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(13) mp 112-113 °C; IR (KBr) 3500-3100 (br, ν(OH)), 1420 cm^{-1}, (W, ν(N=N)); ^{1}H NMR (CDCl$_3$) δ 7.92-6.96 (m, aromatic H's, 8 H), 4.26-3.67 (m, OCH_2, OCH_3, 15 H).
(14) IR (KBr) 1410 (w, ν(N=N)), 1250 cm^{-1} (s, ν(PN)); ^{1}H NMR (CDCl$_3$) δ 7.89-6.93 (m, aromatic H's, 8 H), 4.14-3.60 (m, OCH_2, OCH_3, 15 H); ^{31}P NMR (CDCl$_3$) −8.3 ppm (singlet).
(15) IR (KBr) 1410 (w, ν(N=N)), 1240 cm^{-1} (s, ν(PN)); ^{1}H NMR (CDCl$_3$) δ 7.89-6.92 (m, aromatic H's, 8 H), 4.10-3.66 (m, OCH_2, OCH_3, 15 H); ^{31}P NMR (CDCl$_3$) 18.5 ppm (singlet).

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Liquid Crystalline Side-Chain Phosphazenes

Liquid crystalline polymers can be prepared in a variety of ways. Both main-chain and side-chain liquid crystalline polymers have been reported. The concept of coupling a mesogenic group with a flexible spacer to a polymeric substrate to prepare side-chain liquid crystalline polymers has been demonstrated by Finkelmann and other workers.[1] Our approach has been to attach low molecular weight mesogenic molecules to the phosphazene (PN) backbone via a flexible spacer group (Figure 1). Phosphazenes offer a potential advantage in that a variety of different substituents can be readily attached to a common substrate to yield a wide range of materials with different properties.[2] The mesogenic molecules that are not necessarily liquid crystals are able to induce mesomorphic behavior when attached to a suitable substrate. In our study, both cyclic phosphazenes and linear polymers are used as substrates, since the behavior of these systems is quite different. Cyclic phosphazenes serve mainly as model compounds, but they have some interesting properties of their own and thus are included in this paper.

The initial work was to prepare sutable side-chain compounds (mesogens) with a reactive end group to attach to the phosphazene substrate. For this study, 4-((*n*-butylphenyl)azo)phenol (prepared by the diazotization reaction of 4-*n*-butylaniline with phenol) was reacted with 2-chloroethanol in basic aqueous ethanol containing KI for 14 h to give the desired chain-extended mesogenic alcohol 2-(4-((*n*-butylphenyl)azo)phenoxy)ethanol in 90% yield.[3]

The conversion of hexachlorocyclotriphosphazene to high molecular weight poly(dichlorophosphazene) has been studied extensively in our laboratory.[4] The polymers used in this study were prepared by the bulk thermal polymerization route. The general procedure to prepare the phosphazene derivatives is outlined in Figure 2.

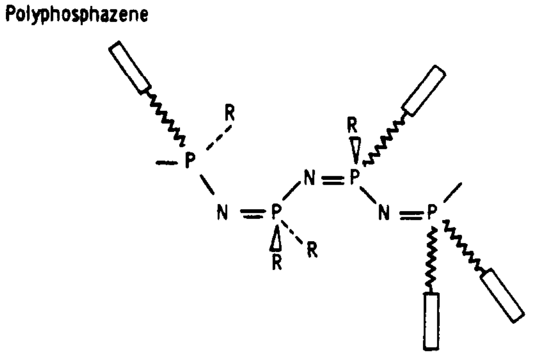

Figure 1. General structure for phosphazenes with mesogenic side groups.

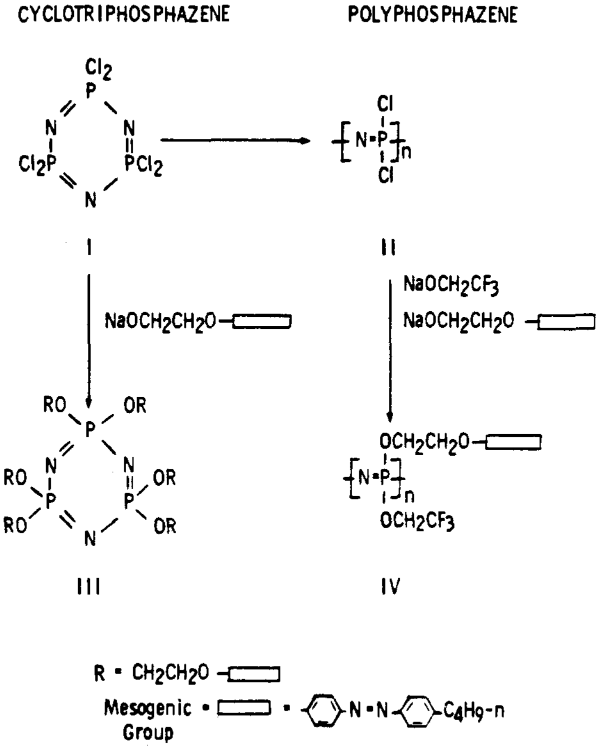

Figure 2. Synthesis of phosphazenes with mesogenic side groups.

A solution of polymer II (4.38 g, 0.038 mol) in 100 mL of dry benzene was added to 18.20 g (0.057 mol) of sodium 2-(4-((*n*-butylphenyl)azo)phenoxy)ethoxide in 200 mL of dry tetrahydrofuran (THF) and heated to reflux over a 4-h period. Next, a solution of sodium trifluoroethoxide (4.64 g, 0.038 mol) in dry THF (50 mL) was added to the reaction, and the resultant mixture was refluxed for an additional 12-h period. The desired polymer IV was isolated by precipitation into pentane and purified by extensive distilled water washing followed by a Soxhlet extraction with pentane. Elemental analysis for polymer IV was consistent with a 1.3:0.7 (mesogen alkoxide:trifluoroethoxide) side-chain composition.[5]

A model cyclic compound (III) was also prepared from hexachlorocyclotriphosphazene (I) and sodium 2-(4-((*n*-butylphenyl)azo)phenoxy)ethanoxide.[6]

Both polymer IV and cyclic phosphazene III were examined with a polarizing microscope fitted with a hot-stage attachment and by differential scanning calorimetry (DSC). Polymer IV strongly exhibited a reversible thermotropic liquid crystalline phase between 123 and 175 °C. Microscopic analysis in the liquid crystalline region is shown in Figure 3. DSC analysis for the polymer shows multiple and very broad transitions in this temperature region, which may be in part due to the irregular distribution of substituents along the polymer backbone (Figure 1).

Observations with the polarized light microscope on the

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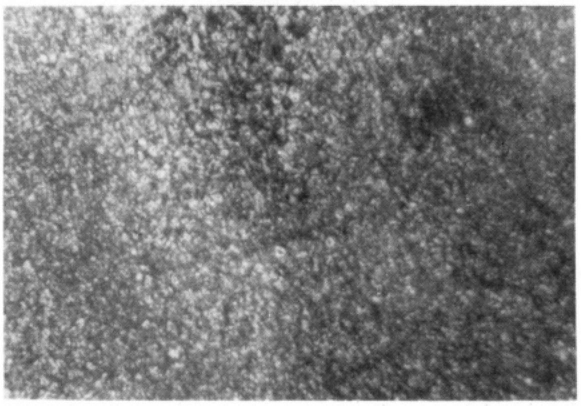

Figure 3. Optical micrograph of polymer IV at 128 °C. Magnification 192×.

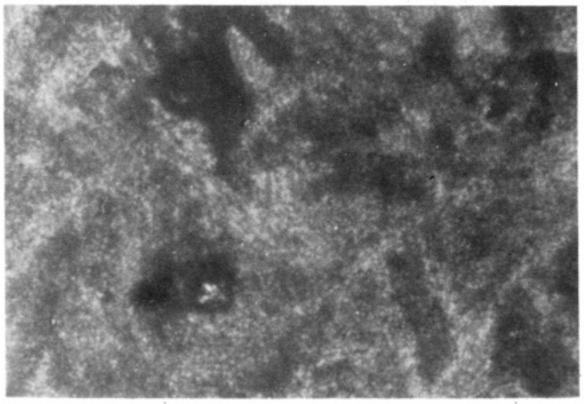

Figure 4. Optical micrograph of compound III at 182 °C. Magnification 192×.

cyclic phosphazene III shows that a reversible thermotropic phase exists between 132 and 188 °C. The texture for this mesophase is shown in Figure 4. The DSC thermogram shows a broad and weak endothermic transition with a peak at approximately 125 °C, which we believe corresponds to a melting transition. A second, much stronger endotherm is obsrved with a peak at approximately 190 °C, and this corresponds very closely with the visually obtained isotropization temperature.

We have thus demonstrated that a thermotropic liquid crystalline phase can be prepared from a polyphosphazene with a suitable side-chain substituent. The nature of this liquid crystalline state appears to be different from the intermediate state of order found in polyphosphazenes with smaller side-chain substituents.[7,8] The nature of the transition for the cyclic phosphazene III is less certain; however, since III and IV are quite different in structure, their mesophases would also be expected to be quite different. Further work is in progress to prepare polyphosphazenes with varied side-chain substituents and to gain a better understanding of the nature of this liquid crystalline state.

Registry No. I, 940-71-6; III, 108347-11-1; HO-$(CH_2)_2OC_6H_4$-*p*-N=NC_6H_4-*p*-C_4H_9, 108347-12-2.

References and Notes

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(3) The 2-(4-((*n*-butylphenyl)azo)phenoxy)ethanol compound gave a consistent chemical analysis: mp 97 °C; ^1H NMR ($CDCl_3$) δ 7.7–8.0 (m, Ar H), 7.2–7.4 (m, Ar H), 6.9–7.1 (m, ArH), 3.9–4.2 (m, OCH_2CH_2O), 2.65 (t, CH_2Ar), 1.1–1.8 (bm, CH_2CH_2), 0.9 (t, CH_3); MS (solid probe EI at 70 eV) *m/e* 298, 253, 165, 161, 137 ($M^+ = C_8H_9O_2$). Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.51; H, 7.44; N, 9.40. Found: C, 72.21; H, 7.46; N, 9.33.

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(5) Polymer phosphazene IV: T_i 175 °C (isotropization temperature); $M_w > 10^6$ (GPC); ^1H NMR ($CDCl_3$) δ 7.5–7.8 (m, Ar H), 7.0–7.4 (m, Ar H), 6.6–6.91 (m, Ar H), 4.1–4.5 (bm, OCH_2CH_2O), 3.7–4.1 bm, OCH_2CF_3), 2.7 (t, CH_2Ar), 1.1–1.8 (bm, CH_2CH_2), 0.9 (t, CH_3). Anal. Calcd for a 1.3:0.7 substituent ratio $C_{24.8}H_{28.7}F_{2.1}N_{3.6}O_{3.3}P_{1.0}$: C, 59.47; H, 5.78; F, 7.97; N, 10.07; P, 6.18. Found: C, 59.12; H, 5.97; F, 7.13; N, 9.88; P, 6.19; Cl, 0.10.

(6) Cyclic phosphazene compound III: T_i 188 °C (isotropization temperature); ^1H NMR ($CDCl_3$) δ 7.6–7.9 (m, Ar H), 7.0–7.4 (m, Ar H), 6.6–6.9 (m, Ar H), 4.0–4.4 (bm, OCH_2CH_2O), 2.6, t, CH_2Ar), 1.1–1.8 (bm, CH_2CH_2), 0.9 (t, CH_3). Anal. Calcd for $C_{108}H_{126}N_{15}O_{12}P_3$: C, 67.63; H, 6.57; N, 10.95; P, 4.84. Found: C, 67.64; H, 6.61; N, 10.98; P, 5.01; Cl, 0.024.

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