The Infra-red Spectrum and Vibrational Assignments of Poly(phosphonitrilic chloride)

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The infra-red spectrum of poly(phosphonitrilic chloride) has been obtained in the region 5 000–20 cm^{-1}. Correlation of the results with the spectra of some phosphonitrilic halide oligomers has enabled characterization of the polymer spectrum to be made and assignments for the phosphorus–halogen and skeletal vibrational modes are given. As expected most of the fundamentals of this molecule appear to lie in the far infra-red region. No line group splitting of these bands was observed. The vibrational spectrum of the polymer supports a distorted helical structure of C_2 *symmetry.*

CYCLIC phosphonitrilic chloride and phosphonitrilic bromide oligomers may be readily converted into a high polymer of the form $(NPX_2)_n$, where X = Cl or Br. Little work appears in the literature on physical methods of analysis of the inorganic polymer $(NPCl_2)_n$ and we are not aware of any infra-red spectroscopic studies. The X-ray pattern of the fibre which crystallizes on stretching was first investigated by Meyer *et al.*[1], who proposed a linear backbone chain of regular conformation with two mono-

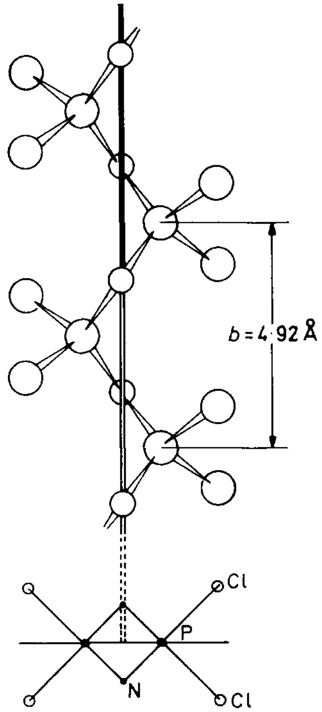

Figure 1 (a)—Uniform helical model of linear $(NPCl_2)_n$

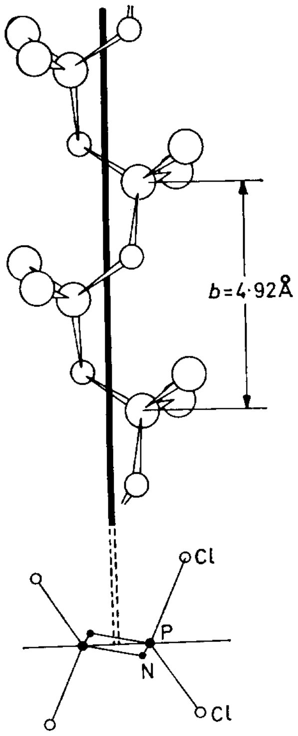

Figure 1(b)—Distorted 'cis-plan' helical model of linear $(NPCl_2)_n$

meric units in the identity period, and deduced an orthorhombic unit cell. Huggins[2] later proposed a uniform helical conformation with two monomeric units in the repeat unit [*Figure 1* (a)], using the electron diffraction results of Brockway and Bright[3] for the molecular structure of $(NPCl_2)_3$.

More recently, Giglio *et al.*[4] have shown that the identity period is not sufficient to define the chain conformation, as the study of many organic high polymers has shown. They interpreted the X-ray fibre results of stretched $(NPCl_2)_n$ by means of Fourier transform methods in an attempt to establish the chain conformation without considering the mode of packing in the crystal lattice. They concluded that the analysis was nearly consistent with a twofold helical conformation which they designate 'cis-plan' [*Figure 1* (b)], the values for the angles of rotation around the P–N and N–P bonds being 156° and 14° respectively. The 'cis-plan' conformation would correspond to angles of rotation of 180° and 0°, respectively. The analysis yielded a P–N bond length for the linear polymer of 1·60 Å, and bond angles $P\hat{N}P = 127°$. $N\hat{P}N = 119°$ and P—Cl = 1·99 Å, $Cl\hat{P}Cl = 102°$. These workers also concluded that the bond angles of the backbone chain in the linear polymer, although not accurately determined in their analysis, were slightly different from those established for $(NPCl_2)_3$ in which $N\hat{P}N = P\hat{N}P = 120°$.

In this investigation the infra-red spectrum of poly(phosphonitrilic chloride) has been examined for both the stretched polymer, and for polymer cast as a thin film on a transparent substrate, and for rubber swollen in carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$). A comparison of the polymer spectrum with the spectra of the oligomers $(NPCl_2)_3$[5,6], $(NPBr_2)_3$[7,8], $(NPCl_2)_4$[7,8] and $(NPBr_2)_4$[7,8] has enabled some characterization of the polymer to be made.

EXPERIMENTAL

Preparation of pure $(NPCl_2)_n$

The polymer was initially prepared as described by Meyer *et al.*[1]. Commercial $(NPCl_2)_3$ (Albright and Wilson) which had been recrystallized from CCl_4 and then sublimed, was heated at 300°C for twelve hours in a glass capsule sealed under vacuum. A brownish-black rubbery plug which could only be removed from the capsule with difficulty was obtained in good yield. After repeating the preparation several times with further purified oligomer over a range of temperatures between 250° and 325°C, the product continued to be a dark rubber.

It was concluded that the 'purified' oligomer used in the preparation still contained traces of an impurity which was characterized by giving a brownish-black polymer, and by being a good catalyst at about 250°C. Subsequently, a sample of poly(phosphonitrilic chloride) was obtained by courtesy of Dr R. O. Colclough. This was very pure and easily worked and was used in some runs. It appeared to be of lower molecular weight and less branched than our material but no significant difference in the spectra was noticed. We concluded that any impurities in our own polymer were not affecting the spectrum. The low molecular weight polymer was prepared by recrystallizing the oligomeric $(NPCl_2)_3$ from CCl_4, followed by refluxing over barium oxide (BaO), and then subliming the product several times, the penultimate sublimation being carried out over a phosphorus pentoxide (P_2O_5) boat, to remove all traces of moisture. The latter can also catalyse polymerization at 250°C. On heating such a sample of $(NPCl_2)_3$ *in vacuo* at 260°C for 72 hours, the product was a milky-white rubbery plug which, when swollen in CCl_4 to remove unconverted oligomer, yielded a colourless polymer[9]

Sampling techniques

In the far infra-red region, three sampling techniques were employed. The 'dry' rubber, obtained by removing all traces of CCl_4 accumulated during swelling, and removal of unconverted oligomer, was stretched and clamped between high density (Rigidex) polyethylene plates. It was found possible to 'cast' thin films of low molecular weight rubber on to a polyethylene substrate by 'smearing' the latter with rubber swollen in CCl_4. The solvent was removed under vacuum and the film clamped (and stretched) between two polyethylene discs, to prevent peeling. High molecular weight polymer was also swollen in CCl_4 and $CHCl_3$, and sections were microtomed for examination between polyethylene windows. The

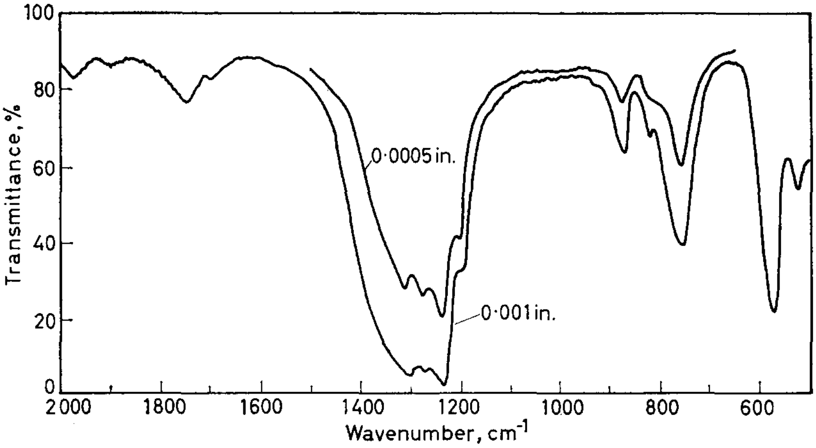

Figure 2—Infra-red spectrum of poly(phosphonitrilic chloride) in the region 2 000–500 cm^{-1}

three types of sample were examined on a Grubb Parsons–NPL interferometer and the Grubb Parsons DM4 and GM3 far infra-red grating spectrometers. The far infra-red spectrum of $(NPCl_2)_n$ film, cast and then stretched on to polyethylene is shown in *Figure 3*. The conventional infra-red spectrum is shown in *Figure 2*.

In the conventional region much thinner specimens of polymer had to be used to produce clear spectra. The three sampling procedures described above were also adapted in this region, substituting potassium bromide windows for the polyethylene plates. The physical properties of the linear

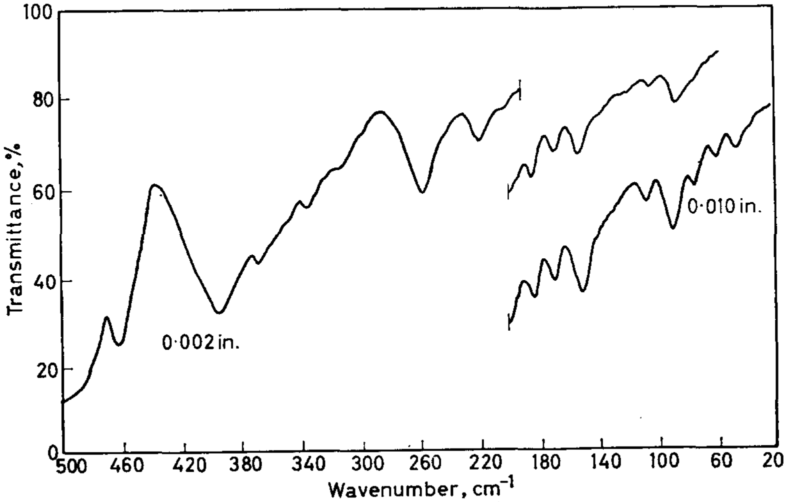

Figure 3—Far infra-red spectrum (500–20 cm^{-1}) of poly(phosphonitrilic chloride)

$(NPCl_2)_n$ rubber made it almost impossible to obtain oriented specimens of suitable thickness by mechanical treatment. The polymer loses its elastic properties on standing at room temperature (thin films are also particularly vulnerable to hydrolysis), the process being accelerated whilst in the beam of the spectrometer and for this reason a study with polarized radiation using oriented samples could not be made.

Assignment of normal modes of vibration of $(NPCl_2)_n$

In attempting to make an assignment of the normal vibrations of the polymer, the two most probable structures for the isolated polymer chain will be considered. These are the normal helical model proposed by Huggins[2] [*Figure 1* (a)] in which $P\text{–}N = 1{\cdot}74$ Å, $P\widehat{N}P = N\widehat{P}N = 120°$, and the distorted 'cis-plan' helical model of Giglio *et al.*[4] [*Figure 1* (b), with $P\text{–}N = 1{\cdot}60$ Å, $P\widehat{N}P = 127°$ and $N\widehat{P}N = 119°$]. The infra-red spectral results will then be applied to the predicted spectrum of each structure in turn in order to assess the best 'structural fit'.

Normal helical model (*Figure 1* (a))

The normal helical model contains two monomeric units in the polymer identity period which constitutes one turn of the helix[4]. The hypothetically infinite and isolated polymer chain possesses four symmetry elements, namely the identity, a twofold screw axis about the fibre axis, and two twofold axes bisecting the $P\widehat{N}P$ and $N\widehat{P}N$ angles, and perpendicular to the screw axis. The factor group of this line group will then be isomorphous to the point group D_2. Since the polymer identity period

$$[\text{—N=(PCl}_2\text{)—N=(PCl}_2\text{)—}]$$

contains eight atoms, the fragment will possess $(3N-4)$ or 20 normal modes of vibration. According to *Table 1*, in the isolated chain, these modes will be distributed as follows:

Table 1. Characters, numbers of normal modes and selection rules for poly(phosphonitrilic chloride) under the group D_2

Species	*E*	$C^1(z)$*	$C_2(y)$	$C_2(x)$	*N*†		
A	1	1	1	1	5	—	$\alpha_{xx}\alpha_{yy}\alpha_{zz}$
B_1	1	1	−1	−1	5	‡T_z (‖), R_z	α_{xy}
B_2	1	−1	1	−1	5	T_y (⊥), R_y	α_{zx}
B_3	1	−1	−1	1	5	T_x (⊥), R_x	α_{yz}

*The symmetry operation C^1 (z) is a rotation of angle π about the axis of the helix followed by a translation along the fibre axis of half the unit cell length.

†*N* is the number of total normal modes under each symmetry species.

‡*T* (‖) and *T*(⊥) are pure translations (denoting infra-red activity) parallel and perpendicular to the helical axis.

R denotes pure rotation about the helical axis.

$$5A + 5B_1 + 5B_2 + 5B_3$$

where the A modes are Raman active, and the B_1, B_2 and B_3 modes are both infra-red and Raman active. The B_1 modes give rise to a transition moment parallel to the helical axis (z axis) and the B_2 and B_3 modes give rise to transition moments perpendicular to the helical axis. In the crystal the only symmetry operations which leave the axis of the chain invariant are the factor group operations E and $C_2(z)$. Consequently the site group in the crystal will be isomorphous to the C_2 point group.

Distorted 'cis-plan' helical model, Figure 1 (b)

The distorted 'cis-plan' helical structure will also contain two monomeric units in the polymer identity period[4] and will comprise one turn of the helix.. The isolated polymer considered as an infinite chain possesses only two symmetry elements, namely the identity and the twofold screw axis about the fibre axis (z axis). The factor group will then be isomorphous to the point group C_2 (also the line group C_2) and according to the characters in *Table 2,* the twenty normal modes of vibration in the isolated chain will then divide as follows

$$10A + 10B$$

where both the A and B modes are infra-red and Raman active. The site group in the crystal will be isomorphous to the C_2 point group, as in the normal helical model.

Table 2. Characters, numbers of normal modes and selection rules for $(NPCl_2)_n$, under the group C_2

Species	E	$C^1(z)$	N		
A	1	1	10	T_z, R_z	$\alpha_{xx}\alpha_{yy}\alpha_{zz}\alpha_{xy}$
B	1	-1	10	T_x, T_y R_x, R_y	$\alpha_{yz}\alpha_{zx}$

Discussion of the vibrational spectrum

Of the 30 bands definitely resolved in the spectrum of the stretched linear polymer on transparent substrates there are 23 in the region where fundamental modes are likely to occur (*Table 3*).

Since the distorted 'cis-plan' model predicts 20 infra-red-active fundamentals and the normal helical model only 15, the infra-red spectral evidence favours the former structure. Further support for the distorted helical model lies in the fact that four bands which could be readily attributed to stretching of the P—N bond are observed. The distorted helix predicts four infra-red-active P—N stretching modes whilst the normal helix predicts only three.

A comparison of the crystal spectra of $(NPCl_2)_3$, $(NPCl_2)_4$ and the 'cast film' spectrum of $(NPCl_2)_n$ reveals that there are a number of bands lying in the far infra-red spectrum common to all three molecules and it is felt that band correlations can be made in most of these cases between the oligomeric and the polymeric vibrational modes. The common bands are nearly all believed to be due essentially to PCl_2 motion. Using these correlations, a tentative assignment for the PCl_2 vibrational modes has been made for the linear polymer, and these are summarized in *Table 4.*

Table 3. Infra-red spectra of poly(phosphonitrilic chloride)

Rubber swollen in CCl_4	*Film stretched on substrate*	*Assignment**
	49 vvw	
	62 vvw	
80 vvw	77 vvw	$\tau_{skeleton}\nu_{10}(A)$
91 vvw	89 vvw	
	105 vvw	
	128 vvw	τPCl_2, $\nu_{20}(B)$
155 vvw	157 vw	$\rho PCl_2+\delta PNP$, $\nu_{15}(B)$
168 vvw	172 vw	τPCl_2, $\nu_5(A)$
183 vvw	185 vw	$\rho PCl_2+\nu PN$, $\nu_9(A)$
	222 vvw	
268 w	262 w	δPCl_2, $\nu_{19}(B)$
	336 sh	$\delta PCl_2/\omega PCl_2$
	368 sh	$\nu_s PCl_2/\omega PCl_2$
400 m, b	397 m	$\nu_s PCl_2$, $\nu_{18}(B)$
460 m, b	464 m	δPNP, $\nu_{13}(B)$
513 w, b	515 w, b	$\nu_{as} PCl_2$, $\nu_7(A)$
580 s, b	565 s, b	$\nu_{as} PCl_2$, $\nu_{12}(B)$
750 m	745 m	δNPN, $\nu_{17}(B)$
821 vvw	815 vvw	565 $(\nu_{12}, B)+262$ $(\nu_{19}, B)=827$
863 vw	872 vw	δNPN, $\nu_2(A)$
	1 194 sh	$\nu P{=}N+\rho PCl_2$, $\nu_{11}(B)$
1 225 vs, b	1 230 vs	$\nu P{=}N+\rho PCl_2$, $\nu_6(A)$
	1 275 vs	$\nu_s P{=}N$, $\nu_1(A)$
1 304 vs, b	1 300 vs, b	$\nu P{=}N+\rho PCl_2$, $\nu_{16}(B)$
1 701 sh	1 700 sh	1 300 $(\nu_{16}, B)+397$ $(\nu_{18}, B)=1\,697$
1 768 w†	1 755 vw, b†	1 300 $(\nu_{18}, B)+464$ $(\nu_{13}, B)=1\,764$
1 981 sh	1 985 sh	1 230 $(\nu_6, A)+745$ $(\nu_{17}, B)=1\,975$
2 120 m†	2 120 vvw, b†	1 275 (ν_1, A) $+464$ $(\nu_{13}, B)+397$ $(\nu_{18}B)=2\,136$
2 930 vw	2 910 vw	

*The assignments are based on the distorted 'cis-plan' helical structure for $(NPCl_2)_n$.
†Bands much stronger in highly branched rubber.

Also included in *Table 4* are approximate descriptions of the normal vibrations involved and the form of their division under the A, B_1, B_2 and B_3 species of the D_2 (normal helix) and the A and B species of the C_2 (distorted helix) line groups. It should be noted that the description of the vibrational modes in terms of simplified group frequencies is very approximate, since appreciable mixing of the various symmetry coordinates does occur for simpler molecules, especially for vibrations occurring at frequencies below 1 300 cm^{-1}.

Assignment of PCl_2 *modes*

(i) PCl_2 *stretching modes*—Four PCl_2 stretching modes are expected, namely $\nu_s PCl_2$ (in-phase), $\nu_s PCl_2$ (out-of-phase), $\nu_{as} PCl_2$ (in-phase) and $\nu_{as} PCl_2$ (out-of-phase). In $(NPCl_2)_3$, $\nu_{as} PCl_2$ (in-phase) occurs strongly at 544 cm^{-1}, and in $(NPCl_2)_4$ it occurs at 521 cm^{-1}. Consequently the weak, broad absorption at 515 cm^{-1} is assigned to this mode (ν_7) in $(NPCl_2)_n$.

Table 4. Assignment of the fundamental modes of vibration of poly(phosphonitrilic chloride)

Line group species (D_2)	*Line group species* (C_2)	*No.*	P	ν_i	*Approximate motion*
A (R)	A (R, IR)	1		1 275	Sym. P=N stretching
		2		872	NPN skeletal deformation
		3		397/368*	PCl_2 sym. stretch, in-phase
		4		336*	PCl_2 deformation, in-phase
		5		172	PCl_2 twisting, out-of-phase
B_1 (R, IR)	A (R, IR)	6	π	1 230	P=N sym. stretching+PCl_2 rocking
		7	π	515	PCl_2 asym. stretch, in-phase
		8	π	336*	PCl_2 wagging, out-of-phase
		9	π	185	PCl_2 rocking+skeletal stretching
		10	π	89	skeletal torsion
B_2 (R, IR)	B (R, IR)	11	σ	1 194	P=N stretching+PCl_2 rocking
		12	σ	565	PCl_2 asym. stretching, out-of-phase
		13	σ	464	PNP skeletal deformation
		14	σ	368/336*	PCl_2 wagging, out-of-phase
		15	σ	157	PCl_2 rocking+PNP deformation
B_3(R, IR)	B (R, IR)	16	σ	1 300	P=N stretching+PCl_2 rocking
		17	σ	745	NPN skeletal deformation
		18	σ	397*	PCl_2 sym. stretching, out-of-phase
		19	σ	262	PCl_2 deformation, out-of-phase
		20	σ	128	PCl_2 twisting, in-phase

*Several alternative assignments are possible for these bands; see text.

Similarly, the broad, strong absorption in $(NPCl_2)_n$ at 565 cm^{-1} (cast film) and ~ 580 cm^{-1} (rubber swollen in CCl_4 is assigned to ν_{as} PCl_2 (out-of-phase), ν_{12}. In $(NPCl_2)_3$ the mode occurs strongly at 582 cm^{-1} and in $(NPCl_2)_4$ at 578 cm^{-1} The symmetric out-of-phase stretching mode, $\nu_s PCl_2$ occurs as a medium band at 404 cm^{-1} in $(NPCl_2)_3$ and at 390 cm^{-1} in $(NPCl_2)_4$ and the medium band at 397 cm^{-1} in $(NPCl_2)_n$ is therefore reasonably attributed to this vibration (ν_{18}). The totally symmetric $\nu_s PCl_2$ (in-phase) mode in $(NPCl_2)_n$ is less readily assigned. In $(NPCl_2)_3$ the mode is believed to occur at 365 cm^{-1} (Raman) and in $(NPCl_2)_4$ at 404 cm^{-1} (Raman). The vibration is expected to occur only weakly in the infrared in $(NPCl_2)_n$ for the distorted C_2 structure and could easily be masked by the medium absorption at 394 cm^{-1}. A pronounced shoulder occurs at 368 cm^{-1} which could also be attributed to this mode. Since the extent of mixing of this vibration with the chain skeleton is unknown in the linear polymer, no assignment can be made with confidence by direct correlation. This mode will be inactive in the normal helical model of $(NPCl_2)_n$.

(ii) PCl_2 *wagging modes*—The two PCl_2 'wagging' modes are the most difficult PCl_2 vibrations to locate, since appreciable mixing of the symmetry coordinates is likely to occur. In $(NPCl_2)_3$ the ωPCl_2 modes are believed to occur in the region 320 to 340 cm^{-1} and in $(NPCl_2)_4$ in the region 340 to 420 cm^{-1}. The only band which can be reasonably assigned to an ωPCl_2 mode in $(NPCl_2)_n$ is the shoulder at 336 cm^{-1}. The medium band at 397 cm^{-1} is very broad on the longer-wave side and it is felt that other bands, as yet unresolved, may contribute to this effect. It seems probable that the other PCl_2 wagging vibration also contributes to this broad shoulder.

(iii) PCl_2 *deformation modes*—The out-of-phase δPCl_2 mode (ν_{19}) is assigned without difficulty in $(NPCl_2)_n$ to the weak band at 262 cm^{-1}. It occurs characteristically in $(NPCl_2)_3$ and $(NPCl_2)_4$ at 260 cm^{-1}, the extent of mixing being only slight. The totally symmetric in-phase δPCl_2 modes in $(NPCl_2)_3$ and $(NPCl_2)_4$ occur as polarized Raman bands at 304 and 352 cm^{-1} respectively. In $(NPCl_2)_n$ it is felt that the broad unresolved shoulder in the region 380 to 300 cm^{-1} contributes to this mode (ν_4).

(iv) PCl_2 *torsional modes*—Characteristic absorption at 177 cm^{-1} in $(NPCl_2)_3$ and 170 cm^{-1} in $(NPCl_2)_4$ has been attributed to out-of-phase PCl_2 torsion, τPCl_2. Since the forms of normal vibration and the extent of coordinate mixing in these τPCl_2 modes appears to be similar in the oligomers and the polymer, the weak absorption at 172 cm^{-1} in $(NPCl_2)_n$ is also assigned to this mode in $(NPCl_2)_n$ (ν_5). This vibration is only infrared active in the distorted helical model for the linear polymer, so if it is correct then it is strong evidence for the presence of the distorted C_2 structure.

The in-phase PCl_2 torsions in $(NPCl_2)_3$ and $(NPCl_2)_4$ are believed to occur at 131 and 137 cm^{-1}, respectively. An extremely weak band at 128 cm^{-1} was observed in $(NPCl_2)_n$ and may be attributable to ν_{20}, τPCl_2 (in-phase).

PCl_2 *rocking modes*—The mixed vibrations due to out-of-phase $[\rho PCl_2 + \delta PNP]$ in $(NPCl_2)_3$ and $(NPCl_2)_4$ are believed to occur at 162 and 158 cm^{-1} respectively. By analogy, the mode in $(NPCl_2)_n$ (ν_{15}) is assigned to the very weak absorption at 157 cm^{-1}.

The assignment of the 'mixed' in-phase PCl_2 rocking mode (ν_9) is in some doubt. A band common to both $(NPCl_2)_4$ and $(NPCl_2)_n$ occurs quite distinctly at 88 cm^{-1}, but is not found in $(NPCl_2)_3$. Since it is the lowest observed fundamental in $(NPCl_2)_4$ it could reasonably be attributed to ρPCl_2 (in-phase). However, in $(NPCl_2)_3$ the lowest fundamental is found at 131 cm^{-1} and this has been assigned to τPCl_2 (in-phase), although it is possible that a lower fundamental remains undetected in this molecule. This PCl_2 rocking mode, which occurs as a mixed (ρPCl_2 + skeletal stretching) mode is tentatively assigned to the very weak band at 185 cm^{-1}, where the mode is believed to occur in $(NPCl_2)_3$.

Skeletal modes

(i) *P=N stretching modes*—The intense, broad absorption in $(NPCl_2)_n$ at ~ 1 300 cm^{-1} is resolved in very thin film specimens into four components at 1 300, 1 275, 1 230 and 1 194 cm^{-1}. There are four infra-red active P=N stretching modes expected in the distorted helical model, only one of these involving essentially symmetric stretching of the P=N bond. The other three vibrations are 'mixed' modes involving

$$(\nu P{=}N + \rho PCl_2),\ \nu_6,\ \nu_{11} \text{ and } \nu_{16}.$$

From a knowledge of the mixed skeletal stretching vibrations occurring in other similar systems[10] we would tentatively assign these frequencies in the order ν_{16} (1 300) > ν_1 (1 275) > ν_6 (1 230) > ν_{11} (1 195). These νP=N frequencies are somewhat lower than those observed in $(NPCl_2)_4$ (which occur in the region 1 360 to 1 300 cm^{-1}) and $(NPCl_2)_3$ (1 370, 1 226 cm^{-1}) which is due to the mixing with the PCl_2 rocking modes, which would appear to occur to a greater extent in the linear polymer.

(ii) PNP *and* NPN *skeletal deformation modes*—A comparison of the infra-red and Raman spectra of $(NPCl_2)_3$ and $(NPCl_2)_4$ with the infra-red spectrum of $(NPCl_2)_n$ reveals that the strong bands assigned to ring ('skeletal') breathing, in-plane deformation and elongation vibrations in the trimer at 877, 785, 671, 601 and 533 cm^{-1} and in the tetramer 894, 794, 752, 725, 667, 602, 538 and 434 cm^{-1}, are absent from the spectrum of the linear polymer. However, it is thought that the infra-red bands occurring in the latter at 872, 815, 745 and 464 cm^{-1} must be due to skeletal modes since they certainly cannot be accounted for as vibrations involving primarily PCl_2 motion.

Due to the lack of polarization measurements, and since a normal coordinate analysis has not been performed on this molecule, there is insufficient evidence for an unambiguous assignment of these skeletal deformation modes. Consequently, their assignment as given in *Table 4* is somewhat arbitrary. However, in orthorhombic polyoxymethylene, which is believed to have a similar helical structure to $(NPCl_2)_n$, characteristic OCO and COC deformation modes (equivalent to ν_{17} and ν_{13} in *Table 4*) do appear strongly in the infra-red at 594 and 430 cm^{-1} respectively[10]. By analogy the infra-red bands of medium intensity at 745 and 464 cm^{-1} in $(NPCl_2)_n$ (all the remaining unassigned bands are very weak) are tentatively assigned to δNPN (ν_{17}) and δPNP (ν_{13}), respectively. The band at 872 cm^{-1} is tentatively attributed to δNPN (A), ν_2. If the latter assignment were correct then the appearance of this band would be further evidence of the distorted C_2 helical structure for $(NPCl_2)_n$. The remaining band unassigned in the region 1 000 to 400 cm^{-1}, namely the extremely weak absorption at 815 cm^{-1}, could be accounted for as the combination tone

$$565 + 262 = 827 \text{ cm}^{-1}$$

(iii) *Skeletal torsional mode*—The torsional vibration of the —P—N—P—N— chain is expected at a very low frequency. Bands in the far infra-red at 89, 77, 62 and 49 cm^{-1} are observed in the spectrum of the stretched film of $(NPCl_2)_n$. Of these the most intense is the absorption at 89 cm^{-1} and this band is therefore tentatively assigned to the skeletal torsional mode, ν_{10}. However, it is possible that the absorption complex at 77, 62 and 49 cm^{-1} is in some way associated with the torsional oscillation of the chain backbone.

Assignment of combination bands

The weak bands as yet unaccounted for at 1 700, 1 755, 1 985 and 2 120 cm^{-1} can only reasonably be accounted for in terms of the following combination tones:

$$1300\,(\nu_{16}) + 397\,(\nu_{18}) = 1\,697 \text{ (Observed 1 700)}$$
$$1300\,(\nu_{16}) + 464\,(\nu_{13}) = 1\,764 \text{ (Observed 1 755)}$$
$$1230\,(\nu_{6}) + 745\,(\nu_{17}) = 1\,975 \text{ (Observed 1 985)}$$
$$1275\,(\nu_{1}) + 464\,(\nu_{13}) + 397\,(\nu_{18}) = 2\,136 \text{ (Observed 2 120)}$$

Discussion

No X-ray information on the number of polymer chains expected in the unit cell in the polymer crystal is available. However, theory predicts that if N polymer chains are placed in the crystal lattice, each of the line group modes should split into N components. In the distorted helical structure all the components arising due to A and B line group splitting would be infra-red active, provided that the intermolecular coupling constants in the crystal are large enough to produce appreciable separation of the energy levels. In the normal helical structure, if N is even, only $N/2$ of the components arising from the A and B_1 line group modes, and all N components of the B_2 and B_3 line group modes will be infra-red active.

No such splitting of any of the bands in the stretched film spectrum of the polymer was observed. There was only slight improvement in resolution in the stretched film spectrum compared to the spectrum of the polymer swollen in CCl_4. No definite conclusions may be drawn from this observation at this stage since the physical nature of the polymer is such that, although stretching does induce crystallization[4] the extent of crystallization in the stretched rubber diminishes over a period of time and is temperature dependent. In addition, even if $N > 1$ the intermolecular coupling in such a sample at room temperature might not be great enough to cause splitting of the vibrational levels.

Although the preliminary evidence present in this study favours the distorted 'cis-plan' helical structure, definite conclusions await the examination of the stretched film in polarized infra-red radiation and at liquid nitrogen temperatures. It is hoped that the experimental difficulties associated with such a study will shortly be overcome, and it is also intended to perform a normal coordinate analysis on the polymer.

The authors are grateful to Messrs Albright and Wilson Ltd, for samples of $(NPCl_2)_3$, *to Dr R. O. Colclough for a sample of pure* $(NPCl_2)_n$ *and to Mr L. H. W. Hallett for his interest. We are indebted to Newcastle Education Committee for the provision of a Research Studentship (to D.A.W.). The work is supported by the Science Research Council.*

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(*Received July 1968*)

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ANNOUNCEMENT

SYMPOSIUM ON 'POLYMERS AND WATER'

The annual Polymer Symposium organized by the Department of Chemistry of the University of Wales Institute of Science and Technology will be held on 4 July and will be concerned with water-soluble polymers and the properties of polymer–water systems. The symposium will be of interest to those concerned with adhesives, packaging, textiles and food science. The following subjects will be discussed under the leadership of the named invited speakers: Polyvinyl alcohol—Dr C. A. Finch; Gelatin and the gelatin–water system—Dr G. Stainsby; Sorption and diffusion of water polymers—Dr J. A. Barrie; and The electrical properties of polymer–water systems—Dr J. A. Medley. Further details are obtainable from the Organizer of Short Courses, U.W.I.S.T., 22 North Road, Cardiff, CF1 3DY.