

Chapter 14

Side-Chain Liquid-Crystalline Polyphosphazenes

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An overview of the synthesis and characterization of a new class of side-chain liquid crystal polymers with a phosphorus-nitrogen backbone is presented. Using poly-(dichlorophosphazene) as a common reactive high polymer intermediate, low-molar-mass aromatic azo and stilbene mesogens with flexible spacer groups have been attached to the phosphazene (P-N) chain. Single-substituent polymers and mixed-substituent polymers, containing mesogen and trifluoroethoxy cosubstituents, have been prepared and studied by differential scanning calorimetry, optical microscopy, and X-ray diffraction. Both nematic and smectic mesophases have been observed. This synthetic approach offers many opportunities, both with molecular weight control and side-chain chemistry, for tailoring molecular structure to prepare different mesophases and optimize physical properties for non-linear optical applications.

The concept of a side chain liquid crystal polymer has been demonstrated in a number of laboratories and is well documented in the literature (1). Most of the side chain liquid crystalline polymers reported to date contain polysiloxane, polyacrylate or polymethacrylate main chains. More recent studies on the effect of backbone flexibility now include the use of flexible poly(ethylene oxide) or more rigid poly(α -chloroacrylate) chains.

Polyphosphazenes represent a new approach to the design and synthesis of side-chain liquid crystal polymers. Polyphosphazenes are inorganic main-chain polymers consisting of alternating phosphorus-nitrogen atoms in the main chain with two substituents attached to each phosphorus atom. The top of Figure 1 shows the general structure for a side chain liquid crystal polymer: a polymer backbone with a side chain comprised of a flexible spacer and a rigid rod (mesogen). The remaining structures in Figure 1 are examples of side-chain liquid crystalline polyphosphazenes. The middle structure represents a phosphazene mixed-substituent "copolymer" which contains a mesogen side chain along with a non-mesogen (R) side chain. Phosphazene homopolymers (Figure 1, bottom) contain two identical substituents attached to phosphorus. Both phosphazene homopolymers and copolymers can be readily synthesized by processes which are described in the next section.

Synthesis

The most commonly used approach (Figure 2) for the synthesis of polyphosphazenes involves a ring-opening polymerization of hexachlorocyclotriphosphazene (trimer) to give open-chain high molecular weight poly(dichlorophosphazene), followed by a substitution process to yield poly(organophosphazenes) (2,3). By using highly purified trimer and by carefully monitoring the polymerization process, one can obtain soluble high molecular weight poly(dichlorophosphazene) and avoid the branching and crosslinking which can lead to a crosslinked matrix, "inorganic rubber". The second step is also critical: poly(dichlorophosphazene) is a reactive inorganic macromolecule, and chlorine substitution is required in order to prepare hydrolytically stable polymers. This also allows one to prepare a variety of different polymers. Shown in Figure 2 are three general examples consisting of alkoxy, aryloxy, and amino substituted phosphazene polymers. Commercial poly(fluoroalkoxy- and aryloxyphosphazene) elastomers have been prepared, where two or more nucleophiles are used in the substitution process (4). Polyphosphazenes which contain organometallic and bioactive side chains have also been reported (4).

The two-step synthesis process shown in Figure 2 affords several possibilities for preparing new side-chain liquid crystal polymers. The polymerization process allows one to vary the molecular weight and molecular weight distribution (MWD), and potentially change the properties of the liquid crystalline state. Most of the polyphosphazenes reported in the literature, including the examples in this paper, are derived from the bulk uncatalyzed process: this generally produces high molecular weight polymer (one million or greater) with a broad MWD. Catalyst systems have been developed which give lower molecular weight poly(dichlorophosphazene) with a narrower MWD (4). One catalyst, boron trichloride, has also been used to prepare poly(dichlorophosphazene) with narrow molecular weight fractions ranging from approximately ten thousand to over one million (5). Thus, it may be possible to prepare side-chain liquid crystal polyphosphazenes with a range of molecular weights and change the properties of the mesophase.

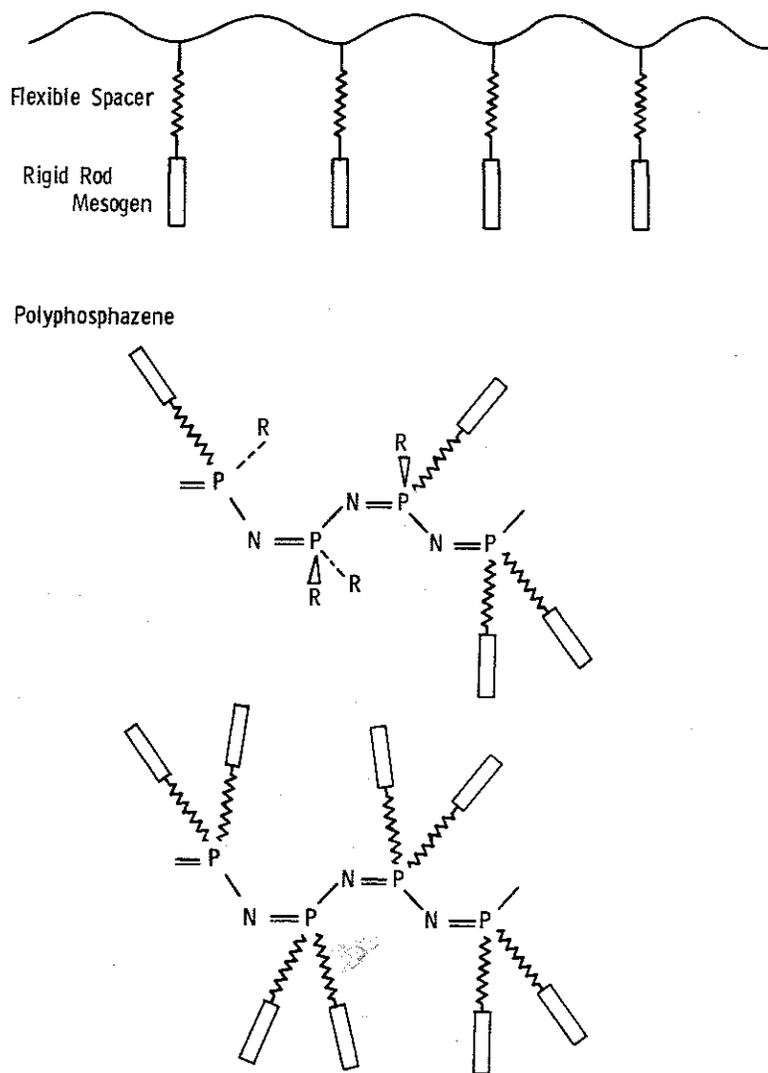


Figure 1. General structures for side-chain liquid crystal polymers.

Polyphosphazene synthesis provides additional possibilities for preparing liquid crystal polymers with different properties. As noted above, the substitution process (Figure 2) enables one to synthesize a wide variety of polymers. The phosphazene inorganic backbone is a highly flexible polymer chain: glass transition temperatures can vary from below room temperature to above 100°C, depending on the size and the nature of the group attached to the P-N backbone (3,6,7). Crystallinity can be altered by preparing mixed-substituent "copolymers" (8). Thus, changing the side-chain substituent affords the potential for varying both the nature and temperature range of the mesophase.

For the synthesis of side chain liquid crystal polyphosphazenes, the most important examples in Figure 2 are the alkoxy- and aryloxy-polymers. Mesophase behavior has been noted with simple side chains, such as trifluoroethoxy and aryloxy side chains (9). This mesophase behavior is not conventional liquid crystal order, but polymers which exist in a conformationally disordered state (10).

Liquid Crystal Polyphosphazenes

In Figure 3 are examples of side-chain liquid crystal polymers. Phosphazene copolymer (I) contains a mixture of an azophenoxy mesogen and a trifluoroethoxy non-mesogen (ca. 1.3:0.7) side chain (11). Structure I in Figure 3 represents only one of the possible repeat units, since the distribution of substituents is presumed to be random (see Figure 1). Although the copolymer (I) contained only slightly greater than one mesogen side chain per repeat unit, it formed a reversible thermotropic liquid crystal phase upon cooling from the isotropic state above 180°C. Analysis by differential scanning calorimetry (DSC) showed no prominent first-order transitions for either the heating or cooling cycles, which may be due to the irregular distribution of substituents along the P-N backbone. Microscopic analysis in the liquid crystalline region is shown in Figure 4. The polymer crystallized upon cooling to room temperature. However, upon heating above 120°C, the polymer transformed back into a mesophase which persisted up to the final clearing point.

High temperature X-ray experiments have been performed on copolymer I in an attempt to obtain a better understanding of the nature of the mesophase. Fibers obtained from I, which were pulled from the melt and quench cooled in water, gave very diffuse patterns. If the fibers were allowed to air cool, the pattern shown in Figure 5 was obtained. It shows a series of sharp arcs centered on the equator and meridian, and the spacings are listed in Table I. More accurate measurements of the low angle equatorial signals were obtained by increasing the specimen to film distance to 170 nm, and the pattern is shown in Figure 6. The reflection at spacing 4.33 Å consists of a full circle but with intensity enhancement at approximately 20-30 degrees off the meridian line. This would approximately place it on a layer line with spacing about 4.9 Å. The equatorial reflections do not index on an obvious lattice. In fact the reflections at 32.4 Å and 25.5 Å are broader than the other reflections, indicating a different origin for these two reflections.

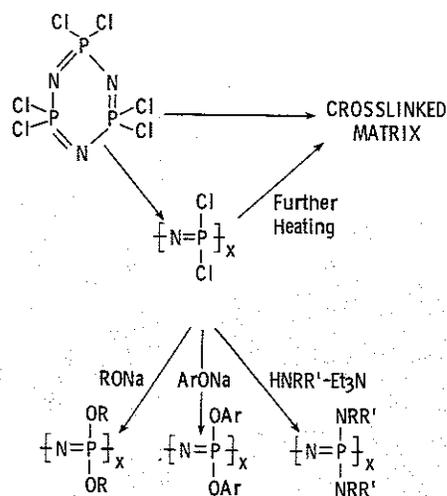


Figure 2. Synthesis of poly(dichlorophosphazene) and poly(organo-phosphazenes).

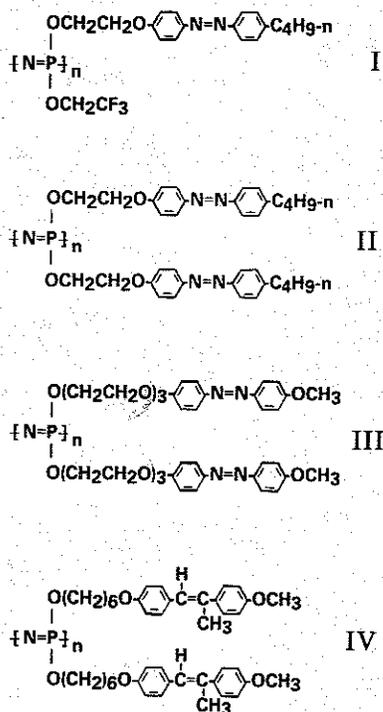


Figure 3. Side-chain liquid crystal polyphosphazenes.

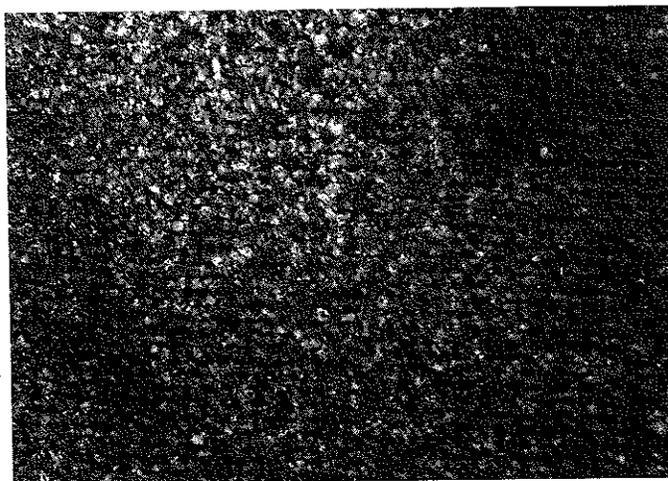


Figure 4. Optical micrograph of polymer I at 128 °C. Crossed polarizers. Magnification 134X. (Reproduced from Ref. 11. Copyright 1987 American Chemical Society.)

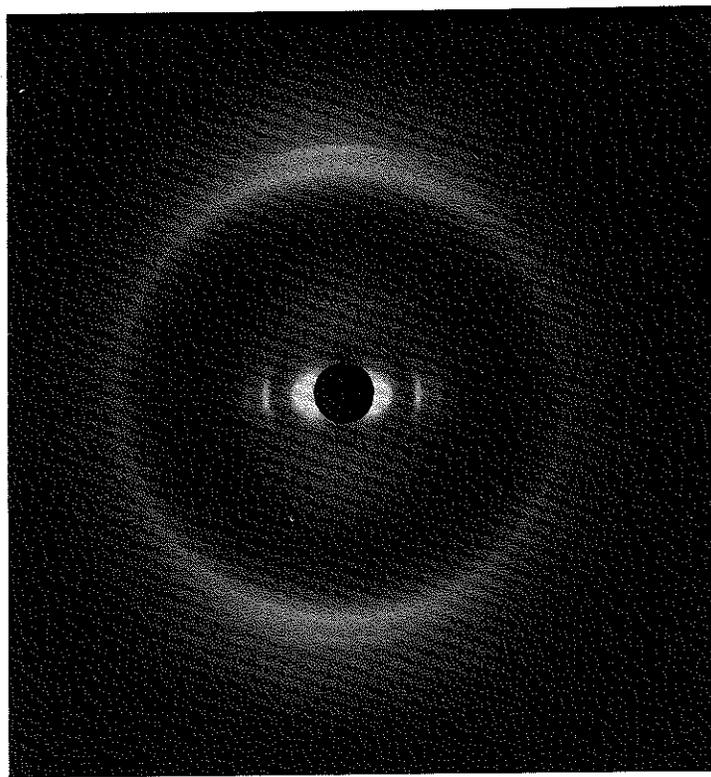


Figure 5. Polymer I. X-ray diffraction pattern obtained from fibers drawn from the melt and cooled in air. Wide-angle pattern.

The sketch of the wide angle pattern is shown in Figure 7. Unit cells taking these two values for the basic parameters \bar{a} and \bar{b} and taking $\bar{c} = 4.9 \text{ \AA}$ do not give the calculated densities that related to the average measured density of 1.2 g/mL.

Table I

Spacing \AA	Description
32.4	Equatorial Arc
25.5	" "
20.4	" "
12.3	" "
9.55	" "
4.33	Ring With Intensity Enhancement in Angle Region $20^\circ - 30^\circ$ From Meridian
3.99	Meridional Arc
3.45	" "

For copolymer I, it is reasonable to relate the diffraction ring at spacing 4.33 \AA (Figure 6) with the stacking of the mesogenic slabs in the side chain. The observation that this interplanar spacing is spherically averaged and other reflections show a respectable degree of orientation argues for two organizational regimes within the sample which of course frustrates the analysis of the X-ray patterns. The fact this material is a copolymer with an irregular distribution of side chains along the polymer main chain probably accounts for the difficulty in indexing the crystalline state and giving a more well defined explanation for the nature of the mesophase.

The situation is quite different for a phosphazene polymer II (Figure 3) containing solely the *n*-butyl phenylazophenoxyethoxy side chain. On cooling from the isotropic state (above 185°C) a viscous mesophase is first observed which shows the characteristic focal conic texture typical of low molar mass smectic A phases. A photomicrograph of the smectic A phase at 162.4°C is shown in Figure 8. As the temperature falls below $160-155^\circ\text{C}$, a smectic C-like mesophase appears. Below $150-145^\circ\text{C}$, the polymer crystallizes, and in the oriented form can be indexed on an orthorhombic unit cell with $\bar{a} = 35.7 \text{ \AA}$, $\bar{b} = 17.85 \text{ \AA}$, and \bar{c} (fiber axis) = 9.85 \AA . The doubling of the 4.9 \AA chain repeat has been reported for other polyphosphazene structures and can arise from alternating perturbations of the side chains or a change in the backbone conformation (12).

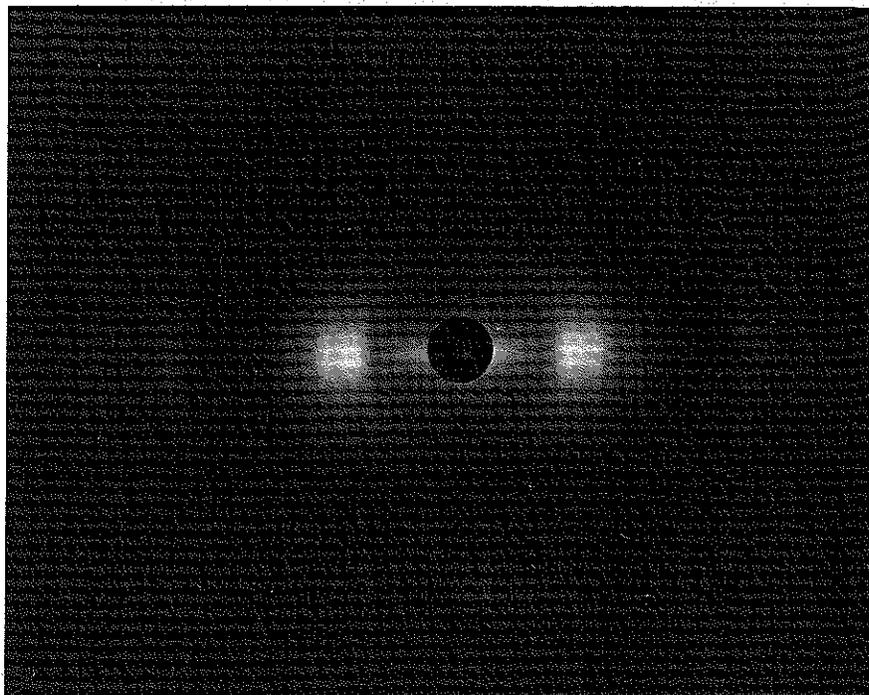


Figure 6. Polymer I. X-ray diffraction pattern obtained from fibers drawn from the melt and cooled in air. Low-angle pattern showing broadness of first two reflections.

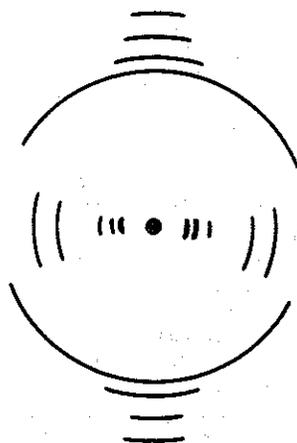


Figure 7. Sketch of wide-angle X-ray pattern for polymer I.

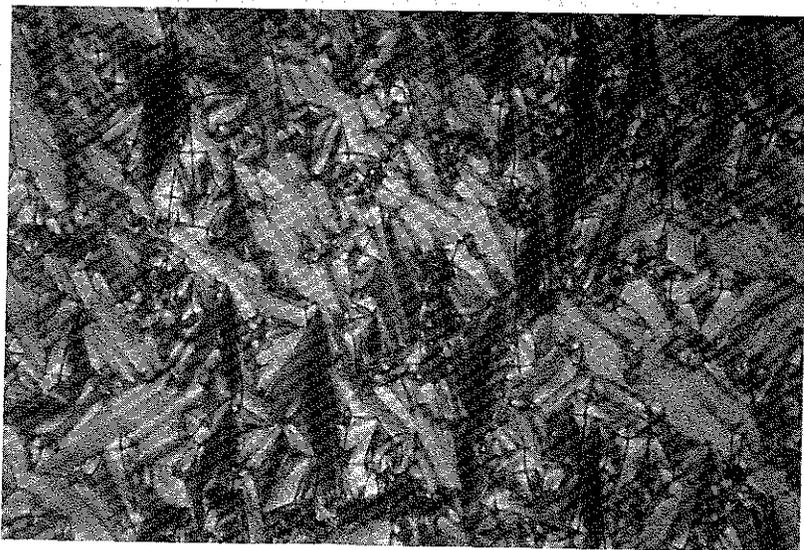


Figure 8. Optical micrograph of polymer II at 162.4 °C. Crossed polarizers. Magnification 200X.

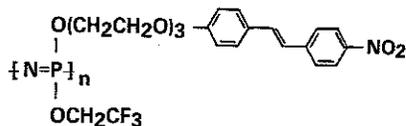
A more extensive series of side-chain liquid crystalline polyphosphazenes and their corresponding cyclic trimers were reported by Allcock and Kim (13,14). The side chain consisted of aromatic azo mesogenic units attached to the phosphorus atoms through flexible oligomeric ethyleneoxy spacer units. Polymers were studied by DSC and optical microscopy. For polymer III, transition from the crystalline to the liquid crystalline state occurred at 118°C, and this phase formed an isotropic fluid at 127°C. On cooling, the transition from the isotropic to the liquid crystalline state occurred at 126°C, with a final crystallization at 94°C. Polarized optical microscopy of the mesophase at 121°C showed a typical nematic pattern. The corresponding cyclic trimer with three ethyleneoxy spacer units did not form a stable mesophase; however the trimer with two ethyleneoxy spacer units (not shown) displayed a typical nematic texture between 192 and 166°C upon cooling from the isotropic phase. This study showed that the terminal para substituent on the mesogen, the length of the spacer unit, and the cyclic or long-chain polymer character of the phosphazene all played a role in determining whether or not the material was liquid crystalline and also played a role in determining the nature of the liquid crystalline state.

The study by Percec, Tomazos and Willingham (15) looked at the influence of polymer backbone flexibility on the phase transition temperatures of side chain liquid crystalline polymethacrylate, polyacrylate, polymethylsiloxane and polyphosphazene containing a stilbene side chain. Upon cooling from the isotropic state, polymer IV displays a monotropic nematic mesophase between 106 and 64°C. In this study, the polymers with the more rigid backbones displayed enantiotropic liquid crystalline behavior, whereas the polymers with the flexible backbones, including the siloxane and the polyphosphazene, displayed monotropic nematic mesophases. The examples in this study demonstrated how kinetically controlled side chain crystallization influences the thermodynamically controlled mesomorphic phase through the flexibility of the polymer backbone.

Nonlinear Optical Polymers

Part of the rationale for investigating liquid crystal polyphosphazenes is for nonlinear optical (NLO) applications. In general, for NLO activity, polymers must either contain noncentrosymmetric side chains (eg., side-chain liquid crystal polymers) or highly delocalized (conjugated) backbones (16). Alternatively, polymers can be doped with low molar mass compounds to obtain NLO activity.

Recently, a mixed-substituent polyphosphazene (polymer V) was synthesized and the second-order NLO properties were investigated (17). The nitrostilbene/trifluoroethoxy ratio was approximately 36:64. Due to the low glass transition temperature of V ($T_g = 25^\circ\text{C}$), the second harmonic signal decayed to zero within a few minutes. However, polymer V is a prototype which offers many opportunities for further tailoring the molecular structure of polyphosphazenes to generate an optimum combination of NLO and physical properties (17).



V

Another recent report (18) involves the evaluation of phosphazenes with nonmesogen side chains that exhibit NLO activity. Modification of the intrinsic optical response of the P-N chain was achieved through substitution of side groups including chloro, anilino, dimethylamino, and trifluoroethoxy. Cyclic phosphazenes were also included in this study. Results suggest that phosphazenes possess inherent NLO activity which can be enhanced by the suitable selection of substituent groups.

Conclusion

At the present time, only a few side-chain liquid crystal polyphosphazenes have been synthesized and investigated. Opportunities exist to prepare a wide variety of side-chain liquid crystalline polyphosphazenes, based on the polymerization-substitution process outlined in Figure 2. Alternative approaches, such as side chain modification of polyphosphazenes prepared by the thermal decomposition of N-silylphosphoranimines (19), may provide even further options for preparing liquid crystal polyphosphazenes.

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