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(13) $^{31}P$ NMR: 4 to −6 ppm (br) ($D_2O/H_3PO_4$). Broadness decreases as the amount of sulfonate groups in the polymer backbone decreases. $^1H$ NMR: 3.7 and 4.2 ppm (br) for $OCH_2$ protons, 3.4 ppm (s) for $OCH_3$ protons, and 1.9 ppm (br) for $SCH_2$ protons [$D_2O$/TMS (ext.)]. IR: 1210–1280 $cm^{-1}$ (b) for $\nu$(P=N) and 1050–1100 $cm^{-1}$ (b) for $\nu(SO_3Na)$.
(14) Stoichiometry of polyphosphazene sulfonate is taken from the integral intensity ratios of appropriate peaks from the $^1H$ NMR spectra.
(15) Stoichiometry is expected on the basis of the general trend observed for the preparation of polymers **3–5** under similar experimental conditions.
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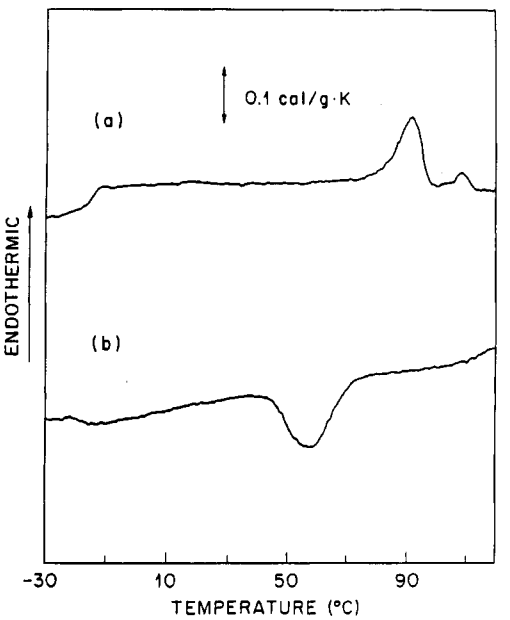


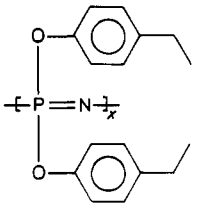

**Figure 1.** DSC scans of PBEBB in the heating (a) and cooling (b) process.

## Multinuclear Solid-State NMR Study of Phase Transitions in Poly[bis(4-ethylphenoxy)phosphazene]

Recently[1-16] much attention has been paid to the structural and thermal properties of poly(organophosphazenes) [—N=P($R_2$)]— in view of the scientific interest and potential applications of these polymers. Polyphosphazenes are unusual polymers that, like silicones and silanes, have an inorganic backbone structure. It is well-known[17] that most polyphosphazenes undergo three transitions, the glass transition $T_g$, the thermotropic transition from crystal to mesophase, so-called $T(1)$, and the melting transition $T_m$. Among these transitions, the thermotropic phase transition in these polymers is most interesting and is responsible for drastic changes in their properties. Furthermore, recently it has been found that some polyphosphazenes have a number of different crystalline modifications or polymorphs below $T(1)$ and their occurrence strongly depends on the crystallization conditions.[18-20]

These crystalline modifications and mesophase have been studied mainly by X-ray diffraction, electron beam diffraction, and thermal analysis. Only a few studies have been done on the dynamic properties of polyphosphazenes.[21-24] Solid-state nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful methods for studying the local dynamics and conformations of polymers. To our knowledge, however, there has been no study of the mesomorphic phase transitions in polyphosphazenes by solid-state, high-resolution NMR. Poly(organophosphazenes) have two kinds of nuclei, $^{31}P$ and $^{13}C$, which are easily accessible to study by solid-state, high-resolution NMR. $^{31}P$ NMR provides information on the conformation and mobility of the backbone, while $^{13}C$ NMR gives information on the conformation, packing, and mobility of the side groups.

In this paper, we report preliminary results from $^{13}P$ and $^{13}C$ NMR studies on the phase transitions of poly[bis(4-ethylphenoxy)phosphazene] (PBEPP)[25,26] along with the results of DSC thermal analysis and X-ray diffraction analysis.




PBEPP

PBEPP was prepared from the Allcock procedure.[27] Polydichlorophosphazene was prepared by heating purified $(NPCl_2)_3$ in a sealed glass tube for 5 days at 250 °C with rigorous exclusion of moisture. Derivitization of $(NPCl_2)_x$ with the 4-ethylphenoxide residue was accomplished by a slight modification of the usual process.[27] Elemental analysis of the polymer showed <0.2% residual chlorine. Gel permeation chromatography indicated an average molecular weight of the order of $10^6$. The polymer was soluble in tetrahydrofuran, chloroform, and benzene. A $^{31}P$ NMR ($C_6H_6$) spectrum of the sample consisted of a sharp singlet at −19.30 ppm (ext. $H_3PO_4$). The $^{31}P$ NMR ($C_6H_6$) spectrum of the corresponding cyclic trimer [NP-($OC_6H_4$-4-$C_2H_5)_2]_3$ exhibited a singlet at 8.80 ppm (ext. $H_3PO_4$). Full details of the sample preparation will be given elsewhere.[28]

$^{31}P$ and $^{13}C$ NMR spectra were recorded on a Varian XL-200 spectrometer at a static magnetic field of 4.7 T. Magic angle sample spinning (MAS) at a speed of ca. 3 kHz was achieved with a Doty Scientific variable-temperature probe, which utilizes a double air bearing design. The temperature was varied from 20 to 135 °C by use of heated flow. Temperature was controlled within ±1 °C. PBEPP in rubbery form was packed in an aluminum oxide rotor with Vespel or Kel-F caps. A 45-kHz radiofrequency field strength was used for dipolar decoupling (DD), with a decoupling period of 200 ms. The optimum cross-polarization (CP) time of $^{13}C$ from $^1H$ was found to be 2 ms at room temperature and we used this value at all the temperatures. The $^{13}C$ spectra were referenced to the resonance of POM (89.1 ppm from TMS) and the $^{31}P$ spectra to the resonance of $H_3PO_4$ (0 ppm).

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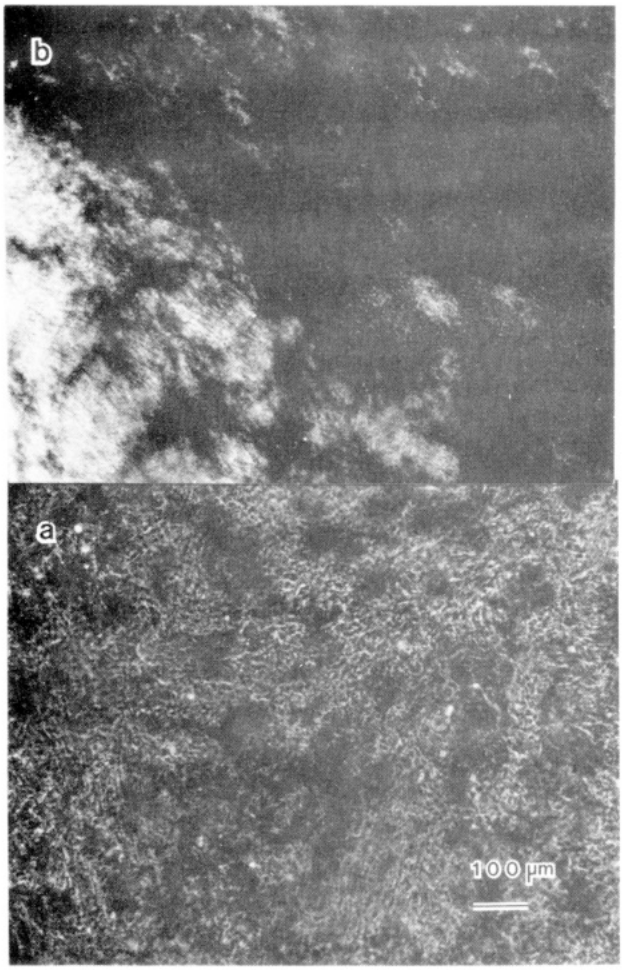


**Figure 2.** Photographs of a spherulite structure observed at 25 °C (a) and a liquid crystalline structure observed at 130 °C (b) with a polarizing microscope.

The phase transitions were also studied by differential scanning calorimetry (Perkin-Elmer DSC-4). Figure 1 shows typical transition behavior in both heating and cooling processes. The glass transition temperature $T_g$ is observed at −16 °C and two other transitions [$T(1)$] are observed at 90 and 110 °C with a heating rate of 10 °C/min. The heats of fusion of these transitions are not very large, indicating either a small difference in order between the crystalline and mesomorphic state or a rather small crystallinity. During the cooling process, with a cooling rate of 10 °C/min, there is only one transition observed. The thermal behavior is very strongly dependent on the thermal history of the sample. The details of the effects of thermal treatment will be discussed elsewhere. The strong dependence of the number of transitions on the crystallization condition suggests the coexistence of more than two kinds of crystalline forms as is the case in poly[bis(4-isopropylphenoxy)phosphazene].[19,20]

The transition was also observed with an optical microscope. On the basis of polarized microscopy observations, we confirm that the transition around 110 °C is from the crystalline to the mesomorphic state. As shown in Figure 2a, there are spherulitic structures below the $T(1)$ transition, while above $T(1)$ there is no spherulitic structure, but a large spatial scale birefringence characteristic of the liquid crystalline state is observed (see Figure 2b). The birefringence of the mesomorphic state remains after annealing at 130 °C for a week, which indicates that the birefringence is from a stable liquid crystalline structure and not from a stress birefringence. The birefringence disappears around 240 °C, which corresponds to the liquid crystalline to isotropic melt transition.

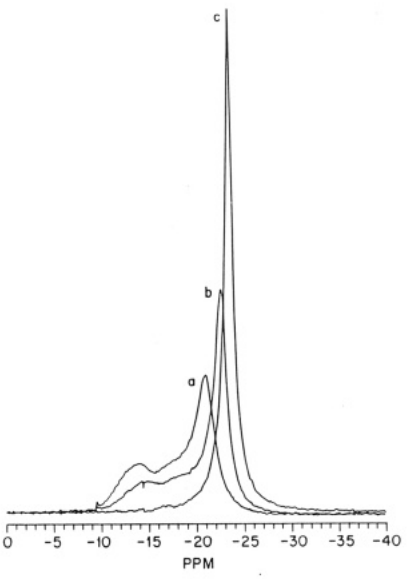


**Figure 3.** $^{31}P$ MAS/DD spectra of PBEPP at (a) 23 °C, (b) 80 °C, and 120 °C.

Figure 3 shows the temperature dependence of the $^{31}P$ MAS/DD spectra of PBEPP. At low temperatures, there are three components with different chemical shifts, which correspond to the crystalline, interfacial, and amorphous phases. This assignment has been confirmed by the real time observation of the crystallization process from the mesophase at 75 °C. The chemical shift of the crystalline phase is least shielded, that of the amorphous phase is most shielded, and that of the interface is intermediate. This is the same order as observed in typical crystalline polymers such as polyethylene[29] and indicates that the conformational order is highest in the crystalline and lowest in the amorphous phase. The intensity corresponding to the crystalline phase is reduced with increased temperature and completely disappears above $T(1)$, which is consistent with the optical microscopy observation. The line width of the amorphous component sharpens with increasing temperature and becomes discontinuously narrow above $T(1)$. In a motional sense, the mesophase is almost the same as the liquid state. The mobility of the amorphous phase below $T(1)$ is suppressed by the geometrical constraints from the crystalline phase, while above $T(1)$ these constraints are absent.

The chemical shift position of the amorphous phase monotonically moves to higher frequency as the temperature increases. This means that the average polymer conformation in the amorphous phase becomes more disordered with temperature and the backbone conformation of the mesophase is also disordered. The bonding in polyphosphazenes is usually interpreted as three-center islands with $\pi$-bonding character, which is interrupted at phosphorous, and thus the bonding is localized.[3,4,30] Furthermore, the nature of the $\pi$-bonding leads to a low torsional potential in such materials.[3,4,31,32] The spin–lattice relaxation time, $T_1$, of the crystalline phase is much longer than the amorphous phase as expected. There is no significant difference in $T_1$ values between the amorphous phase and the mesophase.

Figure 4 shows the $^{13}C$ spectra of the polymer below and above $T(1)$. The resonances are assigned to carbons as shown in the figure. MAS/DD spectra show mainly the $^{13}C$ resonances from the side chains in the mobile amorphous component. The carbon resonances from the phenyl

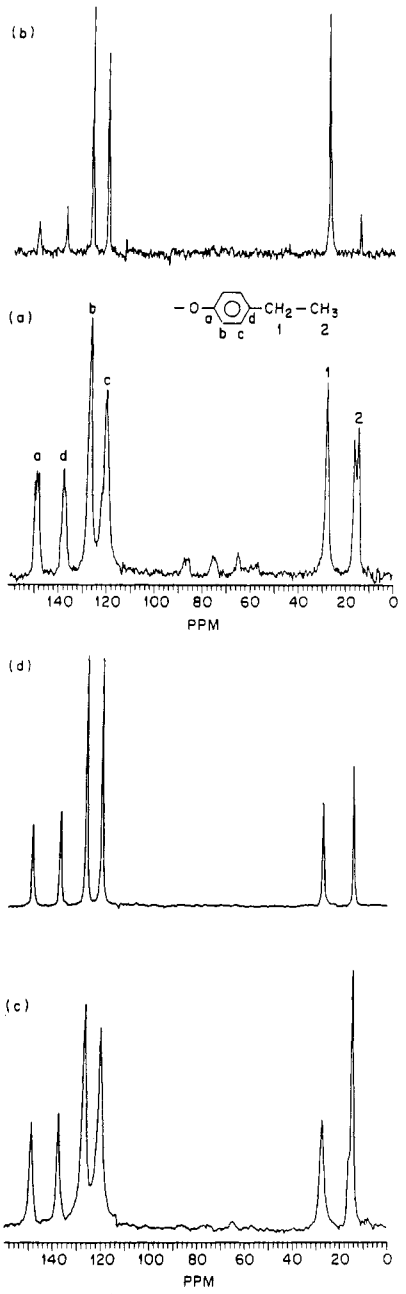


**Figure 4.** $^{13}C$ spectra below and above $T(1)$. (a) CP MAS/DD spectrum at 24 °C. (b) CP MAS/DD spectrum at 120 °C. (c) MAS/DD spectrum at 24 °C. (d) MAS/DD spectrum at 120 °C.

ring, $C_a$, $C_c$, and $C_d$, (especially $C_a$) are split into three resonances in the CP MAS/DD spectrum below $T(1)$. The central resonances are assigned to the amorphous phase by comparison between the CP MAS/DD and MAS/DD spectra. The resonance of the methyl group is split only below $T(1)$. Below $T(1)$, all the peaks split into two or three resonances which reflects the presence of a crystalline structure, while above $T(1)$ only one resonance is observed for each carbon atom. There is a significant difference in $T_{1\rho}$ below and above $T(1)$. The mesophase is very similar to the rubber based on the $T_{1\rho}$ behavior.

Figure 5 shows typical X-ray diffraction patterns of PBEPP both below and above $T(1)$. Below $T(1)$, there are several peaks from the inter- and intramolecular order in the crystalline structure. In the mesophase, however, only one sharp peak, whose position is different from any of the crystal peaks, and which corresponds to intermolecular order in the mesophase, is observed, and no intramolecular order is observed. Below $T(1)$ there is no clear peak corresponding to the mesophase, indicating the absence of significant liquid crystalline order in the amorphous phase. Apparently the geometrical constraints of the crystalline phase do not allow the amorphous phase to have an orientational order at least in the highly crystalline sample. At the present time, we cannot rule out the possibility of liquid crystalline orientational order in a poorly crystalline sample.

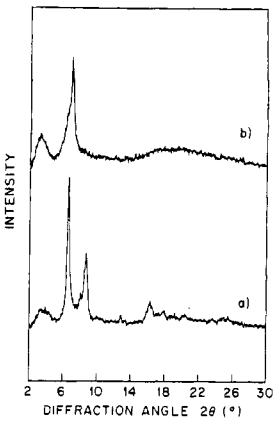


**Figure 5.** X-ray diffractograms of PBEPP at 25 °C (a) and at 120 °C (b).

These results clearly show that the symmetry is completely different between the crystal and the mesophase, which is related to the first-order character of this transition. The structure of the mesophase can be expressed as the hexagonal packing of cylinders which are occupied by the polymer chains with highly mobile backbones and sidegroups. The intermolecular distance in the mesophase is between the lattice spacings of the $a$ and $b$ direction of the crystalline phase, indicating disorder of the backbones and side groups of the mesophase. The broad halo in the mesophase diffractogram indicates the absence of intramolecular order in the chain, which is consistent with the dynamic disorder along the $c$ axis observed by $^{31}P$ NMR. The phase transition may be caused by the interplay between the van der Waals forces which stabilize the crystal and the thermal energy which activates the rotational motion of chain segments. Below $T_m$, however, the thermal energy is not large enough to activate the highest rotation barrier which causes loss of symmetry along the $c$-axis.

Finally, we briefly discuss the nature of the liquid crystalline phase in poly(organophosphazenes).[31,32] As studied by Allcock et al.,[33,34] the backbone of the polyphosphazenes is very flexible because of the nature of the bonding, which is evidenced by the low $T_g$. The rotational barriers for the backbone are governed by steric interactions between side groups. $^{31}P$ NMR results support the flexibility and conformational disorder in the backbone of the amorphous and the mesophase. Both $^{13}C$ and $^{31}P$ NMR show that there are no significant differences in the motions and conformations of the backbone and the substituents between the amorphous and the mesophase of PBEPP. The absence of liquid crystalline order below $T(1)$ in the amorphous phase may be ascribed to the geometrical constraints provided by the crystalline phase.

The rather low crystallinity of PBEPP may be attributed to its lack of flexibility as a result of the bulky substituent. Polyphosphazenes have the flexibility necessary to form a crystal, yet are sufficiently rigid to form a liquid crystalline phase. The rigidity mainly comes from the bulkiness of the substituent. In this regard, we are studying the effect of side-group bulkiness by changing the terminal substituent of the phenoxy group. The results will be published elsewhere.

In this paper, we reported a study of the motional and conformational states of the backbone and substituents of poly[bis(4-ethylphenoxy)phosphazene] through both $^{31}P$ and $^{13}C$ NMR spectra and focused our attention on the crystalline to mesophase transition. A more detailed study including the crystalline polymorphs in this polymer and the dynamics of its molecular motion will be published elsewhere.

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