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Technical Report No. 8

INFLUENCE OF SIDE-GROUPS ON
THERMOTROPIC BEHAVIOR OF
POLYORGANOPHOSPHAZENES

MATERIALS SCIENCE AND ENGINEERING

University of Pittsburgh

Pittsburgh, Pennsylvania 15261



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by

**M. Kojima and J. H. Magill
Department of Materials Science and Engineering
University of Pittsburgh
Pittsburgh, PA 15261**

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INFLUENCE OF SIDE-GROUPS ON THERMOTROPIC BEHAVIOR OF POLYORGANOPHOSPHAZENES

M. Kojima* and J. H. Magill**
Department of Materials Science and Engineering
University of Pittsburgh
Pittsburgh, PA 15261 USA

SUMMARY

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 DSC, 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 shows 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.

*Permanent address: Chisso Corporation, 2-7-3 Marunouchi, Chiyoda-ku, Tokyo

**Also Chemical and Petroleum Engineering Department

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 the thermotropic behavior [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 make polyphosphazenes very versatile property-wise and expand their uses as new material. The thermotropic behavior 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 synthesized the liquid crystalline polyphosphazene in which a mesogenic aromatic azo unit was linked to phosphorus via an adequately flexible spacer unit [11]. A similar topic, chemistry, has been discussed by R. E. Singler et al. [12]. (Possibly the behavior will be practically applicable as liquid crystalline materials.) The structure of polyphosphazenes with different lengths of side n-aliphatic groups has been studied, too [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]. The present paper deals with structural and morphological investigations of polyphosphazenes with different kinds of side groups that influence thermotropic behavior.



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EXPERIMENTAL

MATERIAL

Polyphosphazenes with different kinds of side group illustrated in Table 1 were synthesized by (i) solution and (ii) bulk polymerization procedures.

FILMS

Relatively thick films for x-ray diffraction measurements were made from concentrated solutions typically of several wt% concentration.

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

SOLUTION GROWN CRYSTALS

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

DIFFERENTIAL SCANNING CALORIMETRY

A Perkin-Elmer DSC 2 calorimeter with an IBM PC computer for data analysis was used. Measurements covering temperature ranges through T_g , $T(1)$ and often extending 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 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 200 kV.

RESULTS AND DISCUSSION

DSC 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 behavior have been investigated for PBPP [4,9,15]. The results by DSC measurements for polyphosphazenes are summarized in Table 2. It has been established that an empirical relationship (Figure 1) exists amongst T_g, T(1), and T_m for polyphosphazenes exhibiting thermotropic behavior [4]. Note, however, that the T(1) temperature is dependent on thermal history of the specimens. Namely, the form $(T_m - T(g))/(T_m - T(1))$ is proportional to T(1)/T_m in the range of $0.5 \leq T(1)/T_m \leq 0.9$ [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 consideration 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 2,c), which is characterized by three rings. PBFP (Figure 2,a), PBPP (Figure 2,b), and PB(4-F)PP all show sharp inner reflection but a second reflection is also seen in PB(4-F)PP. PB(2-Np)P (Figure 2,d) and PB(4-Ph)PP (Figure 2,e) which possess rather larger and conformationally stiffer side groups display diffuse inner diffraction pattern in contrast to those seen in Figure 2 (a), (b), and (c). These inner diffraction rings result from the existence of long range ordering transverse to the chain direction, i.e. lateral dimensions, $10 \text{ \AA} \sim 15 \text{ \AA}$ (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. Of course, the mobility of -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 2D pseudo-hexagonal δ -form^{*} to the orthorhombic γ -form seems to occur in all polyphosphazenes that exhibit thermotropic behavior [2,4,9]. 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 $1/2 d(100)_{\gamma}$ spacing (i.e. d_{200}) being close to the $d(100)_{\delta}$ value [9]. However, the transformation to the δ phase from the 3D 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 room temperature and also below $T(1)$ for each polymer are obtained from the innermost diffraction ring of the 3D polymer crystals. Crystals of polyphosphazene homopolymers formed from solution are lamellar and most

* This transformation path, hexagonal to orthorhombic, is common in several polymers, polyethylene being well known example.

likely comprised of folded chain molecules, however well organized. After heating above $T(1)$ and cooling back to room temperature, chain extension occurs that is commensurate with an increase in specimen crystallinity which can exceed 90% for smaller side group polymers. The larger the side group, the more difficult the packing and lower the crystallinity. The difference of the d values at room temperature for some polyphosphazenes in Figure 3, is associated with this remarkable increase of the crystallinity by chain-extended crystallization after heating specimens above $T(1)$ and cooling again. Of course, kinetics 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% larger than that of PBFP. PBFP possess the smaller side group size. PBFP exhibits the $T(1)$ transition, typically at 79°C . Note that the d value increases suddenly in the vicinity of 240°C . Figure 4 is an x-ray diffraction pattern of PBFP at 240°C (a) and 290°C (b). 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 ($50^{\circ}\text{C} > T_m$), although appears as diffuse halo. This may be interpreted to mean that two dimensional ordering still remains in this "isotropic state" giving 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 ordering seems to persist in the molten state [16]. The DSC 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 temperature 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 and in this respect is similar to the behavior of PBFP also 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 behavior. On the other hand, poly[bis(dimethyl)phosphazene]-PBMeP which possesses rather small side group shows a single first order endothermic peak at 146°C with classical melting.

X-ray diffraction patterns of PBMeP are shown in Figure 5 at different temperature. However, the crystallinity increases with increasing specimen temperature. Compare Figure 5(a) (at room temperature) with Figure 5(b) (at 140°C). The d value of the lattice plane which corresponds to the innermost diffuse ring in Figure 5(a) is still clear even in the highly crystalline specimen, Figure 5(b), and is estimated to be 1.35 nm at room temperature. This d value coincides with the results 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]. The diffuseness of the diffraction ring suggests a defect hexagonal array of molecular chains in the (100) plane. It is not known at this time if the location and the diffuseness of the ring is related with the thermotropic state of PBMeP. The x-ray diffraction measurement supports an amorphous state for PBMeP above 146°C as illustrated in Figure 5(c). 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 polyphosphazenes, together with the interplanar distances, $d(100)_\delta$, measured in the thermotropic state at selected temperatures (referred to Figure 2). Some

thermotropic polyphosphazenes exhibit polymorphism when the monoclinic form transforms into an orthorhombic form upon passage through the pseudo-hexagonal thermotropic state. Volume of the unit cell of the polyphosphazenes crystal largely depends on the size of the side groups as well as 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 surprisingly show a linear dependence upon side group dimension as in Figure 6. Note also that T_g and the $T(1)$ are also roughly related linearly with the size of the side groups (see Figure 6) even though $T(1)$ depends somewhat upon the thermal history [14]. 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 too. ^{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. Overall however, 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.

CONCLUSION

1. The empirical relationship that $(T_m - T_g)/(T_m - T(1))$ is proportional to $T(1)/T_m$ in range of $0.5 \leq T(1)/T_m \leq 0.9$ is valid for many polyphosphazenes.

2. The T_g and the $T(1)$ for each polyphosphazenes are roughly linearly related 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.
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 behavior.
6. Semicrystalline linear polyphosphazenes may be classified as thermotropic or non-thermotropic depending upon the side group type and size.

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FIGURE LEGENDS

- Figure 1 $(T_m - T_g)/(T_m - T(1))$ vs. $T(1)/T_m$ 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).
- Figure 3 Interplanar distances, $d(100)_\delta$ of polyphosphazenes plotted as a function of sample temperature.
- Figure 4 X-ray diffraction patterns of PBFP at above T_m , 240°C (a) and 290°C (b).
- 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 ($> T_m$).
- Figure 6 Interplanar distances, $d(100)_\delta$, T_g , and $T(1)$ of polyphosphazenes as a function of the size of side group.

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- Table 1 Characteristics of Polyphosphazenes $(R_2PN)_n$ Used in Present Study
- Table 2 Results of Thermal Analysis Parameters for Polyphosphazenes
- Table 3 Results of X-ray and Electron Diffraction Measurements for Some Polyphosphazenes

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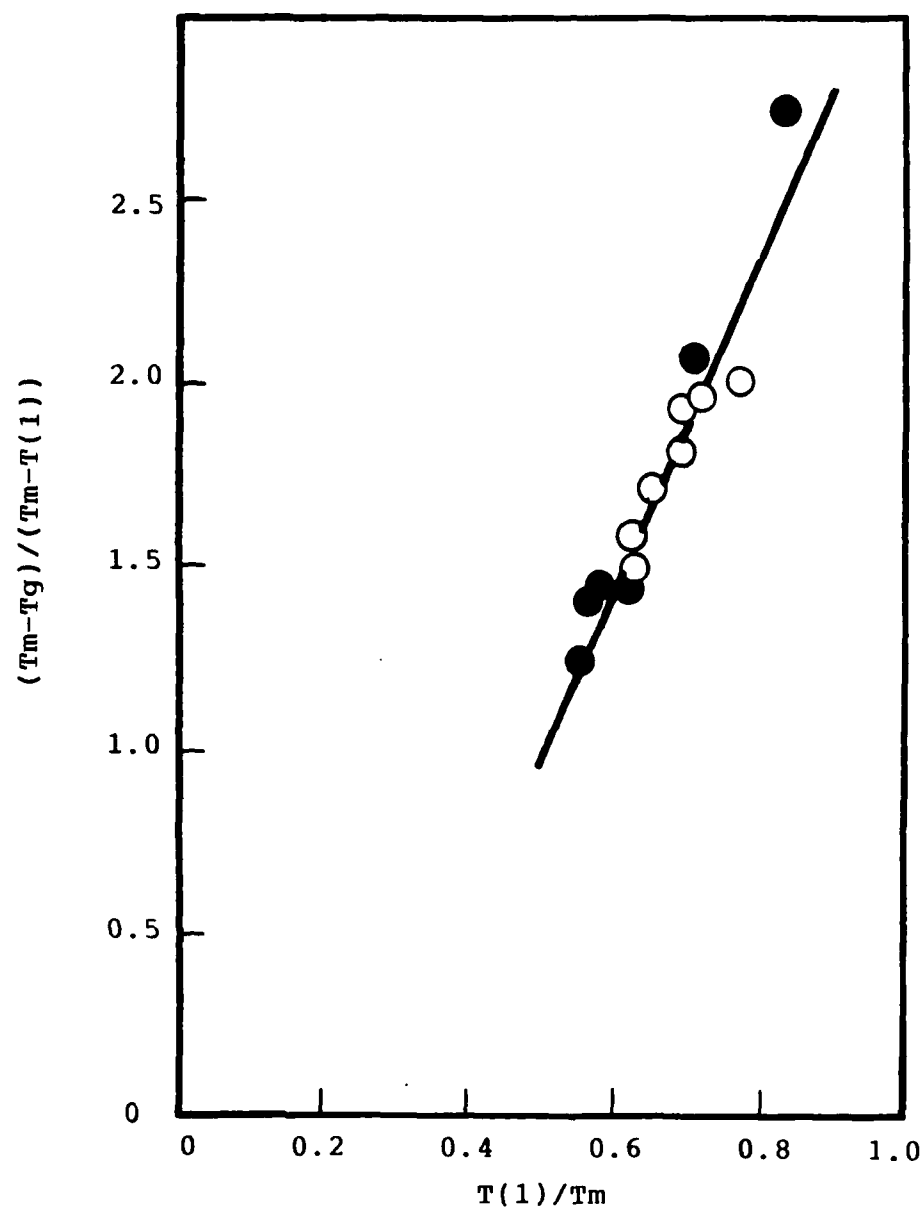
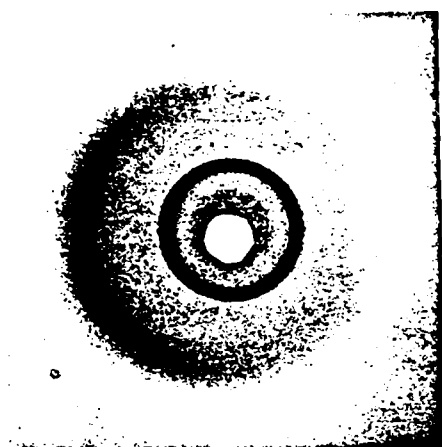


Figure 1. $(T_m - T_g) / (T_m - T(1))$ vs $T(1) / T_m$ for polyphosphazenes where T_g , $T(1)$, and T_m are the glass transition temperature, thermotropic transition temperature, and melting temperature, respectively.



(a)



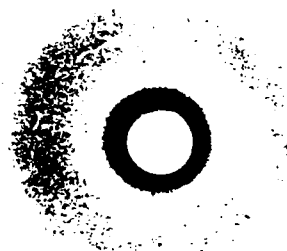
(b)



(c)



(d)



(e)

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(2-Np)P (at 200 °C), and (e) PB(4-Ph)PP(at 250 °C).

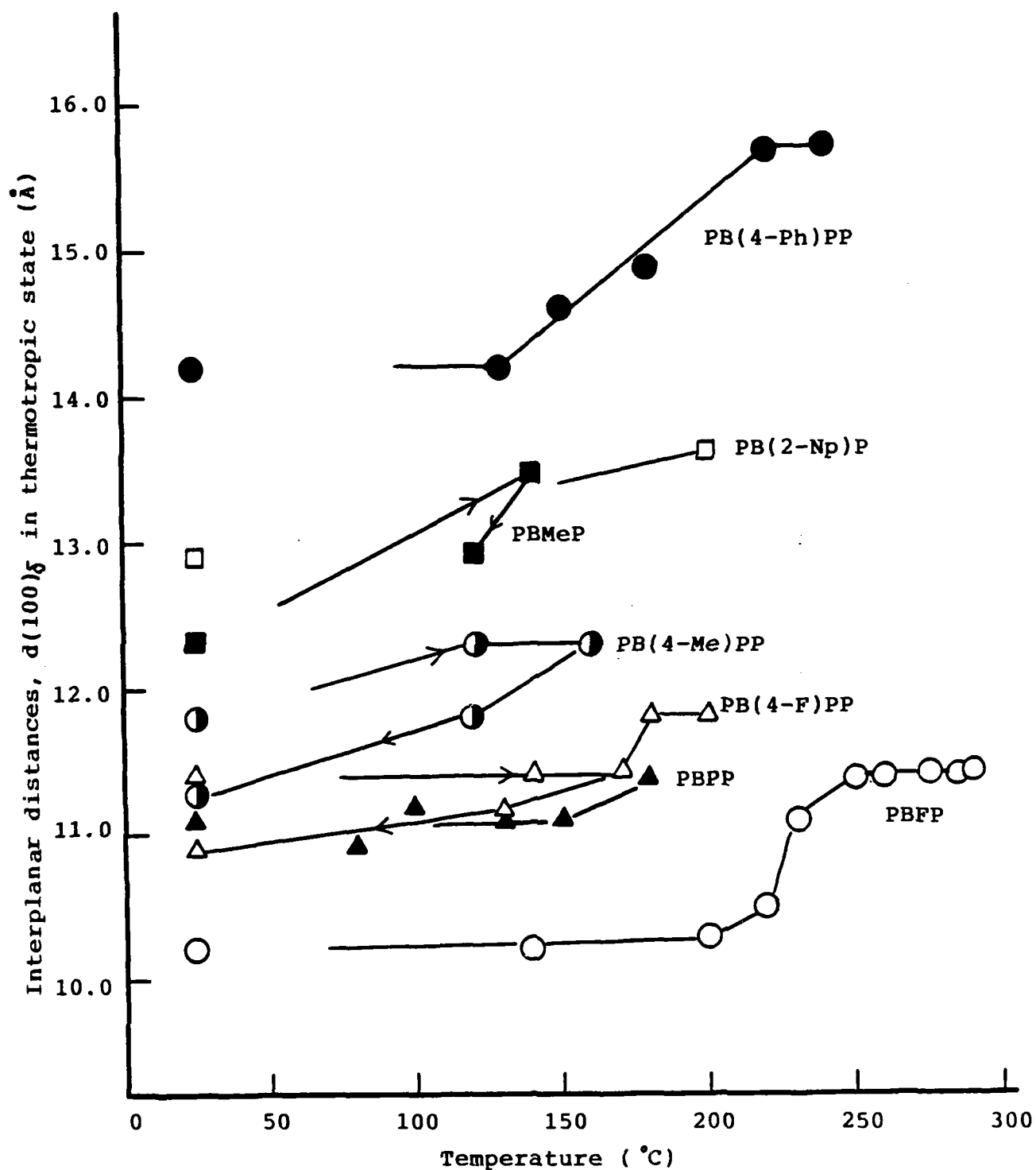
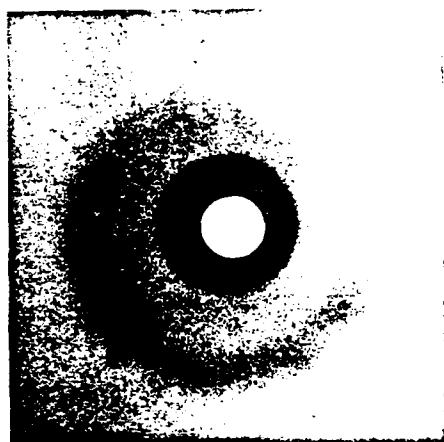


Figure 3. Interplanar distances, $d(100)$ of polyphosphazenes as a function of temperature.

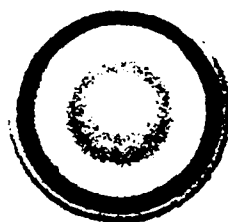


(a)



(b)

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



(a)



(b)



(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 ($> T_m$).

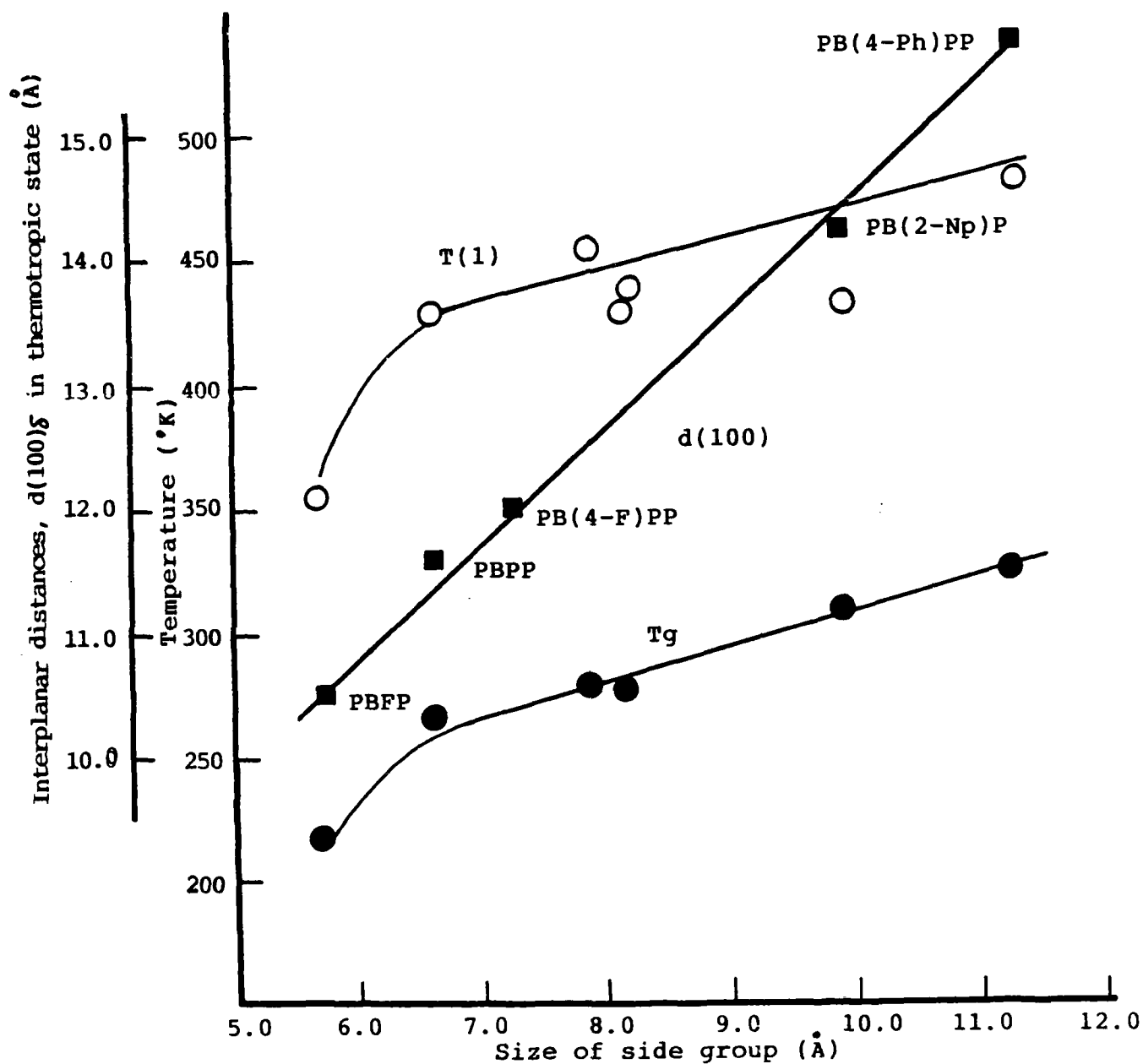


Figure 6. Interplanar distances, $d(100)\delta$, T_g , and $T(1)$ of polyphosphazenes as a function of the size of side group

Table 1 Characteristics of Polyphosphazenes (R₂PN)_n used in present study.

R	Notation	Mn	Mw X10 ⁴	Mw/Mn
OC ₆ H ₄ F a)	PB(4-F)PP	3.91	16.3	4.16 *
OC ₆ H ₄ Cl	PB(4-Cl)PP	5.285	6.277	1.19
OC ₆ H ₄ Br	PB(4-Br)PP			
OC ₆ H ₅	PBPP			>6
OC ₆ H ₄ C ₆ H ₅	PB(4-Ph)PP			
OC ₆ H ₄ CH ₃ b)	PB(4-Me)PP			>10
OC ₁₀ H ₇	PB(2-Np)P	9.364	72.851	7.78
OCH ₂ CF ₃ b)	PBFP			>10
CH ₃ c)	PBMeP	6.364	10.830	1.7 **

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** R.H.Neilson, R.Hani, P.Wisian-Neilson, J.J.Meister,
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Table 2 Results of DSC 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.

Table 3 Results of x-ray and electron diffraction measurements of polyphosphazenes.

Polymer	Crystal form & unit cell dimensions Å	$d(100)_g^*$ Å
PB(4-F)PP	mono. (α); $a=26.4, b=19.2, c=4.91, \gamma=86^\circ$ (T. Masuko et al.) ortho. (γ); $a=27.3, b=19.5, c=4.75$	11.8 (200 °C)
PB(4-Cl)PP	ortho.; $a=13.08, b=20.23, c=4.90$ (S.M. Bishop et al.)	
PB(4-Br)PP	$c=4.84$	
PBPP	mono. (α); $a=16.6, b=13.8, c=9.70, \gamma=83^\circ$ ortho. (γ); $a=19.2, b=11.5, c=9.70$	11.4 (180 °C)
PB(4-Ph)PP	ortho. $a=41.8, b=18.3, c=9.57$	15.7 (220 °C)
PB(4-Me)PP	ortho. $a=14.52, b=18.62, c=4.87$ (J.J. Beres et al.)	
PB(2-N _p)P	(mono. $a=22.4, b=13.9, \gamma=93^\circ$)	13.8 (200 °C)
PBMeP	ortho. $a=13.9, b=5.98, c=4.90$	
PBFP	ortho. (α); $a=10.16, b=9.35, c=4.86$ mono. (β); $a=10.03, b=9.37, c=4.86, \gamma=91^\circ$ ortho. (γ); $a=20.06, b=9.40, c=4.86$	10.3 (200 °C)

* Interplanar distance, $d(100)_g$ in thermotropic state

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