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Influence of side groups on thermotropic behaviour of polyorganophosphazenes

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Structural and morphological investigations of polyphosphazenes with different kinds of side groups have been made in an attempt to understand the $T(1)$ thermotropic transitions. Solution grown crystals and cast films of phosphazene homopolymers were prepared and investigated by d.s.c., electron microscopy and X-ray diffraction. It has been established that the $T(1)$ and the T_g values are roughly linearly related with the size of side groups. The interplanar distances expressed as $d(100)_\delta$ in thermotropic state also show a linear relation with the side group dimensions. Polymorphic forms have been found for most polyphosphazenes that exhibit a $T(1)$ temperature, the location of which is influenced by the side groups.

(Keywords: side group dimensions; thermotropic transition; cast film; solution grown crystals; X-ray diffraction; polymorphism; interplanar distance)

INTRODUCTION

Some semicrystalline phosphazene homopolymers exhibit a thermotropic transition above which temperature polymers exist in a disordered state. Structural and morphological investigations of such polymers have been made in order to understand the nature of their thermotropic behaviour[1–10].

Polyphosphazenes are composed of a relatively flexible -P=N- backbone with alkyl, aryl, or amide groups connected to the phosphorus via oxygen, or even directly. Specific physical and chemical properties are introduced depending on the type, size and flexibility of the side groups. Therefore, variations in side group chemistry mean that polyphosphazenes have very versatile properties. This expands their uses as new materials.

The thermotropic behaviour is one of the most interesting features in polyphosphazenes. The liquid crystal-forming ability of polyphosphazenes has been discussed[4]. Recently, H. R. Allcock and C. Kim[11] synthesized a liquid crystalline polyphosphazene in which a mesogenic aromatic azo unit was linked to phosphorus via an adequately flexible spacer unit. A similar topic has been discussed by R. E. Singler *et al.*[12]. This behaviour may be practically applicable in the manufacture of liquid crystalline materials.

The structure of polyphosphazenes with different lengths of side n-aliphatic groups has also been studied[13]. It has been demonstrated that the crystalline state exists only when the length of side chains for the polyalkoxyphosphazene are large. The interplanar distances, d, obtained from the innermost reflection of X-ray diffraction patterns at room temperature for each polymer are a function of the number of carbon atoms in side groups[13]. This paper deals with structural and morphological investigations of polyphosphazenes with different kinds of side groups which influence thermotropic behaviour.

EXPERIMENTAL

Materials

Polyphosphazenes with different kinds of side groups are illustrated in *Table 1*. They were synthesized by solution and by bulk polymerization procedures.

Films

Relatively thick films for X-ray diffraction measurements were made from concentrated solutions typically of several weight percent concentrations.

Pressed sheets from polymers as-synthesized were also prepared for X-ray diffraction measurements. Thin films were prepared from a dilute solution for electron microscopy examination.

Table 1 Characteristics of polyphosphazenes $(R_2PN)_n$ used in this study

R	Notation	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n
$OC_6H_4F^a$	PB(4-F)PP	3.91	16.3	4.16*
OC_6H_4Cl	PB(4-Cl)PP	5.285	6.277	1.19
OC_6H_4Br	PB(4-Br)PP			
OC_6H_5	PBPP			>6
$OC_6H_4C_6H_5$	PB(4-Ph)PP			
$OC_6H_4CH_3^b$	PB(4-Me)PP			>10
$OC_{10}H_7$	PB(2-Np)P	9.364	72.851	7.78
$OCH_2CF_3^b$	PBFP			>10
CH_3^c	PBMeP	6.364	10.830	1.7†

[a] Kindly supplied by T. Masuko (Yamagata University, Japan)
[b] Supplied by R. E. Singler and G. L. Hagnauer (AMMRC)
[c] Supplied by R. H. Neilson (Texas Christian University)
* T. Masuko, M. Hori, J. Kitami and K. Yonetake (unpublished work)
† R. H. Neilson, R. Hani, P. Wisian-Neilson, J. J. Meister, A. K. Roy and G. L. Hagnauer, *Macromolecules*, 1987, **20**, 910

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Table 2 Results of d.s.c. measurements

Polymer	T_g (°C)	$T(1)$* (°C)	T_m† or T_d (°C)
PBPP	−4	159	~390
PB(4-F)PP	−14	169	365
PB(4-Cl)PP	7	180	360
PB(4-Br)PP		162	
PB(4-Me)PP	1	154	~417
PB(4-Ph)PP	52	(206)	
PB(2-Np)P	34	(158)	
PBMeP		–	146
PBFP	−57	66	240

* $T(1)$ depends on thermal history of the specimen

† T_m, melting temperature; T_d, degradation temperature. Some polyphosphazenes indicate $T_d < T_m$

Solution grown crystals

These were made by isothermal crystallization from dilute solution. For example, poly-bis(phenoxy)phosphazene crystals were precipitated from 0.03% w/w polymer in xylene solution at 60°C for 20 h isothermally.

Differential scanning calorimetry

A Perkin-Elmer DSC 2 calorimeter with an IBM PC computer for data analysis was used. Measurements covered temperature ranges through T_g, $T(1)$ and often extended through the melting temperature T_m if polymers were stable.

X-ray diffraction measurements

X-ray diffraction measurements were made using a Statton-type vacuum camera fitted with a heater and temperature control system. Ni-filtered Cu(K_α) radiation was used at 35 kV.

Electron microscopy

Specimens were examined with a Jeol JEM-200 CX electron microscope at 200kV.

RESULTS AND DISCUSSION

D.s.c. heating curves of semicrystalline polyphosphazenes show single or double endothermic peaks for the $T(1)$ transition to the thermotropic phase and are associated with structural modifications[14]. For instance, the thermotropic behaviour has been investigated for PPP[4,9,15]. The results of d.s.c. measurements for polyphosphazenes are summarized in *Table 2*. It has been established that an empirical relationship exists amongst T_g, $T(1)$, and T_m for polyphosphazenes which exhibit thermotropic behaviour[4] (*Figure 1*). Note, however, that the $T(1)$ temperature is dependent on the thermal history of the specimens. Specifically, the form $(T_m - T_g)/(T_m - T(1))$ is proportional to $T(1)/T_m$ in the range of $0.5 \leqslant T(1)/T_m \leqslant 0.9$ (ref. 4). The parameters used are listed in *Table 2*. Interestingly, the ratio of the thermotropic temperature span divided by the difference in the extreme T_g and T_m scales as the ratio of the two first order transitions $T(1)/T_m$. Consequently, the side chain mobility and the temperature range of conformational disorder, $T_m - T(1)$, is governed by steric considerations between side chains. Subsequent correlations bear out this point.

Figure 2 shows X-ray diffraction patterns obtained for several polyphosphazenes in their thermotropic states. Each pattern exhibits two reflections, with the exception of PB(4-F)PP (*Figure 2c*), which is characterized by three rings. PBFP (*Figure 2a*), PBPP (*Figure 2b*), and PB(4-F)PP all show sharp inner reflections. A second reflection is also seen in PB(4-F)PP. PB(2-Np)P (*Figure 2d*) and PB(4-Ph)PP (*Figure 2e*), which possess rather larger and conformationally stiffer side groups, display diffuse inner diffraction patterns in contrast to those seen in *Figures 2a, b* and *c*. These inner diffraction rings result from the existence of long-range ordering transverse to the chain direction, i.e. lateral dimensions, 10–15 Å (or even larger) depending upon the dimensions of the side group and its chemistry, of hexagonally packed molecular chains in the thermotropic state of respective polyphosphazenes.

The mobility of the –P=N– chain backbone, which must be thermally activated upon passing through $T(1)$, is coupled with side group motions. It is commonly found that the structural transformation from the two dimensional pseudohexagonal δ-form to the orthorhombic γ-form seems to occur in all the polyphosphazenes that exhibit thermotropic behaviour[2,4,9]. This hexagonal to orthorhombic transformation path is common in several polymers. Polyethylene is a well known example.

In this $\delta \rightarrow \gamma$ transformation the $[100]_\gamma$ direction is parallel to the $[100]_\delta$ direction. Contraction takes place during the transformation process and this generally results in the $1/2d(100)_\gamma$ spacing (i.e. d_{200}) being close to the $d(100)_\delta$ value[9]. However, the transformation to the δ phase from the three-dimensional state involves unit cell expansion[2]. The interplanar distance $d(100)_\delta$ in the thermotropic state for selected polyphosphazenes examined with X-ray diffraction at elevated temperature is illustrated as a function of temperature in *Figure 3*. Here the d values measured at both room temperature and below $T(1)$ for each polymer are obtained from the innermost diffraction ring of the three dimensional polymer crystals.

Crystals of polyphosphazene homopolymers formed

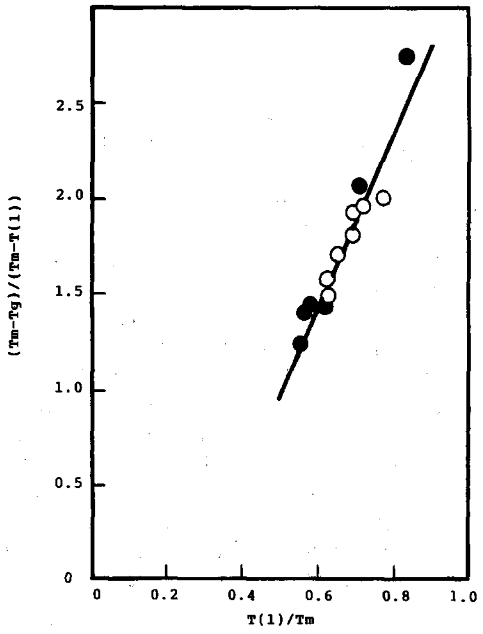

Figure 1 $(T_m - T_g)/(T_m - T(1))$ *versus* $T(1)/T_m$ for polyphosphazenes where T_g, $T(1)$ and T_m are the glass transition temperature, thermotropic transition temperature, and melting temperature, respectively

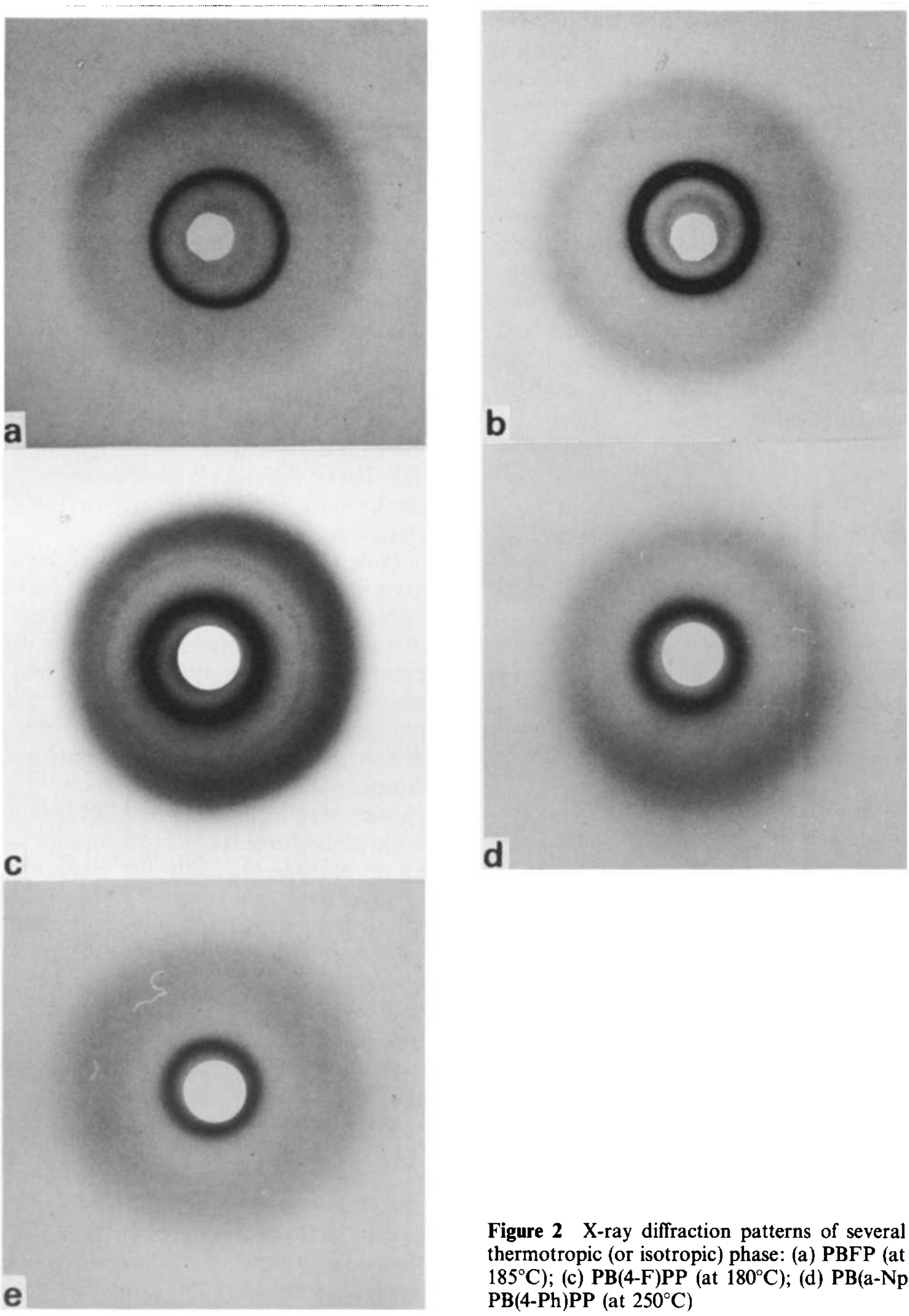

Figure 2 X-ray diffraction patterns of several polyphosphazenes in thermotropic (or isotropic) phase: (a) PBFP (at 200°C); (b) PBPP (at 185°C); (c) PB(4-F)PP (at 180°C); (d) PB(a-Np)P (at 200°C), and (e) PB(4-Ph)PP (at 250°C)

from solution are lamellar and are probably comprised of folded chain molecules, however organized. After heating above $T(1)$ and cooling back to room temperature, chain extension that is commensurate with an increase in specimen crystallinity occurs. It can exceed 90% for smaller side group polymers. The larger the side group, the more difficult the packing and the lower the crystallinity. The difference between the *d* values at room temperature for some polyphosphazenes in *Figure 3*, is associated with this remarkable increase in the crystallinity by chain-extended crystallization after heating specimens above $T(1)$ and cooling again.

Kinetics also play an important role. The bulkier the side group, the more difficult the transformation. The interplanar separation of chains increases with increasing temperature above $T(1)$ and also depends upon the size of the side group and its ability to pack. The *d* values for each polyphosphazene reflects this ability at 150°C. PB(4-Ph)PP, the largest side group used in this study, has a *d* value 40% higher than that of PBFP. PBFP possesses the smaller side group size. PBFP typically exhibits the $T(1)$ transition at 79°C. Note that the *d* value increases suddenly in the vicinity of 240°C.

Figure 4 shows an X-ray diffraction pattern of PBFP at 240°C and 290°C. It is observed that the reflection corresponding to that from the $(100)_\delta$ plane in the thermotropic or pseudohexagonal state remains even after fusion, at 290°C ($50°C > T_m$), although it appears as diffuse halo. This may mean that two-dimensional ordering still remains in this 'isotropic state' and gives rise to the diffuse X-ray scattering associated with lateral stacking of chain molecules in some fashion as yet unknown.

Investigation of PBFP *in situ* using synchrotron radiation, also exhibited similar features where lateral long range order seems to persist in the molten state[16]. The d.s.c. heating curve of PB(4-Ph)PP shows a typical first order endothermic enthalpy change at 205°C. Relative birefringence measurements of this polymer made over a range of temperatures also exhibit a rapid decrease in retardation to zero at 205°C[17]. Surprisingly, the X-ray diffuse scattering halo is still observed well above 205°C. In this respect it is similar to the behaviour of PBFP above its T_m of 240°C. Consequently, one may question the state of PBFP and PB(4-Ph)PP above their respective temperatures. Probably other polyphosphazenes will show similar behaviour. On the other hand, poly[bis(dimethyl)-phosphazene]-PBMeP which possesses rather small side groups shows a single first order endothermic peak at 146°C with classical melting.

X-ray diffraction patterns of PBMeP at different temperatures are shown in *Figure 5*. The crystallinity increases with increasing specimen temperature. Compare *Figure 5a* (measured at room temperature) with *Figure 5b* (measured at 140°C). The *d* value of the lattice plane which corresponds to the innermost diffuse ring in *Figure 5a* is still clear even in the highly crystalline specimens represented in *Figure 5b*, and is estimated to be 1.35 nm at room temperature. This *d* value is in agreement with the results obtained by electron diffraction measurement for solution-grown PBMeP crystals in which the unit cell dimensions $a = 1.35$ nm, $b = 0.598$ nm and $c = 0.490$ nm (orthorhombic form) have been established[18].

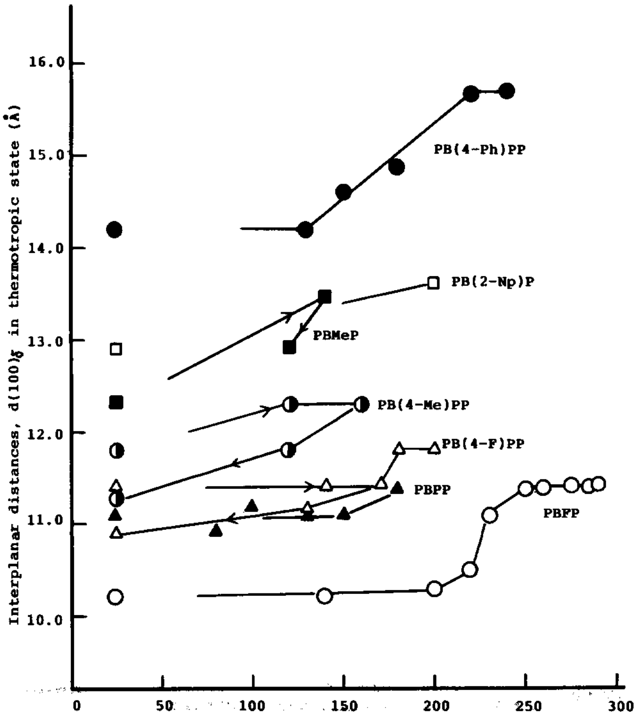

Figure 3 Interplanar distances, $d(100)_\delta$ of polyphosphazenes plotted as a function of sample temperature

The diffuseness of the diffraction ring suggests a defective hexagonal array of molecular chains in the (100) plane. It is not known if the location and the diffuseness of the ring is related to the thermotropic state of PBMeP. The X-ray diffraction measurement supports an amorphous state for PBMeP above 146°C as illustrated in *Figure 5c*.

Note that PBMeP does not exhibit a $T(1)$ transition or crystal modification as in PBFP,PBPP, and so on (see *Table 3*). This table contains the crystal form and unit cell dimensions estimated from electron diffraction measurements of solution-grown crystals and X-ray diffraction measurements of cast films of each of the polyphosphazenes, together with the interplanar distances, $d(100)_\delta$, measured in the thermotropic state at selected temperatures (refer to *Figure 2*). Some thermotropic polyphosphazenes exhibit polymorphism when the monoclinic form transforms into an orthorhombic form upon passage through the pseudohexagonal thermotropic state. The volume of the unit cell of the polyphosphazene crystal largely depends on the size of the side groups and on the interplanar distance $d(100)_\delta$ associated with 'packing' in the thermotropic state. The interplanar distances for polyalkoxyphosphazenes at room temperature have been expressed as a function of the number of carbon atoms in the side groups[13]. When the size of the side groups of each polyphosphazene is estimated based upon the atomic radius of each atom of the side groups, the interplanar distances in the thermotropic state of each polymer show a surprisingly linear dependence upon side group dimension as shown in *Figure 6*. Note also that T_g and the $T(1)$ also roughly relate linearly with the size of the side groups (see *Figure 6*) even though $T(1)$ depends somewhat upon the thermal history[14].

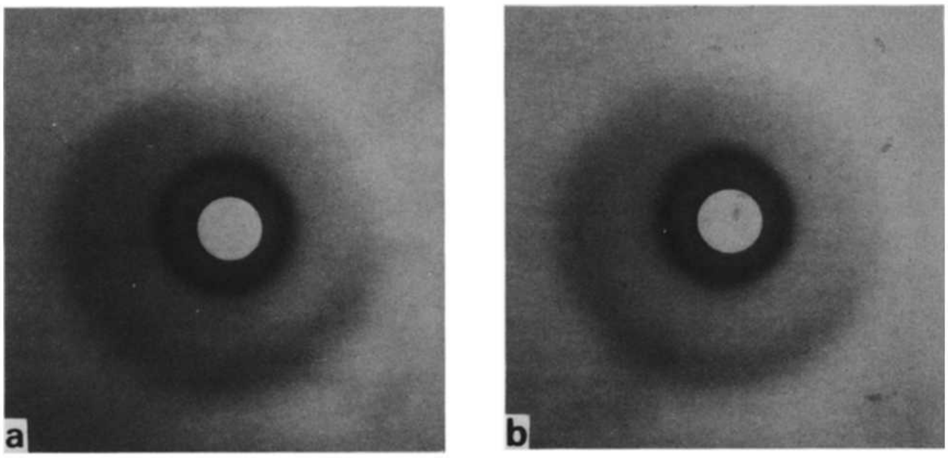

Figure 4 X-ray diffraction patterns of PBFP at above T_m. (a) 240°C; (b) 290°C

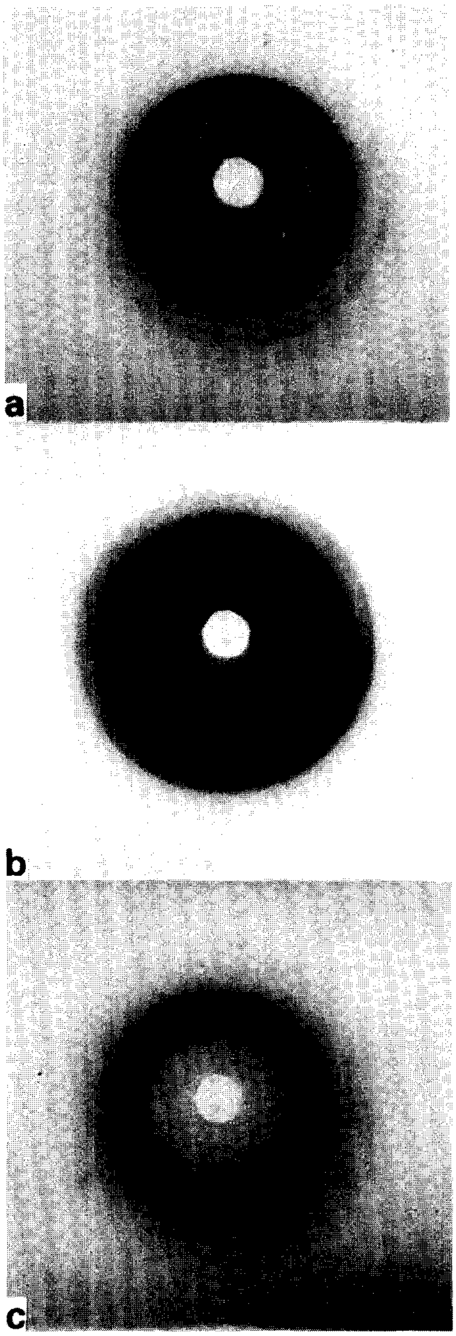

Figure 5 X-ray diffraction patterns of THF solution cast PBMeP films (a) at room temperature; (b) at 140°C ($<T_m$); (c) at 160°C ($>T_m$)

These empirical correlations depicted in *Figures 1* and *6* are not mutually exclusive. Rather, these correlations depict how steric interactions associated with side group chemistry and dimensions influence the conformation of side groups which is thermally activated and dependent *inter alia* upon backbone flexibility. ^{13}C and ^{31}P spectral line broadening in the solid state[19] and measured through $T(1)$ for several polyphosphazenes in our laboratory supports this hypothesis. However, overall it appears that the semicrystalline polyphosphazenes can be classified simply as thermotropic or non-thermotropic depending upon the type and size of the side groups.

CONCLUSIONS

1. The empirical relationship $(T_m - T_g)/(T_m - T(1))$ is proportional to $T(1)/T_m$ in range of $0.5 \leqslant T(1)/T_m \leqslant 0.9$ is valid for many polyphosphazenes.
2. The T_g and the $T(1)$ for each polyphosphazene are roughly related linearly with size of the side group.
3. The interplanar $(100)_\delta$ distance obtained in the thermotropic state for polyphosphazenes also shows a linear relation with the side group dimensions.

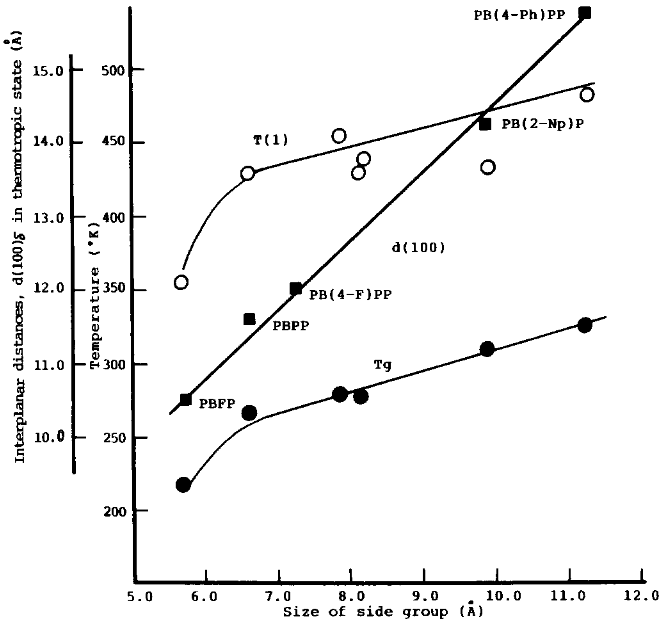

Figure 6 Interplanar distances, $d(100)_\delta$, T_g, and $T(1)$ of polyphosphazenes as a function of the size of side group

Table 3 Results of X-ray and electron diffraction measurements of polyphosphazenes

Polymer	Crystal form and unit cell dimensions† (Å)						$d(100)_\delta$* (Å)
PB(4-F)PP	M (α);	$a=26.4$,	$b=19.2$,	$c=4.91$,	$\gamma=86°$	(ref. 20)	11.8 (200°C)
	O (γ);	$a=27.3$,	$b=19.5$,	$c=4.75$			
PB(4-Cl)PP	O;	$a=13.08$,	$b=20.23$,	$c=4.90$			
PB(4-Br)PP				$c=4.84$		(ref. 21)	
PBPP	M (α);	$a=16.6$,	$b=13.8$,	$c=9.70$,	$\gamma=83°$		11.4 (180°C)
	O (γ);	$a=19.2$,	$b=11.5$,	$c=9.70$			
PB(4-P_h)PP	O;	$a=41.8$,	$b=18.3$,	$c=9.57$			15.7 (220°C)
PB(4-Me)PP	O;	$a=14.52$,	$b=18.62$,	$c=4.87$		(ref. 22)	
(PB(2-N_p)P	M;	$a=22.4$,	$b=13.9$		$\gamma=93°$)		13.8 (200°C)
PBMeP	O;	$a=13.9$,	$b=5.98$,	$c=4.90$			
PBFP	O (α);	$a=10.16$,	$b=9.35$,	$c=4.86$			10.3 (200°C)
	M (β);	$a=10.03$,	$b=9.37$,	$c=4.86$,	$\gamma=91°$		
	O (γ);	$a=20.06$,	$b=9.40$,	$c=4.86$			

* Interplanar distance, $d(100)_\delta$ in thermotropic state
† M = monoclinic; O = orthorhombic

4. In the isotropic state ordering appears to persist between aligned chains for some polyphosphazenes.
5. Polymorphism is very common in polyphosphazenes that also exhibit thermotropic behaviour.
6. Semicrystalline linear polyphosphazenes may be classified as thermotropic or non-thermotropic depending upon the side group type and size.

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