Macromolecules **1995**, *28*, 1668−1672

Liquid Crystalline Behavior of Poly[((6-(4-phenylphenoxy)hexyl)oxy)(trifluoroethoxy)-phosphazene]

Adam J. Jaglowski[†] and Robert E. Singler[*]

Polymer Research Branch, U.S. Army Research Laboratory,
Watertown, Massachusetts 02172-0001

Edward D. T. Atkins

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue,
Bristol BS8 1TL, U.K.

Received July 5, 1994; Revised Manuscript Received November 29, 1994[®]

ABSTRACT: The thermotropic liquid crystalline behavior of a mixed-substituent poly(organophosphazene) containing trifluoroethoxy and (6-(4-phenylphenoxy)hexyl)oxy side chain groups has been investigated by differential scanning calorimetry, polarized optical microscopy, and X-ray diffraction. Upon cooling from the isotropic liquid a "batonnet" texture mesophase formed, which is indicative of a smectic-like structure as compared to low molar mass molecules. The texture grows and coalesces to a final texture. The X-ray diffraction pattern of the "captured" structure upon quench-cooling from the mesophase indicated a mixture of smectic C- and A-like phases. The phosphazene backbone layer thickness is approximately 2.4 nm, and the mesogenic (6-(4-phenylphenoxy)hexyl)oxy side chain overlaps in an antiparallel, interdigitated structure within this layered interval. Mesophase formation in the mixed-substituent polyphosphazene is due largely to the chemical inhomogeneity of the side chain groups, since the single-substituent polyphosphazene containing the same biphenyl side chain does not exhibit a liquid crystalline phase.

Introduction

The structure−property relationships of side chain liquid crystalline polymers (SCLCP) have been well documented in the literature.[1] Although the majority of the work on SCLCP has focused on polysiloxanes, polyacrylates, and polymethacrylates, a few studies have been reported on polyphosphazenes.[2−8] These polyphosphazenes have either exhibited a nematic-like mesophase[2−4] or a smectic-like mesophase.[6,7] Polyphosphazenes are inorganic polymers that consist of alternating phosphorus and nitrogen atoms in the main chain with two substituents attached to the phosphorus atom (Figure 1). The two substituents can be identical as in **1** ("single substituent") or different as in **2** ("mixed-substituent"). In mixed-substituent SCLC polyphosphazenes, the side chain groups are mesogenic and nonmesogenic (denoted as R in Figure 1) and are randomly distributed along the phosphazene backbone. In the single-substituent SCLC polyphosphazenes, the side chain groups are all mesogenic.

In continuing our investigations of liquid crystalline behavior in polyphosphazenes, this paper describes the synthesis, structural determination, thermal analysis, optical microscopy, and X-ray diffraction data for the poly(organophosphazenes) **5** and **6** (Scheme 1).

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**3**) was purified by recrystallization from *n*-heptane followed by vacuum sublimation at 90 °C (0.1 Torr). Poly(dichlorophosphazene) (**4**) was prepared by the ring-opening polymerization of **3** at 245 °C for 260 h (Scheme 1) and purified in 26% yield according to procedures previously described.[9] Toluene and pentane were distilled from CaH_2. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled in a dry nitrogen atmosphere before use. Reagent grade cyclohexane was stored over 4-Å molecular sieves prior to use. Sodium hydride (60% dispersion in oil) was purified by washing three times with cyclohexane and twice with pentane and stored under nitrogen

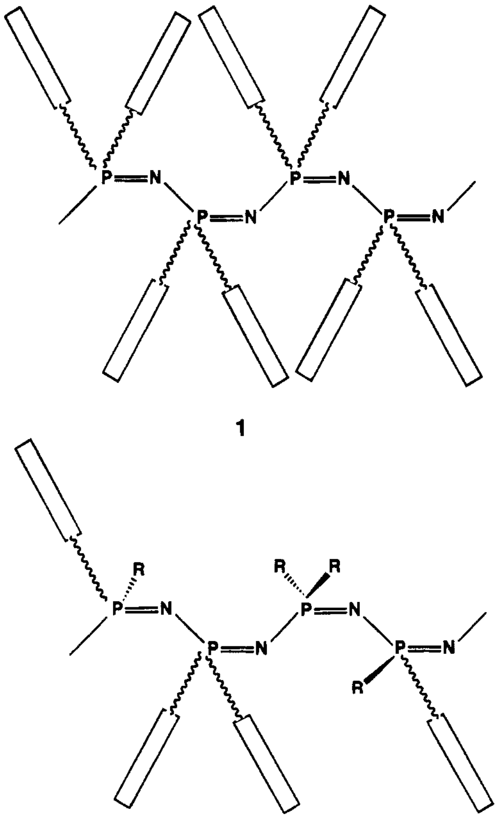


Figure 1. Side chain liquid crystalline polyphosphazenes.

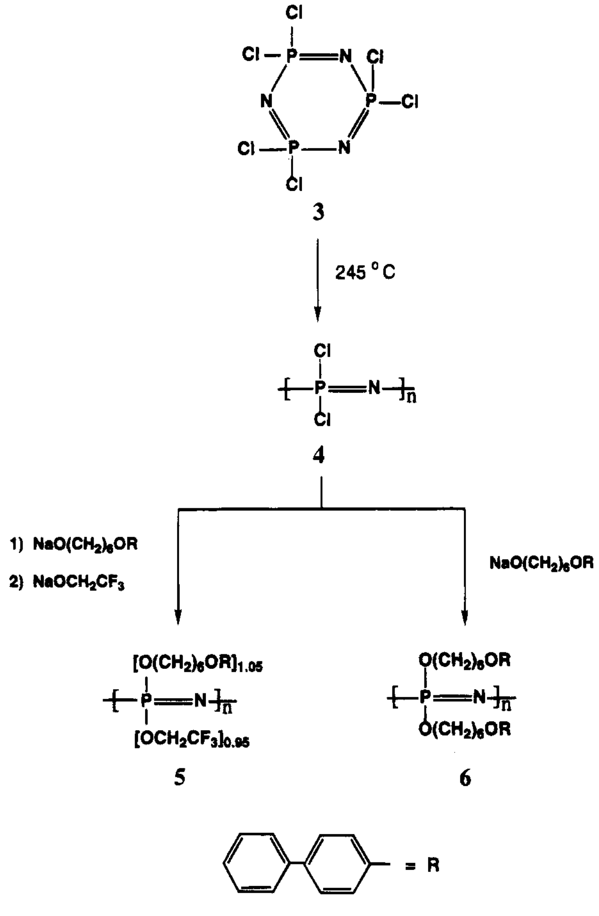
---

[*] To whom correspondence should be addressed.

[†] Current address: Globe Manufacturing Co., Fall River, MA 02720.

[®] Abstract published in *Advance ACS Abstracts*, January 15, 1995.

Scheme 1



prior to use. 4-Phenylphenol was purified by vacuum sublimation. All other solvents and reagents were used as received.

Instrumentation. All glassware was oven-dried prior to use. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded as a thin film between NaCl plates or a KBr pellet with a Perkin-Elmer 1740 FTIR spectrometer. The IR spectra are reported in cm^{-1} along with some definitive absorption assignments. Proton (^{1}H) NMR spectra were obtained with a Varian XL-200 spectrometer operating at 200 MHz. The chemical shifts are reported in ppm relative to an internal standard, tetramethylsilane. Mass spectra were obtained with a Hewlett-Packard 5995C mass spectrometer operating at 70 eV and using a direct insertion method. The filtered mass spectrum reported below is limited to *m/z* values which exceed 10% relative intensity. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Weight-average molecular weight was determined by light scattering at 25 °C via a Zimm plot analysis. Light-scattering measurements were performed on a Brookhaven Instruments BI-200SM goniometer coupled with a Melles Griot 5-mW He–Ne laser light source operating at 632.8 nm. The refractive index increment of **5** in THF was 0.085 mL/g as measured by a Wyatt Optilab 903. Intrinsic viscosity measurements of **5** in THF were made with a Cannon-Ubbelohde viscometer at 25.0 ± 0.1 °C.

The thermal behavior of polymer samples was studied using a Perkin-Elmer DSC-7 differential scanning calorimeter. All DSC samples were under 10 mg and were heated and cooled at 10 °C/min in crimped aluminum pans.

The optical textures were obtained with a Nikon polarizing microscope equipped with a Mettler FP52 hot stage upon slow cooling from the isotropic state.

Oriented samples were obtained by drawing fibers from the material at 115 ± 2 °C and quench-cooling. At 115 °C the mixed-substituent polymer exhibited mesophase behavior and was just below the isotropization temperature (T_i = 117 °C) for the polymer. The X-ray diffraction patterns were recorded in an evacuated flat-plate Statton camera with pinhole collimation and nickel-filtered Cu Kα radiation.

Preparation of 6-(4-Phenylphenoxy)hexanol. An ethanolic solution (100 mL) of 4-phenylphenol (10.0 g, 59 mmol), potassium hydroxide (3.95 g, 70 mmol), and potassium iodide (0.98 g, 5.9 mmol) was stirred at room temperature for 2 h. 6-Bromo-1-hexanol (10.5 mL, 80 mmol) was added to the pink ethanolic solution. The reaction mixture was refluxed for 24 h, cooled to room temperature, and poured into chilled aqueous sodium hydroxide (5 wt %, 500 mL). A solid precipitate was collected by filtration, washed with water (800 mL), and air-dried. The crude product was recrystallized from ethanol to afford 13.46 g (85%) of a white solid: mp 101–102.5 °C (lit.[10] mp 104–105 °C); IR (KBr) 3312 (OH), 3060 (aryl CH), 3033 (aryl CH), 2936 (alkyl CH), 2866 (alkyl CH), 1608 (unsaturated CC), 1520 (unsaturated CC), 1487 (unsaturated CC), 1253, 1078, 837, 764, 697; MS, *m/z* (relative intensity) 270 (M$^+$, 13), 171 (14), 170 (100), 55 (10), 31 (10). Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.24; H, 8.21.

Preparation of Poly[((6-(4-phenylphenoxy)hexyl)oxy)(trifluoroethoxy)phosphazene] (5). A suspension of sodium 6-(4-phenylphenoxy)hexoxide in THF (50 mL) was prepared from the reaction of 6-(4-phenylphenoxy)hexanol (2.72 g, 10.0 mmol), sodium hydride (0.24 g, 10.0 mmol), and tetrabutylammonium bromide (0.81 g, 2.52 mmol, anhydrous) under a blanket of nitrogen at refluxing conditions for 9 h. A toluene solution (50 mL) of poly(dichlorophosphazene) (**4**) (0.585 g, 5.0 mmol) was added dropwise to the sodium hexoxide mixture, and the reaction mixture was heated at reflux for 16 h and then cooled to room temperature. A sodium trifluoroethoxide solution was prepared from trifluoroethanol (0.50 g, 5.0 mmol), sodium hydride (0.12 g, 5.0 mmol), and THF (25 mL). The sodium trifluoroethoxide solution was added dropwise to the polymer reaction mixture, and the resulting mixture was heated to reflux. After 16 h, the reaction mixture was poured into pentane (1 L), and the crude polymer was collected by gravity filtration. The product was washed with water (10 × 500 mL) over a 10 day period and purified by dissolving in THF and precipitating in methanol to afford 1.55 g (76% yield) of a white powder after vacuum-drying: mp 135–140 °C; IR (film) 3032 (aryl CH), 2942 (alkyl CH), 2865 (alkyl CH), 1608 (unsaturated CC), 1522 (unsaturated CC), 1490 (unsaturated CC), 1286 (PN), 1248 (PN), 1172 (alkyl CF_3), 1085 (alkyl CF_3), 963, 833, 763, 695; ^{1}H NMR ($CDCl_3$) δ 7.1–7.6 (7H, m, ArH), 6.6–6.95 (2H, m, ArH), 4.5–4.15 (2H, m, OCH_2CF_3), 3.65–4.1 (4H, m, $POCH_2$ and $ArOCH_2$), 1.1–2.05 (8H, m, CH_2). Molecular weight analysis: light scattering M_w = 1.39 × 10^6; intrinsic viscosity, $[\eta]$ = 0.85 dL/g. Anal. Calcd for $C_{19.2}H_{22.05}NO_{2.95}PF_{3.15}$: C, 56.95; H, 5.49; N, 3.46; P, 7.66; F, 14.78; Cl, 0.00. Found: C, 57.46; H, 5.67; N, 2.66; P, 7.48; F, 14.42; Cl, 0.072.

Preparation of Poly[bis[(6-(4-phenylphenoxy)hexyl)oxy]phosphazene] (6). A suspension of sodium 6-(4-phenylphenoxy)hexoxide in THF (70 mL) was prepared from the reaction of 6-(4-phenylphenoxy)hexanol (5.27 g, 19.5 mmol), sodium hydride (0.47 g, 19.5 mmol), and tetrabutylammonium bromide (1.57 g, 4.9 mmol, anhydrous) at refluxing conditions for 6 h. A toluene solution (50 mL) of poly(dichlorophosphazene) (**4**) (0.76 g, 6.5 mmol) was added dropwise to the sodium hexoxide suspension. The reaction mixture was heated at reflux for 16 h, cooled to room temperature, and poured into pentane (1 L). The crude polymer was collected by gravity filtration and washed with water (6 × 250 mL) over several days. The product was purified by dissolving in THF and precipitating in methanol twice to afford 3.0 g of a white powder after vacuum-drying: mp 115–116 °C; IR (film) 3033 (aryl CH), 2939 (alkyl CH), 2861 (alkyl CH), 1609 (unsaturated CC), 1521 (unsaturated CC), 1489 (unsaturated CC), 1244 (PN), 1102–906, 832, 760, 693; ^{1}H NMR ($CDCl_3$) δ 7–7.6 (7H, m, ArH), 6.7–7 (2H, m, ArH), 3.6–4.3 (4H, m, $ArOCH_2$ and $POCH_2$), 1.1–2.0 (8H, m, CH_2). Anal. Calcd for $C_{36}H_{42}NO_4P$: C, 73.85; H, 7.52; N, 2.39; P, 5.30; Cl, 0.0. Found: C, 71.49; H, 7.18; N, 3.16; P, 5.57; Cl, 2.14.

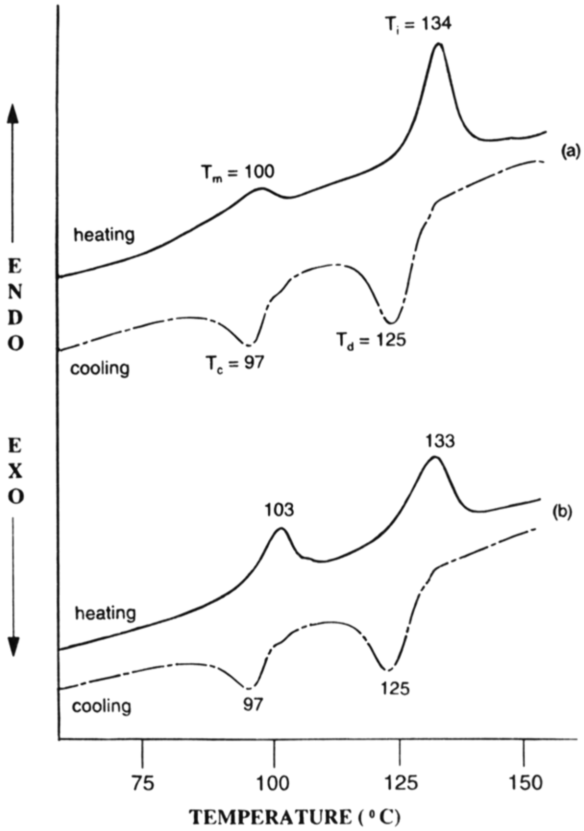


Figure 2. DSC heating and cooling traces of polymer **5** at 10 °C/min: (a) first run; (b) second run. T_m, T_i, T_c, and T_d are defined as the melting, isotropization, crystallization, and deisotropization temperatures, respectively.

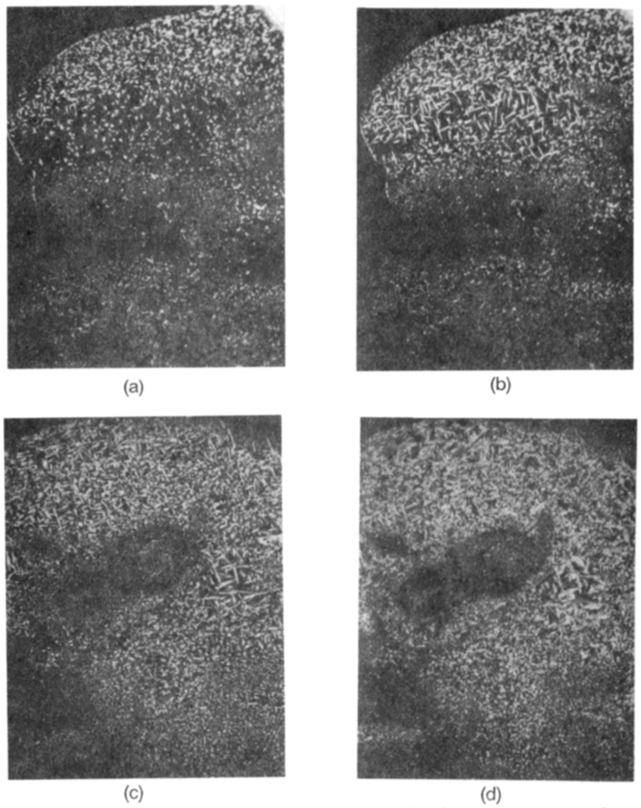


Figure 3. Optical photomicrographs of polymer **5** (magnification 100×): (a) 118.8 °C on cooling; (b) 118 °C on cooling; (c) 115.2 °C on cooling; (d) 108.3 °C on cooling.

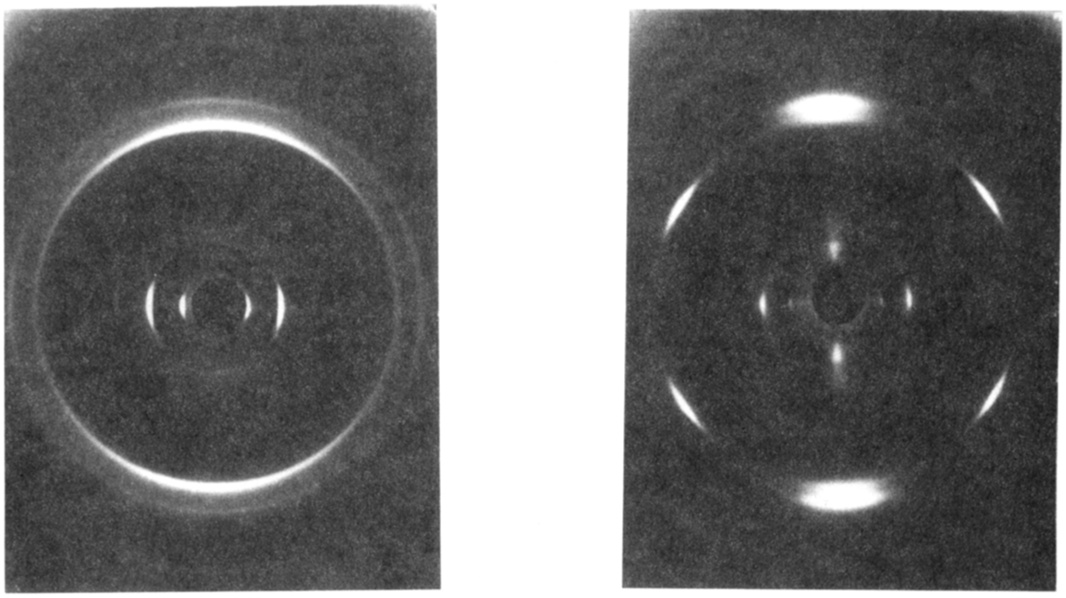
Results and Discussion

Synthesis and Characterization. Synthesis of 6-(4-phenylphenoxy)-1-hexanol was accomplished using a procedure similar to that previously described,[10] and the structure was confirmed by IR spectroscopy, mass spectrometry, and elemental analysis (see Experimental Section). The single-substituent and mixed-substituent polymers **5** and **6**, respectively, were prepared from poly(dichlorophosphazene) and appropriate sodium alkoxides as illustrated in Scheme 1. Structural assignments of **5** and **6** were achieved by IR and ^{1}H NMR spectroscopy and elemental analysis (Experimental Section). The IR spectra of **5** and **6** showed absorptions for the biphenyl group, methylene spacer group, and phosphazene (−PN−) backbone. Although the trifluoroethoxy group absorption appeared in the IR spectrum of **5**, the substituent ratio was undetermined. However, the proton integration from the NMR spectrum of **5** indicated that the biphenyl mesogen to trifluoroethoxy ratio is approximately 1:1. Elemental analysis of **5** showed that the ratio of (6-(4-phenylphenoxy)hexyl)oxy to trifluoroethoxy is 0.95:1.05, which is consistent with the ratio obtained by ^{1}H NMR. Elemental analysis of **6** revealed that the polymer contains approximately 2% residual chlorine. Both **5** and **6** are clearly polymeric as evidenced by drawing fibers for X-ray diffraction studies.

Differential Scanning Calorimetry. The DSC traces of polymer **5** in Figure 2 were obtained from the first and second heating/cooling cycles. The first heating shows two endotherms at $T_m = 100$ °C and $T_i = 134$ °C. On the first cooling, two distinct exotherms are observed, $T_d = 125$ °C and $T_c = 97$ °C. Both exotherms appear to have a shoulder. On the second heating two endotherms at $T_m = 103$ °C and $T_i = 133$ °C are recorded. The T_m endotherm has a slight shoulder. Upon cooling, the same curve trace is observed as in the first cooling. The DSC traces of additional heating and cooling runs were unaffected. The temperature range of the liquid crystal phase was approximately 30 °C on heating and 28 °C on cooling.

However, polymer **6** does not exhibit liquid crystalline behavior as evidenced by only a melting transition at 117 °C and a crystallization at 108 °C in the DSC trace. This type of transitional behavior has also been observed in a related single-substituent polyphosphazene of 8-(4-phenylphenoxy)-3,6-dioxa-1-octanol.[7] In both these systems, it is believed that the biphenyl side chain groups begin to crystallize and the high flexibility of the −PN− backbone accommodates this crystallization. These observations are consistent with conclusions made by Percec and co-workers[6] on the influence of the polymer backbone flexibility on phase transitions. As noted above, multiple endotherms and exotherms are observed when a nonmesogenic trifluoroethoxy group and a (biphenylhexyl)oxy group are incorporated into a polyphosphazene.

Optical Microscopy. Upon first-time heating of the amorphous polymer **5**, birefringence is observed at 114 °C and persists up to 140 °C. Upon cooling from the isotropic liquid, a texture is observed at the deisotropization point, T_d, in the form of "batonnets", which is indicative of a smectic texture (see Figure 3a). On subsequent cooling, the texture grows (Figure 3b,c) and coalesces to a final texture (Figure 3d). Little change in the texture is shown upon cooling to room temperature. The mechanical displacement of the coverslip is possible in the mesophase region. Conversely, polyphosphazene **6** does not exhibit a mesophase texture but



(a) **(b)**

Figure 4. (a) X-ray diffraction pattern. Obtained from the quenched-cooled mesophase (cooled from 115 °C) of the mixed-substituent polymer **5**, (orientation direction vertical). The equatorial arcs are successive orders of a 2.4 nm spacing. (b) X-ray diffraction pattern obtained from quenched-cooled single-substituent polymer **6** from just below the isotropization temperature (orientation direction vertical). The majority of the equatorial arcs are successive orders of 2.12 nm spacing and other wide-angle reflections fall on layer lines with spacing 0.85 nm.

a crystalline texture upon cooling from the isotropic state.

X-ray Diffraction. The X-ray diffraction pattern of the mixed-substituent polymer **5**, obtained by quenching from the mesophase, is shown in Figure 4a. The diffraction arcs on the equator are the first, second, and third orders of a 2.4 nm spacing. In addition, there are three wide-angle diffraction rings at spacings 0.456, 0.405, and 0.325 nm. The intensity of the inner ring is noticeably enhanced in the meridional region, and on close inspection, there is a variation of intensity in the other two rings. The spacings fall on a layer line with spacing 0.49 nm, which is commensurate with the $-PN-$ backbone repeat and has been reported for other polyphosphazenes.[4,11,12] The diffraction pattern confirms that the $-PN-$ backbone runs parallel to the orientation direction but has no regular structure, such as the twofold crankshaft conformation reported for crystalline polyphosphazenes.[12,13] The molecules pack in smectic-like layers with a spacing of 2.4 nm as illustrated in Figure 5. The layers themselves are reasonably well aligned as can be seen from the limited arcing of the equatorial diffraction signals. A noticeable feature of the X-ray diffraction pattern is the substantially greater angular arcing of the wide-angle diffraction signals relative to equatorial reflections, even allowing for the increased distance from the origin of the diffraction pattern. The angular spread of the prominent wide-angle meridional arc at spacing 0.456 nm, for example, is approximately 3 times greater than the equatorial reflections (half-angle ≈45° for the 0.456 nm diffraction signal compared with half-angle ≈15° for the orders of 2.4 nm). The major contribution to this wide-angle diffraction signal is the stacking of the side chain aromatic mesogenic units. The substantial angular spread (half-angle 45°) indicates that the mesogenic side chains cover a range of angles, from perpendicular to the smectic layers to oblique angles. Thus the organization encompasses both smectic A- and C-like character, as illustrated in Figure 5, in the quenched-cooled samples from the mesophase. The simultaneous occurrence of both smectic C- and A-like texture is not surprising in this instance. The disorder, 50% of randomly placed trifluoroethoxy side groups, has blurred the boundary between the higher order smectic C-like texture and smectic A-like texture. The rather crude quench-cooling of oriented samples has not yielded sufficiently fine temperature control to separate both textures and as such both have been "captured" in the experiment.

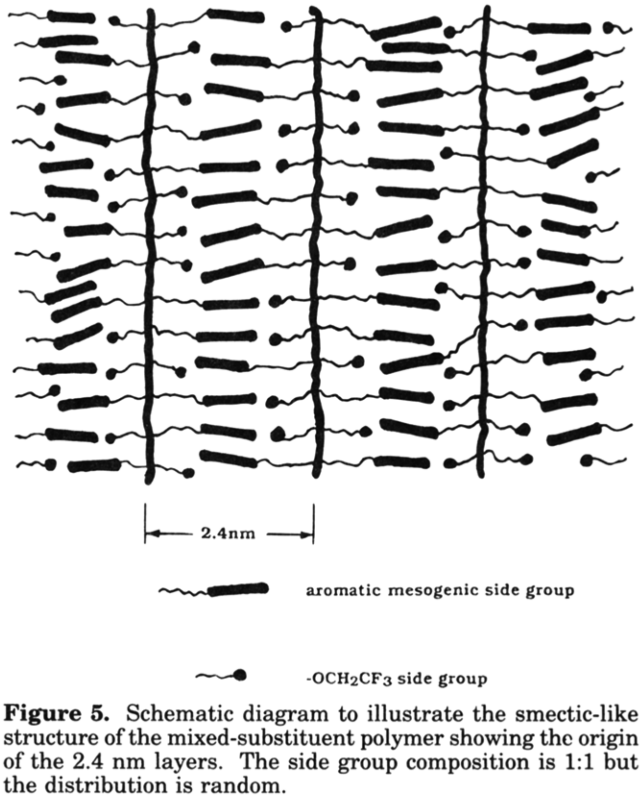


Figure 5. Schematic diagram to illustrate the smectic-like structure of the mixed-substituent polymer showing the origin of the 2.4 nm layers. The side group composition is 1:1 but the distribution is random.

Table 1. Spacings of the Equatorial and Meridional Reflections of Single-Substituent Polymer 6

spacing, nm (error ±0.002)	description
2.123	equatorial arc
1.060	equatorial arc
0.707	equatorial arc
0.530	equatorial arc
0.422	equatorial arc
1.750	equatorial arc
0.983	equatorial arc
0.450	meridional arc
0.418	meridional arc
0.450	off meridional
0.328	off meridional

Figure 4b shows the X-ray diffraction pattern obtained from an oriented sample of the polymer **6** after quench-cooling from the isotropization temperature, $T_{\rm i}$, of 117 °C. The pattern indicates that the sample is crystalline, and the spacings of the reflections are listed in Table 1. The X-ray pattern bears a relationship to that of the mixed-substituent polymer **5**. The majority of the equatorial reflections are successive orders of a 2.12 nm spacing, and the wide-angle reflection confirms the presence of layer lines. Five of the equatorial reflections are successive orders of 2.12 nm. These well-developed layers are spaced 12% closer than for the mixed-substituent polymer **5**. Allowing for the additional side group space needed by the single-substituent polymer, this means a noticeable decrease in the volume occupied by the molecules and is commensurate with the increased crystallinity. The development of order within the layers is supported by the occurrence of additional equatorial reflections (Table 1) indicating three-dimensional ordering. In addition, the strong set of reflections at about 45° (spacing 0.450 nm) to the meridian indicate the development of a layer line with double the spacing of that noticed in the X-ray pattern from the mixed-substituent polymer **5**. The occurrence of a layer line at approximately 0.98 nm has been observed for other polyphosphazenes.[4,11,12] It develops when the −PN− backbone conformation approaches a twofold crankshaft-like conformation.[12,13] A pair of diffraction signals with identical spacing to those at 45° (0.450 nm) occur on the meridian. It is believed this arises from a different crystalline phase of the single-substituent polymer that overlays the structure described above. Thus it will serve no useful purpose to attempt a definitive three-dimensional indexing of these structures.

Conclusions

Polarized optical microscopy, DSC thermal analysis, and X-ray diffraction results indicated that mixed-substituent polyphosphazene **5** exhibits an enantiotropic smectic-like mesophase, and that the single-substituent polymer **6** does not exhibit liquid crystalline behavior. DSC results of **5** indicated that the temperature range of the liquid crystalline phase is approximately 30 °C upon heating and cooling. The X-ray results of the quench-cooled oriented samples from the mesophase of polymer **5** encompass a mixture of smectic C- and A-like structures as illustrated in Figure 5. Finer temperature control together with annealing would be needed to massage in the higher order wholly smectic C-like structure. This has been achieved using the heating stage in the optical microscopy experiments, where the observation of the "batonnet" texture indicates a smectic C-like structure, as illustrated in Figure 3. The phosphazene backbones are thought to lie in parallel planes within the smectic-like layers of the mesogenic side chain groups. The length of the mesogen is approximately 1.8 nm, and therefore there is sufficiently ample space for the group to pack in both smectic A- and C-like configurations within the 2.4 nm intervals of the phosphazene backbone. The flexibility of the −PN− backbone and methylene spacer and the incorporation of the nonmesogenic trifluoroethoxy group allow the biphenyl mesogenic groups to order in a layered, antiparallel, interdigitated structure. Since the single-substituent polymer **6** does not exhibit a mesophase, clearly the chemical inhomogeneity in the side chain groups of **5** is frustating higher levels of order toward the crystalline phase. A comparison of the behavior of polymers **5** and **6** illustrates how the stereochemistry of the side group decoration pattern influences the chain−chain interactions and organization of the mesogenic side chains. This difference in behavior between single- and mixed-substituent polyphosphazenes has been previously documented.[8] The additional inhomogeneity in the side chain stereochemistry in polymer **5** opens up a technologically useful thermotropic mesophasic window for this polymer compared with the parent single-substituent polymer.

Acknowledgment. We gratefully acknowledge the technical assistance of Ms. Marie Potts for viscosity and light scattering measurements, Mr. David Bulpett for mass spectrometry analysis, Dr. James Sloan for IR spectroscopy analysis, and Dr. Richard Desper for review and comments on the manuscript.

References and Notes

(1) McArdle, C. B., Ed. *Side-Chain Liquid Crystal Polymers*; Blackie, Chapman and Hall: New York, 1989.
(2) Allcock, H. R.; Kim, C. *Macromolecules* **1989**, *22*, 2596.
(3) Allcock, H. R.; Kim, C. *Macromolecules* **1987**, *20*, 1926.
(4) Singler, R. E.; Willingham, R. A.; Noel, C.; Friedich, C.; Bosio, L.; Atkins, E. *Macromolecules* **1991**, *24*, 510.
(5) Singler, R. E.; Willingham, R. A.; Lenz, R. W.; Furukawa, A.; Finkelmann, H. *Macromolecules* **1987**, *20*, 1727.
(6) Percec, V.; Tomazos, D.; Willingham, R. A. *Polym. Bull.* **1989**, *22*, 199.
(7) Allcock, H. R.; Kim, C. *Macromolecules* **1990**, *23*, 3881.
(8) Singler, R. E.; Willingham, R. A.; Noel, C.; Friedich, C.; Bosio, L.; Atkins, E.; Lenz, R. W. In *Liquid-Crystalline Polymers*; Weiss, R. A., Ober, C. K., Eds.; ACS Symposium Series 435; American Chemical Society: Washington, DC, 1990; Chapter 14.
(9) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; LaLiberte, B. R.; Sacher, R. E.; Matton, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 433.
(10) Bresci, B.; Frosini, V.; Lupinacci, D.; Magagnini, P. L. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 183.
(11) Burkhart, C. W.; Gillette, P. C.; Lando, J. B.; Beres, J. J. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 2349.
(12) Meille, S. V.; Porzio, W.; Allegra, G.; Audisio, G.; Gleria, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 217.
(13) Bishop, S. M.; Hall, I. H. *Br. Polym. J.* **1974**, *6*, 193.

MA9412391