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A Liquid Crystalline Poly(organophosphazene)

Polyphosphazenes comprise a broad class of macromolecules with the general formula $(NPR_2)_n$.[1-4] The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone, with specific physical or chemical characteristics imposed by the side groups. This side-group influence depends on the size, shape, polarity, and flexibility of the side units.[4]

In earlier work, we have explored the influence on the polymer properties exerted by flexible aliphatic side groups[4-6] or rigid units such as phthalocyanine,[7] TCNQ,[8] steroidal,[9] and other planar or rigid structures, both linked directly to the chain and separated from it by flexible spacer groups. One objective of these studies was to identify those molecular structural features that might lead to side-chain liquid crystalline behavior.[10,11] A conclusion reached from these studies was that liquid crystalline behavior was probably accessible provided the appropriate mesogenic groups could be linked to the polyphosphazene chain through a sufficiently flexible spacer unit.

Thus, our recent studies have focused on the synthesis of polymer 1, a species in which the mesogenic aromatic azo unit is linked to the polymer chain through tri(ethylene oxide) spacer groups.
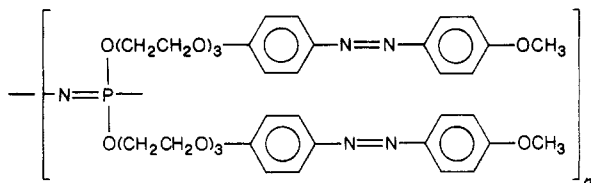
Species 1 was synthesized by the reaction of poly(dichlorophosphazene) with $NaO(CH_2CH_2O)_3C_6H_4N{=}NC_6$-$H_4OCH_3$. Poly(dichlorophosphazene) was prepared by the well-known polymerization of the cyclic trimer $(NPCl_2)_3$.[1-3] p-(Methoxyphenyl)azophenol was prepared by a diazo coupling reaction between p-anisidine and phenol. The hydroxyl group of 2-[2-(2-chloroethoxy)ethoxy]ethanol was protected by dihydropyran in methylene chloride with the use of pyridinium p-toluenesulfonate as a catalyst at 25 °C for 5 h.[12] The protected spacer unit was allowed to react with p-(methoxyphenyl)azophenol and sodium hydroxide in dimethyl sulfoxide in the presence of tetra-n-butylammonium bromide at 100 °C for 10 h. The coupled
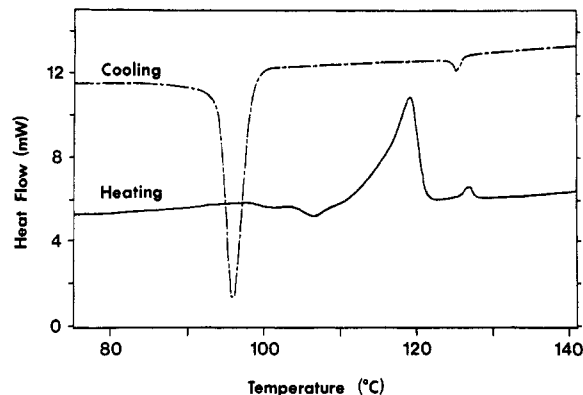
Figure 1. DSC thermograms of polymer 1 at a scanning rate of 10 °C/min.

product was then deprotected in ethanol with pyridinium p-toluenesulfonate. The resultant alcohol was recrystallized from ethanol.[13]

Polymer 1 was then prepared by the reaction of poly-(dichlorophosphazene) with the sodium salt of this alcohol in tetrahydrofuran at reflux temperature for 6 h. The final polymer was purified by precipitation from warm tetrahydrofuran into water, ethanol, and 50 vol % acetone in hexane.[14] On the basis of gel permeation chromatography data in THF solvent, $M_w = 6.8 \times 10^6$ and $M_n = 3.3 \times 10^5$.

The synthesis of 1 was preceded by trial reactions carried out with the cyclic trimeric chlorophosphazene $(NPCl_2)_3$ (2). Reaction of 2 with $NaO(CH_2CH_2O)_3C_6H_4N{=}NC_6$-$H_4OCH_3$ yielded the corresponding organophosphazene trimer, $[NP(O(CH_2CH_2O)_3C_6H_4N{=}NC_6H_4OCH_3)_2]_3$ (3). This compound was characterized by NMR and infrared techniques.[15]

Polymer 1 was isolated as a pale yellow material that shows typical microcrystalline, thermoplastic properties at temperatures below 118 °C. Above 118 °C a mesophase is formed, detectable by optical microscopy with crossed polarizers and by differential scanning calorimetry (Figure 1). Melting of the mesophase occurs above 127 °C during the heating cycle to give the isotropic melt. Formation of the mesophase during the cooling cycle occurs at 126 °C. In the cooling cycle, supercooling is detected for the mesophase–crystalline phase transition (94 °C). Several cycles of heating and cooling within the temperature range of −100 to +200 °C showed that the phenomenon could be recycled. No evidence of thermal decomposition was detected.

Polymer 1 is the first polyphosphazene synthesized in our laboratory that shows definite thermotropic liquid crystalline character. A wide range of related derivatives have been prepared and studied, including examples in which aromatic Schiff's base units, aromatic ester groups, and aromatic amide groups have been linked to the backbone or ring through oxygen atoms in mixed-substituent polymers.[6] None of these was liquid crystalline. The analogue of 1 that lacks the terminal methoxy groups has been synthesized but has not yet shown evidence of liquid crystalline character

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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.

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
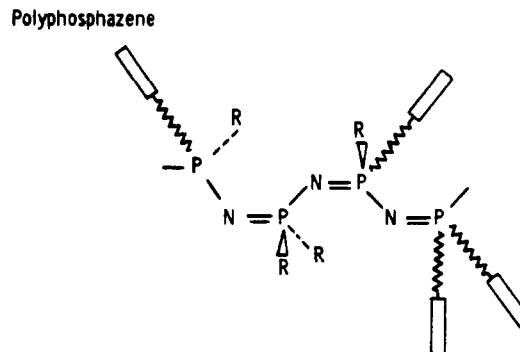

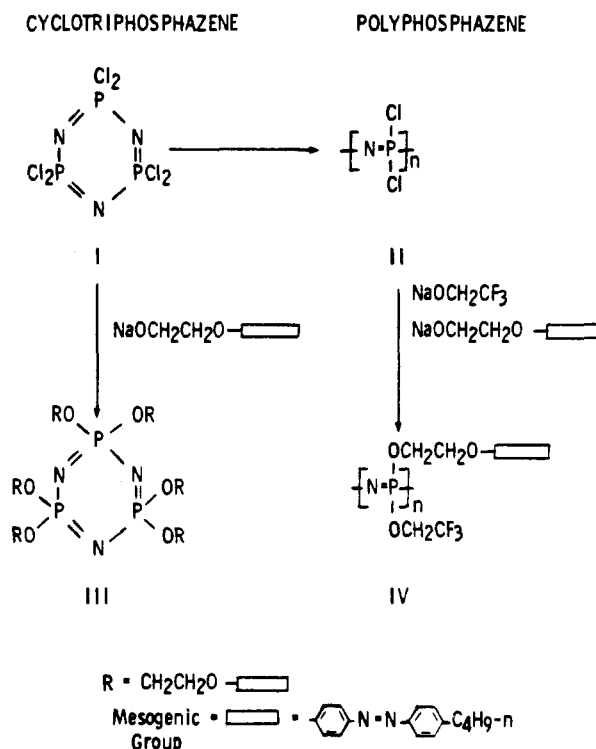**Figure 1.** General structure for phosphazenes with mesogenic side groups.

Figure 2. Synthesis of phosphazenes with mesogenic side groups.

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