X-Ray Examination of the Structure of Poly(difluorophosphazene)

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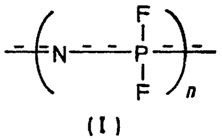
Summary *X*-Ray diffraction photographs of oriented poly(difluorophosphazene) fibres reveal the existence of two molecular conformers, one of which occupies a *cis–trans*-planar conformation: ^{19}F n.m.r. results and elasticity data indicate an unusually high chain flexibility.

WE report the results of an *X*-ray diffraction examination of high molecular weight poly(difluorophosphazene), (I), also known as poly(difluorophosphonitrile). *X*-Ray diffraction patterns of oriented fibres of poly(dichlorophosphazene), $(NPCl_2)_n$, have been studied in some detail,[1–5] and a repeating distance of 4·92 Å along the chain axis has been calculated from the relatively sharp fibre axis reflections. Giglio, Pompa, and Ripamonti[3] used these data to suggest an approximately *cis–trans*-planar chain conformation, and a recent i.r. study[6] has provided some confirmation for this interpretation. *X*-Ray repeating distances of radiation-produced poly(dibromophosphazene), $(NPBr_2)_n$, apparently show sharp Debye–Scherrer-type rings with spacings which correspond closely to those of the chloropolymer.[4] Thermally-produced poly(dibromophosphazene) was reported to be amorphous.[4] No previous attempts to examine the structure of $(NPF_2)_n$ have been reported.

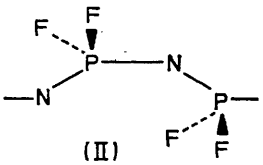


(I)

We have prepared high molecular weight $(NPF_2)_n$ by the high pressure, high temperature polymerization of the cyclic trimer, $(NPF_2)_3$, using a modification of the method reported by Seel and Langer.[7] The polymer is a transparent, hydrolytically-unstable elastomer which can be crystallized and oriented by the stretching of fibres. Analytical and i.r. data were consistent with structure (I). Low temperature X-ray fibre photographs obtained with a cylindrical camera using Cu-K_α radiation revealed two different diffraction patterns, one at temperatures between 25 and −36° (conformer A), and the second in the region of −56° (conformer B). Both showed well-resolved zero, first, and second layer line reflections.

The layer line spacings for conformer A indicated a fibre axis repeating distance of 6·49 ± 0·05 Å. A weak meridional reflection on the *hk*2 layer line (*d* = 3·20 Å) underwent a marked sharpening and intensification when the fibre axis was inclined by 15° or when the fibre was oscillated normal to the *c* axis. The unit cell was provisionally assigned to the tetragonal class with $a = b = 8{\cdot}05$ Å, although several orthorhombic cells could also be justified. A number of possible chain arrangements, including helical structures, are currently being considered for this conformer.

Conformer B provided more detailed photographs, which showed 11 *hk*0, 4 *hk*1, and 3 *hk*2 reflections. The fibre repeat distance is 4·86 ± 0·10 Å, which corresponds closely to the value of 4·92 Å reported for poly(dichlorophosphazene).[1,3,5] All the reflections for conformer B were indexed by reciprocal lattice methods for an orthorhombic cell of dimensions $a = 8{\cdot}69$, $b = 5{\cdot}38$, $c = 4{\cdot}86$ Å, with hkl; $h + k = 2n$: $hk0$; $h + k = 2n$: $0kl$; $k = 2n$: $00l$; $l = 2n$. The space group was assigned to $Cmc2_1$. A D_m of 1·84 (by flotation techniques at 25°) is undoubtedly too low to correspond to the crystalline regions of the polymer. If 4 monomer units are assumed to occupy the cell, the D_c of 2·25—2·42 corresponds closely to the known density of 2·2 for crystalline $(NPF_2)_3$.[8] Furthermore, by the use of the structural parameters, ∠P–N–P = 137, ∠N–P–N = 120, ∠F–P–F = 99·9°, P–N = 1·51, and P–F = 1·52 Å, obtained from crystal-structure work on the trimer and tetramer,[8,9] two *cis–trans*-planar chains (II), each with two monomer units per repeat, can be shown to occupy the *c*-centred cell. Fourier calculations based on this structure show good agreement with the observed intensities.



(II)

It is interesting to note that $(NPF_2)_n$ is elastomeric down to temperatures of −80° to −95° [compared with −63° for $(NPCl_2)_n$[10] and −15° for $(NPBr_2)_n$[5]], and that the ^{19}F n.m.r. spectrum of the unstretched solid remains a sharp doublet at least down to −70°. These facts indicate considerable backbone torsional mobility in this molecule and we believe that this is consistent with the low intramolecular interactions calculated for $(NPF_2)_n$.[11]

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