and polarization corrections, together with absorption correction (via crystal face indexing procedure) were applied. The structure was solved by direct methods using SIR-92 [11] and refined by full-matrix least squares using SHELXL-97 [12]. Hydrogen atoms were included at the calculated positions and refined in the riding mode. Final wR_2 value was 0.087. Atomic coordinates are given in Table 2 and relevant bond distances, bond angles and torsion angles are given in Table 3.

A view of the cyclic trimer is shown in Fig. 3. From Table 3 it can easily be seen that all P–N distances are almost equal, as in TDEP. The ring is nearly planar as for TDEP and TDMP [13]; the deviations from planarity are comparable with those in TDEP.

Table 3
Molecular dimensions for TDPrP

Bond lengths (Å)		Bond angles (deg.)	
P(1)–N(1)	1.6056(18)	N(1)–P(1)–N(1A)	116.50(13)
P(1)–C(1)	1.799(2)	N(1)–P(1)–C(1A)	110.05(11)
P(2)–N(2)	1.5969(13)	N(1A)–P(1)–C(1A)	108.41(11)
P(2)–N(1)	1.6020(19)	N(1)–P(1)–C(1)	108.41(11)
P(2)–C(7)	1.801(2)	N(1A)–P(1)–C(1)	110.05(11)
P(2)–C(4)	1.811(2)	C(1A)–P(1)–C(1)	102.50(16)
C(1)–C(2)	1.503(3)	N(2)–P(2)–N(1)	116.99(10)
C(2)–C(3)	1.510(4)	N(2)–P(2)–C(7)	108.28(10)
C(4)–C(5)	1.509(3)	N(1)–P(2)–C(7)	109.04(11)
C(5)–C(6)	1.513(4)	N(2)–P(2)–C(4)	107.78(9)
C(7)–C(8)	1.513(3)	N(1)–P(2)–C(4)	109.74(11)
C(8)–C(9)	1.519(3)	C(7)–P(2)–C(4)	104.26(11)
Torsion angles (deg.)		P(2)–N(1)–P(1)	122.43(11)
N(2)–P(2)–N(1)–P(1)	− 13.83(16)	P(2)–N(2)–P(2A)	122.50(16)
N(1A) –P(1)–N(1)–P(2)	7.17(9)	C(2)–C(1)–P(1)	115.29(17)
N(1)–P(2)–N(2)–P(2A)	6.62(8)	C(1)–C(2)–C(3)	113.9(2)
N(1)–P(1)–C(1)–C(2)	73.7(2)	C(5)–C(4)–P(2)	116.45(17)
N(1A) –P(1)–C(1)–C(2)	54.8(2)	C(4)–C(5)–C(6)	113.7(2)
N(1)–P(2)–C(4)–C(5)	52.5(2)	C(8)–C(7)–P(2)	114.09(17)
N(1)–P(2)–C(7)–C(8)	69.9(2)	C(7)–C(8)–C(9)	112.6(2)
N(2)–P(2)–C(4)–C(5)	− 179.04(19)		
N(2)–P(2)–C(7)–C(8)	− 58.3(2)		

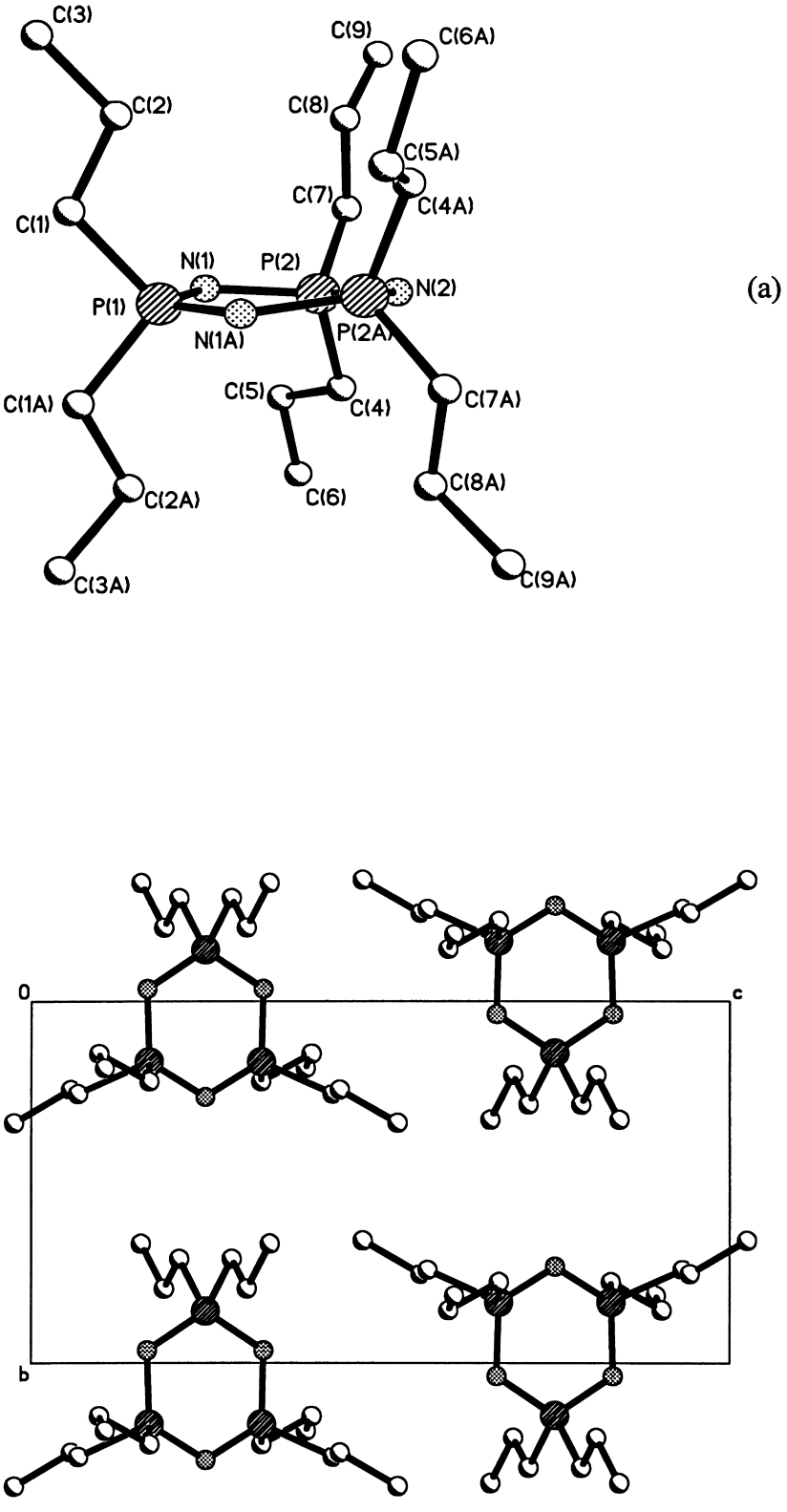

Fig. 3. Structure of the cyclic trimer (a) and packing (b) viewed down the *a* axis.

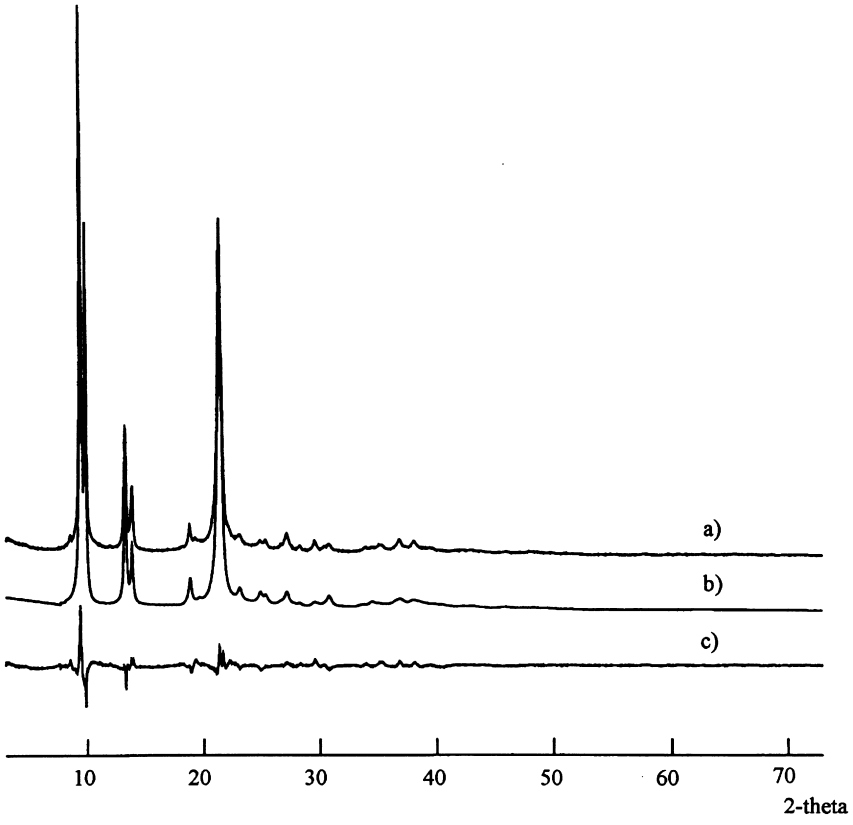

Fig. 4. X-ray diffraction pattern of PDPrP: (a) observed profile; (b) calculated profile; (c) difference curve.

The crystallographic two-fold axis contains P(1) and N(2) and is the only intramolecular symmetry element; the glide plane relates the two trimers in the unit cell. The conformations of the propyl chains resemble those of TDEP and PDEP [14]: while the two chains on P(1) have both a *gauche* conformation with respect to N atoms, one of the two chains on P(2) and one on P(2A) has a *trans* conformation with respect to one N atom.

3.2.2. Polymer

The determination of the crystal structure of poly(dipropylphosphazene) was performed uniquely from powder data since fibers could not be obtained due to the relatively low molecular weights. The spectra collected both for PDPrP-30 and PDPrP-6 are identical and show many resolved and very sharp peaks (Fig. 4). Considering that we are dealing with a polymer, the set of experimental data is indeed quite good, probably because of the relatively low molecular weight and the small polydispersity of the sample: in fact, hardly any amorphous contribution is apparent. Many intense diffraction peaks occur also at relatively high angle, suggesting a considerable degree of tridimensional order. Powder diffraction patterns were obtained both from a native sample and a melt-crystallized sample, but no significant differences were observed.

Table 4
Refined atomic parameters of non-hydrogen atoms in PDPrP

	X	*Y*	*Z*	*B* (Å^2)
N	− 0.0467(2)	0.3214(6)	0.2317(7)	14
P	0.0780(3)	0.5005(7)	0.2699(1)	14
C1	0.2521(2)	0.4310(9)	0.2321(3)	14
C2	0.2634(7)	0.5363(10)	0.2563(2)	14
C3	0.4233(6)	0.5382(7)	0.1329 (4)	14
C4	0.1062(7)	0.3882(15)	0.3595(6)	14
C5	0.2155(10)	0.5657(14)	0.4035(3)	14
C6	0.2211(15)	0.4843(18)	0.4817(3)	14

The close similarity of the chain periodicities of differently substituted polyphosphazenes suggested a plausible axial length of about 4.9 Å: starting from this assumption, indexing of the well defined reflections led to a monoclinic cell which was subsequently refined to the following values: $a = 9.10(5)$ Å; $b = 4.88(4)$ Å (molecular axis); $c = 19.05(10)$ Å; $\beta = 92.43(1)$. Space group $P2_1/c$ was chosen, on the basis of the systematic absences, and later confirmed by satisfactory refinement. With four monomer units in the unit cell, the calculated density is 1.03 g/cm^3, in good agreement with the experimental value of 1.04 g/cm^3. The four monomer units belong to two different polymeric chains: with the assumed unit cell the molecular axis is parallel to the unique axis and, unless disorder involving fractional occupancy factors is assumed, the chain axis must coincide with the crystallographic 2_1 screw axis.

The crystal structure was refined using the Rietveld

Table 5
Refined internal coordinates for PDPrP. Estimated standard deviations on bond angles vary between 0.5° and 1.0°, estimated standard deviations on torsion angles vary between 1.5° and 2.0°

Bond lengths (Å)			
N–P	1.590[a]	P–C	1.800[a]
P–N′	1.590[a]	C–C	1.540[a]
Bond angles (deg.)			
N–P–N′	114.2	N–P–C	109.17
P–N′–P′	132.6	P–C–C	114.00[a]
C–P–C	103.2	C–C–C	112.00[a]
Torsion angles (deg.)			
N–P–N′–P′	− 4.8	P–C1–C2–C3	164.9
P–N′–P′–N″	− 170.7	P–C4–C5–C6	173.5
N–P–C1–C2	71.6		
N–P–C4–C5	− 167.1		

[a] Values not refined.

technique, i.e. by the best fitting of the whole X-ray powder pattern profile. Since a priori structural information such as bond lengths and angles were available from poly(dimethylphosphazene), poly(dichlorophosphazene) and oligomeric systems, we used the program 'Debvin' [15–17], which allows for constrained refinements.

The final disagreement factor $R_2{}'$ ($R_2{}' = \Sigma|I_{obs} - I_{calc}|/\Sigma I_{net}$ where $I_{net} = I_{obs} - I_{bkg}$) is 0.13. In Fig. 4 the observed (a) and calculated (b) profiles are reported together with the difference curve (c). In Table 4 we report the refined atomic parameters of all non-hydrogen atoms and in Table 5 all the refined internal coordinates for PDPrP are listed. Views of the refined molecular conformation and of the packing are shown in Fig. 5.

The value of axial periodicity close to 4.9 Å implies the usual *cis–trans* planar conformation for the main chain (the same established for PDMP and PDCP). The N–P and P–C bond lengths were set respectively to 1.590 Å and 1.800 Å: these values correspond well to those determined for both cyclic [18–20] and linear phosphazenes [21,22]. C–C bond lengths were fixed to 1.540 Å, while C–C–C and P–C–C bond angles were set to 112° and 114°, respectively, and not refined. Hydrogen atoms were located at calculated positions after completing a few refinement cycles.

Refined bond angles on the main chain (P–N–P: 132.6; N–P–N: 114.2; C–P–C: 103.2, with estimated standard deviations between 0.5° and 1.0°) are comparable with those found in PDMP (respectively 135.9, 110.1, 103.5); the *cis* torsion angle (− 4.8°) appears to be smaller than in PDMP and in PDCP.

Propyl side chains were modeled considering available data relative to TDEP and TDPrP, non bonding contacts between the two propyl groups and overall pattern fitting. In our best model an almost *trans* conformation is adopted around one P–C bond and a nearly *gauche* one around the other, which is consistent with NMR results [23].

Intermolecular distances reach values that allow the coexistence of the two chains in the unit cell: the shortest involve methyl–methyl contacts and measure 4.5 Å, all others being larger than 4.8 Å. The shortest intramolecular distances between non-hydrogen atoms separated by more than three bonds are 3.2 Å (N–C1, N–C4), while all the others are larger than 4.5 Å. The relatively large packing contact distances suggest the possibility of disorder in the structure, probably associated with the side chains, consistent with the high values of the refined temperature factors (14 $Å^2$). This also agrees with a substantially lower density of the polymer compared with the trimer (1.03 and 1.10 g/cm^3, respectively), whereas crystalline polydimethylphosphazene, for which disordering of the side chains is irrelevant, shows higher density than the corresponding trimer (1.24 compared with 1.22 g/cm^3).

Non-structural parameters were refined as well and are listed in Table 6. A zero correction was applied to the whole profile pattern. The background level was modeled using a segmented line, defined by 14 points arbitrarily located on the 2θ scale and refined on the intensity scale. A Cauchy function was used to fit peak shapes; peak asymmetry was assumed and described using two half-peak functions with different half-height widths. In the last few cycles, crystallite dimensions were refined: half height widths of each reflection in the whole diffraction profile are considered directly related to the Miller indices *hkl* and to the mean crystallite dimensions along the three crystallographic axes [24,25]. Refinement of *U*, *V* and *W* parameters in the Caglioti and Cox [26] equation led to values of crystallite dimensions of 143 Å, 91.2 Å, and 154.7 Å, consistent with the hypothesis that the chain runs parallel to the *b*-axis. A preferred orientation parameter was taken into account along the 010 direction.

4. Concluding remarks

From the discussion of the structure and thermal behavior of PDPrP, a better understanding of the influence of side chain dimensions and molecular weight on mesophase formation in polyphosphazenes was reached. We recall that in the case of the methyl and ethyl derivatives we do not have any evidence indicating the formation of a columnar mesophase, while in the case of PDPrP only the high molecular mass polymers have a mesophase stable in a wide range of temperatures.

The mechanism leading to the formation of the mesophase probably involves, in the case of PDPrP, some side chain disorder already present in the crystal. Additional disordering of the relatively large side chains, associated with disorder of the main chain, allows the formation of a mesomorphic phase probably characterized by 2D order. In this transition, the great loss of crystalline cohesion is balanced by the entropy gain due to the disordering process.

The influence of molecular weight on the formation of a probably columnar mesophase can be understood

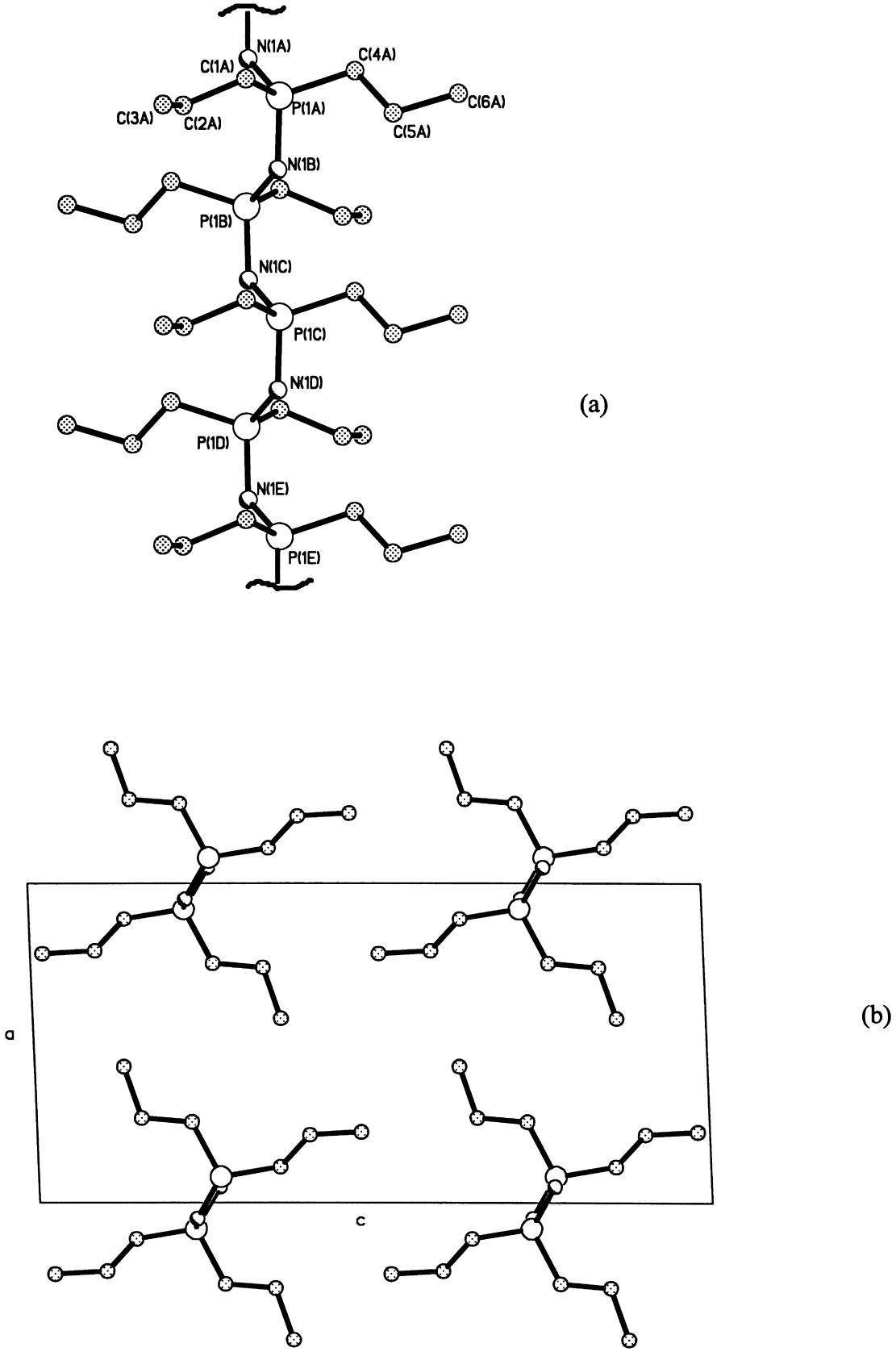

Fig. 5. Structure of PDPrP (a) and packing (b) viewed down the *b* axis.

Table 6
Refined non structural parameters

Zero correction (2θ) (deg.)	− 0.133
Profile function parameters[a]	
U	4.5630
V	− 0.5178
W	0.0403
A[b]	18.651
Preferred orientation parameter[c]	
G	0.242
Background parameters	
Segmented line points location 2θ°	Intensity (counts 10^{-3})
3	0.09426
8	0.05528
13	0.05921
18	0.05239
23	0.06807
28	0.04510
33	0.04000
38	0.05160
43	0.03632
48	0.03507
53	0.02716
58	0.02724
63	0.02887
68	0.02726
Average crystallite dimensions (Å)	
L_a	143.3
L_b	91.2
L_c	154.7

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

[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 $PO = \exp(-G\alpha_k^2)$ 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 the input file, in this case 010.

considering the free energy versus temperature diagrams discussed by Percec and Keller [27]: defects and polymeric chain ends only slightly alter the entropic contribution to the free energy of the crystal and the mesophase, but they increase the entropy of the melt, thus reducing the upper limit of existence range of the mesophase. This may explain why with very low molecular weights the columnar phase is not observed.

The presence of disorder in the PDPrP crystal is also suggested by the value of ΔH associated with the first transition of PDPrP which is comparable with those obtained for the melting of the methyl and the ethyl derivatives (see Table 1). Similar conclusions are implied by the high melting point of the 3D PDPrP crystal which is about 100°C higher than that of the ordered PDMP and very close to that observed for the ethyl derivative in which side chain disordering has been proved to occur prior to melting, thus entropically stabilizing the crystal. Again, not withstanding the very high crystallinity (~ 85% according to X-ray diffraction) the melting enthalpy of PDPrP is only ~ 60% of the global isotropization enthalpy of the trimer (respectively 8.2 and 14.4 kJ/mol monomer unit).

Considering the excellent level of the disagreement factor, no attempt was made to model disorder in more detailed ways in PDPrP crystals. Although only one conformation is given for the propyl side chains (which appears prevalent) the degree and mode of disorder present in PDPrP crystals remains therefore open for a more detailed characterization.

References

[1] Allcock HR. Phosphorous–nitrogen compounds. New York: Academic Press, 1972.
[2] Allcock HR, Arcus RA, Stroh EG. Macromolecules 1980;13:919.
[3] Allcock HR, Patterson DB, Evans TL. Macromolecules 1979;12:172.
[4] Kojima M, Magill JH. Makromol Chem 1992;193:2731.
[5] Rieck U, Magill JH. Polymer Commun 1987;28:107.
[6] Meille SV, Poletti AR, Gallazzi MC, Gleria M, Brückner S. Polymer 1992;33:2364.
[7] Meille SV, Farina A, Gallazzi MC, Sozzani P, Simonutti R, Comotti A. Macromolecules 1995;28:1893.
[8] Neilson RH, Hani R, Wisian-Neilson P, Meister JJ, Roy AK, Hagnauer GL. Macromolecules 1987;20:910.
[9] Neilson RH, Wisian-Neilson P. Chem Rev 1988;88:541.
[10] Gallazzi MC, Freddi G, Sanvito G, Viscardi G. Journal of Inorganic and Organometallic Polymers 1996;6:277.
[11] Altomare A, Cascarano G, Guagliardi A. J Appl Cryst 1993;26:343–350.
[12] Sheldrick GM. SHELXL97, Program for crystal structure refinement. University of Göttingen, Germany, 1997.
[13] Oakley RT, Paddock NL, Rettig SJ, Trotter J. Can J Chem 1977;55:4206.
[14] Farina A, Corradi E, Gallazzi MC, Meille SV. In preparation.
[15] Immirzi A. Acta Crystallogr 1978;A34:S348.
[16] Immirzi A. Acta Crystallogr 1980;B36:2378.
[17] Millini R, Perego G, Bruckner S. Mater Sci Forum 1991;71/82:239.
[18] Dougill MW, Sheldrick B. Acta Crystallogr 1977;B33:295.
[19] Hartsuiker JG, Wagner AJ. J Chem Soc, Dalton Trans 1968;1069.
[20] Dougill MW, Paddock NL. J Chem Soc, Dalton Trans 1974;1022.
[21] Allcock HR, Ngo DC, Parvez M, Visscher KB. Inorg Chem 1994;33:2090.
[22] Allcock HR, Tollefson NM, Arcus RA, Whittle RR. J Am Chem Soc 1985;107:5166.
[23] Simonutti R, Veeman WS, Ruhnau FC, Gallazzi MC, Sozzani P. Macromolecules 1996;29:4958.
[24] Allegra G, Bassi IW, Meille SV. Acta Crystallogr 1978;A34:652.
[25] Perego G, Cesari M, Allegra G. J Appl Crystallography 1984;17:403.
[26] Caglioti G, Paoletti A, Ricci FP. Nucl Instrum Methods 1958;3:223.
[27] Percec V, Keller A. Macromolecules 1990;23:4347.