Poly(organophosphazenes) with Azoxybenzene Side Groups. Synthesis and Morphology

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ABSTRACT: Azoxybenzene derivatives with chiral alkoxy terminal units were introduced as side chains in poly(organophosphazenes). The thermal behavior, morphology, and related electrical properties were investigated by using differential scanning calorimetry (DSC), X-ray diffraction, and measurements of the pyroelectric coefficient. From the DSC studies, suppression of side-chain crystallization by the azoxy group was evident. The thermal behavior was dependent on the spacer length and on the structure of the terminal units on the azoxybenzene group. A polyphosphazene with triethyleneoxy spacer units and azoxybenzene groups, with a 2-octoxy terminal unit at the para position, was amorphous and showed only a glass transition. However, 2-butoxy and 2-methyl-1-butoxy terminal groups imposed a layered morphology on the polymers. An X-ray diffraction study suggested that these polymers have a tilted layer morphology. Spontaneous polarization for the aligned polyphosphazenes was measured by integration of the pyroelectric coefficient with respect to temperature.

Introduction

Poly(organophosphazenes) are a class of semiinorganic polymers with backbones composed of alternating phosphorus and nitrogen atoms.[1-5] The unusual thermotropic behavior of alkoxy- or aryloxy-substituted poly(organophosphazenes) has been studied in detail.[6-16] Furthermore, polyphosphazenes have been studied recently as side-chain liquid crystalline systems.[17-21] The presence of two identical side groups on the phosphorus atoms in single-substituent polymers, together with the flexibility of the phosphorus-nitrogen backbone, is believed to give rise to substantial uniqueness in terms of liquid crystalline behavior compared with organic polymeric systems.

Since Meyer reported the ferroelectric behavior of chiral smectic C and H phases, tilted smectic phases with optically active constituent molecules have been of great interest because of their ferroelectric properties.[22,23] An extension of this approach to polymeric systems was reported first by Shibaev and co-workers by the use of side-chain liquid crystalline polymethacrylates.[24] They observed a chiral smectic C phase and measured the spontaneous polarization by an integration of the pyroelectric coefficient with respect to temperature. However, only a few published results exist related to tilted smectics derived from polymeric systems.[25-32] In addition to liquid crystalline chiral smectic C, I, and F phases, aligned tilted crystalline smectic phases can be ferroelectric when their constituent molecules are optically active.[33] Therefore, a need exists to synthesize novel polymeric systems with tilted smectic morphology and with optically active moieties.

In this paper, the synthesis is described of poly(organophosphazenes) with tilted layer morphology and with optically active groups in the structure. Azoxybenzene derivatives were linked to the skeleton of polyphosphazenes via flexible spacer units to repress the side-chain crystallization.

Results and Discussion

Synthesis. The synthetic pathways used to prepare azoxybenzene groups with optically active alkoxy substituents are summarized in Scheme I. A literature procedure was employed for the preparation of 4,4′-dihydroxyazoxybenzene (1).[34] The chiral moiety was linked to 4,4′-dihydroxyazoxybenzene by use of commercially available (*R*)-(−)-2-octanol (2), (*R*)-(−)-2-butanol (3), and (*S*)-(−)-2-methyl-1-butanol (4). During the monoetherification of compound 1 with 2–4, racemization was avoided by using the Mitsunobu reaction, which involves strict inversion of the chiral reaction center.[35,36] For compound 4, the chiral carbon was not directly involved in the reactions and this maintained its configuration through the whole synthetic route. After monoetherification, one of the azoxybenzene isomers was isolated by column chromatography (see Experimental Section). Determination of the optical purity of the product by the use of chiral shift reagents was not successful. The chirality of the compounds was checked by measurement of the optical rotation. The azoxy compounds 5–7 were coupled to the oligomeric ethyleneoxy spacer units by use of a standard procedure under basic conditions to yield compounds 8–12. The characterization of compounds 5–12 was carried out by use of ^{1}H NMR and IR spectroscopy, mass spectrometry, optical rotation measurements with a polarimeter, and melting points.

Poly(organophosphazenes) 15–19 were prepared by the nucleophilic displacement of chlorine atoms from poly(dichlorophosphazene) (14), which itself was produced by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene (13) as described in Scheme II. The structural characterization of the polyphosphazenes was performed by ^{1}H NMR, ^{31}P NMR, and IR spectroscopies and by elemental analysis (Table I). The total replacement of chlorine atoms by the reaction with the sodium salts of compounds 8–12 was confirmed by a singlet resonance in the ^{31}P NMR spectrum for each polyphosphazene. Elemental microanalysis showed that the residual chlorine content was less than 0.3%. All the polymers 15–19 were soluble in THF.

The general properties of the polymers were dependent on the terminal substituents and the spacer length. Polymer 15, with a 2-octoxy terminal unit and a triethyleneoxy spacer group, was an adhesive material. As the terminal units and the spacer moieties became shorter, the polymeric products became fibrous (17 and 19) or glassy (16 and 18). All are film-forming polymers. The molecular weight data for polymers 15–19 were obtained by the use of gel permeation chromatography. Values of M_w >

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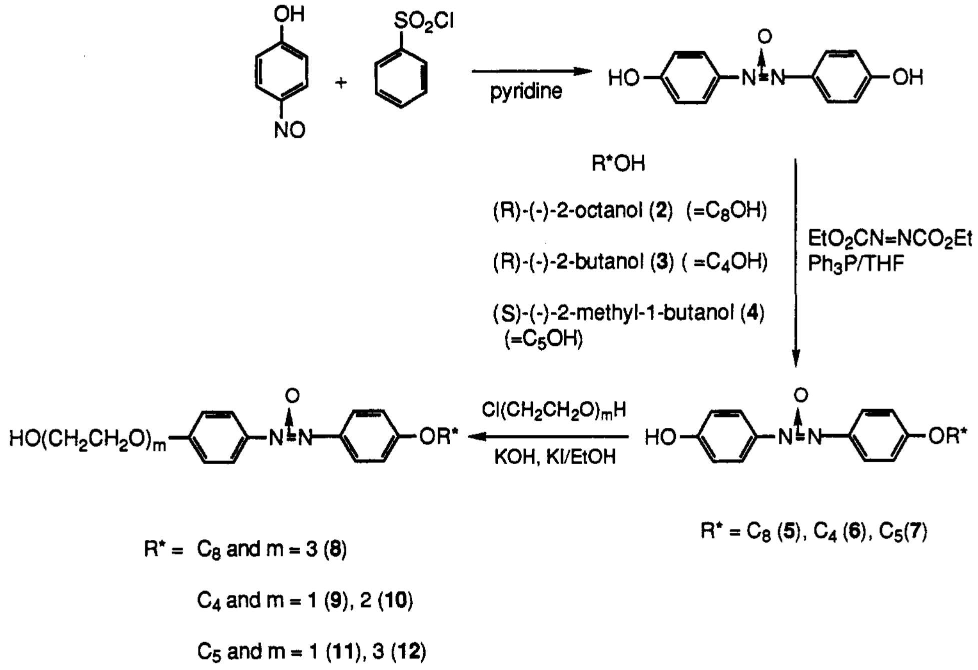
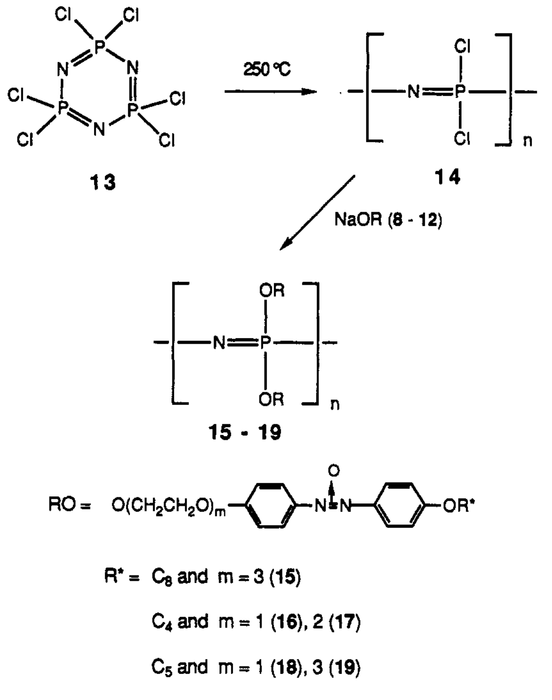
Scheme I



Scheme II



10^6 were found. The polydispersity (M_w/M_n) was in the range of 13–32.

Thermal and X-ray Studies. The morphological aspects of the polymer products were investigated by the use of differential scanning calorimetry (DSC) and X-ray diffraction experiments. The thermal analysis and X-ray diffraction results are summarized in Table II.

The thermal behavior of polymers 15–19 was affected by both the spacer length and the structure of the terminal units. Polymer 15, with the 2-octoxy terminal unit and the triethyleneoxy spacer group, was amorphous, with a glass transition temperature at −35 °C. The X-ray study showed no distinctive diffraction except for a diffuse diffraction between 4 and 6 Å, which is typical for amorphous polymers. Polymers 16–19 showed both a glass transition and a melting transition to an isotropic liquid. A comparison of the thermal transition temperatures of 16–19 showed that both the T_g and T_m were lowered as the length of the spacer unit increased. A trend also existed in which the 2-methyl-1-butoxy terminal substituent generated a much higher isotropization temperature than did the 2-butoxy terminal unit polymers. The enthalpies of isotropization were in the range of 0.6–1.4 kcal/mru (mru is the mole repeat unit).

An X-ray diffraction study of polymers 16–19 provided detailed morphological information, especially for the layer spacing. X-ray diffraction of polymer 16 (Figure 1) showed small-angle diffraction of 29.9 Å, which corresponds to the layer spacing. The estimated length of the extended side group is 17.4 Å. Therefore, more than one side group is involved in the formation of one layer. Two side groups could be involved in the formation of each layer. There are two possibilities for the formation of a layer with two side groups. The first is to have interdigitated side groups in the direction normal to the layer. However, an interdigitated structure is unlikely in this case because of the steric branching of the side-group structure. The second possibility is a tilted layer structure. If two side groups are stacked perpendicular to the layer, the layer spacing should be more than 35 Å. Therefore, the side groups are probably tilted to generate the layer spacing of 29.9 Å. The discrete sharp diffraction at 4.8 Å reflects the ordered side-chain structure in the layer. The diffraction at 10.5 Å has not yet been assigned.

The X-ray diffraction data for polymer 17 were similar to that of 16 except that 17 showed diffuse diffraction between 4 and 5 Å. Polymer 17 showed a layer spacing of 33.1 Å in the small-angle range. The estimated length of the extended side group for polymer 17 is 20.8 Å. Therefore, the two side groups must be tilted in each layer. In addition, the diffuse diffraction that corresponds to a 4–5-Å spacing (interchain distance) reflects the liquidlike order of the side chains in the layer in contrast to polymer 16. The origin of the diffraction at 11.5 Å is not clear.

Polymers 18 (Figure 1) and 19 showed diffraction patterns similar to that of polymer 17. They too are believed to have a tilted layer morphology. For polymer 18, the layer spacing was 33.9 Å, and the diffuse diffraction at 4–5 Å also indicated the liquidlike order of the chains in the layer. The calculated length of the side group in

Table I
Polyphosphazene Characterization Data

polymer	IR,[a] cm^{-1}	^{1}H NMR,[b] δ	^{31}P NMR,[b] ppm	mol wt (GPC)		elem anal.	
				M_w	M_w/M_n	calcd	found
15	1240 (PN)	8.20–7.90 (br, ArH, 4 H), 7.10–6.70 (br, ArH, 4 H), 4.50–4.10 (br, OCH, OCH$_2$, 5 H), 4.00–3.60 (br, m, OCH$_2$, 8 H), 1.75 (br, m, CH_2, 1 H), 1.62 (br, m, CH_2, 1 H), 1.50–1.15 (br, m, CH$_2$, CH$_3$, 11 H), 0.85 (br, CH$_3$, 3 H)	−8.2 (s)	1.4×10^4	22	C, 62.97; H, 7.47; N, 7.06; Cl, 0	C, 62.14; H, 7.19; N, 7.24; Cl, 0.02
16	1240 (PN)	8.20–7.90 (br, ArH, 4 H), 7.05–6.65 (br, ArH, 4 H), 4.50–4.15 (br, OCH, OCH$_2$, 5 H), 1.70 (br, m, CH_2, 1 H), 1.58 (br, m, CH_2, 1 H), 1.25 (br, CH$_3$, 3 H), 0.96 (br, CH$_3$, 3 H)	−8.0 (s)	1.6×10^6	19	C, 61.44; H, 6.02; N, 9.95; Cl, 0	C, 60.38; H, 5.36; N, 9.78; Cl, 0.20
17	1250 (PN)	8.20–7.95 (br, ArH, 4 H), 7.05–6.70 (br, ArH, 4 H), 4.50–4.15 (br, OCH, OCH$_2$, 5 H), 4.05–3.60 (br, OCH$_2$, 4 H), 1.70 (br, m, CH_2, 1 H), 1.55 (br, m, CH_2, 1 H), 1.25 (br, CH$_3$, 3 H), 0.95 (br, CH$_3$, 3 H)	−8.1 (s)	5×10^5	13	C, 60.67; H, 6.37; N, 8.84; Cl, 0	C, 60.08; H, 6.43; N, 8.95; Cl, 0.032
18	1240 (PN)	8.20–7.80 (br, ArH, 4 H), 7.00–6.60 (br, ArH, 4 H), 4.60–3.50 (br, m, OCH$_2$, 6 H), 1.80 (br, CH, 1 H), 1.55 (br, CH_2, 1 H), 1.20 (br, CH_2, 1 H), 1.10–0.85 (br, m, CH$_3$, 6 H)	−8.1 (s)	8×10^5	16	C, 62.37; H, 6.34; N, 9.57; Cl, 0	C, 60.45; H, 6.22; N, 9.44; Cl, 0.31
19	1240 (PN)	8.35–8.05 (br, ArH, 4 H), 7.05–6.80 (br, ArH, 4 H), 4.29 (br, OCH$_2$, 2 H), 4.05 (br, OCH$_2$, 2 H), 3.95–3.55 (br, OCH$_2$, 10 H), 1.82 (br, CH, 1 H), 1.60 (br, m, CH_2, 1 H), 1.25 (br, m, CH_2, 1 H), 1.15–0.90 (br, m, CH$_3$, 6 H)	−7.9 (s)	7×10^5	18	C, 60.85; H, 6.88; N, 7.71; Cl, 0	C, 59.89; H, 6.93; N, 7.77; Cl, 0.057

[a] Thin film on KBr. [b] In THF-d_8.

Table II
Thermal Analysis and X-ray Diffraction Data for Polymers 15–19

polymer	T_g, °C	T_i,[a] °C	ΔH_i,[a] kcal/mru	d_1, Å	d_2, Å	d_3, Å
15	−35					
16	36	118 (75)	0.77 (0.83)	4.8	10.5	29.9
17	18	102 (93)	0.92 (0.97)	4–5	11.5	33.1
18	48	193 (185)	0.66 (0.78)	4–5	11.5	33.9
19	8	142 (137)	1.44 (1.93)	4–5	13.9 (8.4)	39.9

[a] Values in parentheses were measured on cooling.

polymer 18 was 19.5 Å. Polymer 19 has an interlayer spacing of 39.9 Å, with the length of 26.3 Å for the extended side group. This is also consistent with a tilted layer structure.

The morphologies of polymers 17–19 are similar, since all possess tilted layer structures and lack interchain order in the layer. Polymer 16 also showed a similar tilted layer structure. However, 16 has more order in the layer than do polymers 17–19. Polymers 16–19 could be crystalline tilted smectic systems with optically active molecular moieties in the structure. In this case, it is possible that an aligned phase can possess spontaneous polarization.[33]

A preliminary study of the measurement of spontaneous polarization of the aligned polymers with tilted layer morphology was carried out by the integration of the pyroelectric coefficient with respect to the temperature. Polymer films were cast on an indium–tin oxide (ITO) glass, and a gold electrode was deposited on each polymer film and on the reverse side of the ITO glass. This placed the polymer film between two electrodes. The film thickness was in the range of 0.07–0.12 mm. The temperature was elevated above the glass transition, and an electric field (10^2 kv/cm) was applied to align the dipoles in the tilted layer. The temperature was then lowered below T_g and the field was removed. Thereafter, the pyroelectric coefficients were measured by elevating the temperature at a rate of 4 °C/min.

A representative data curve for polymer 17 is illustrated in Figure 2. A pyroelectric peak appears near T_g. This suggests that the frozen aligned dipoles relax as the glass transition occurs. The magnitude of the polarization for the aligned sample of 17 was 90 nC/cm^2. For 16, a very similar relaxation pattern was observed with a very large polarization value (140 nC/cm^2). The magnitude of the polarization for 18 was 30 nC/cm^2, as shown in Figure 2b. For polymer 19, current flow was followed by the pyroelectric peak near T_g, which caused difficulties in measuring the polarization value. The reason for this is not clear.

The magnitude of the spontaneous polarization for the aligned polyphosphazenes is in a range that is typical of organic materials. However, the flexible phosphazene chain could facilitate the electrical reversal of the polarization compared with organic polymers. Future studies will be focused on this aspect.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and was distilled under nitrogen before use. Hexachlorocyclotriphosphazene (Ethyl Corp.) was purified by recrystallization from *n*-hexane followed by sublimation at 40 °C (0.5 mmHg). Poly(dichlorophosphazene) was prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250 °C. An average conversion was 25–35%. The compound *p*-nitrosophenol was obtained from Tokyo Kasei and was used as received. Diethyl azocarboxylate, (*R*)-(−)-2-octanol, (*R*)-(−)-2-butanol, and (*S*)-(−)-2-methyl-1-butanol, obtained from Aldrich, were dried over molecular sieves (4 Å) before use. All the other reagents were obtained from Aldrich and were used as received. Silica gel (60–20 mesh, Fisher) was used for column chromatography. For thin-layer chromatography (TLC), TLC plates precoated with silica gel, 250 μm (J. T. Baker), were used.

Instruments. ^{1}H NMR spectra were recorded with the use of a Bruker WP-360 spectrometer operated at 360 MHz. Chemical shifts are relative to tetramethylsilane at $\delta = 0$. ^{31}P NMR (^{1}H-decoupled) spectra were obtained with a JEOL FX90Q NMR spectrometer operated at 36.2 MHz or a Bruker WP-360 spectrometer operated at 144.8 MHz. ^{31}P NMR chemical shifts are relative to 85% H$_3$PO$_4$ at 0 ppm with positive shift values downfield from the reference. Infrared spectra were recorded with use of a Perkin-Elmer Model 1710 FT-IR spectrophotometer. Electron impact mass spectra were obtained with the use of a Kratos M59/50 spectrometer. Optical rotation was

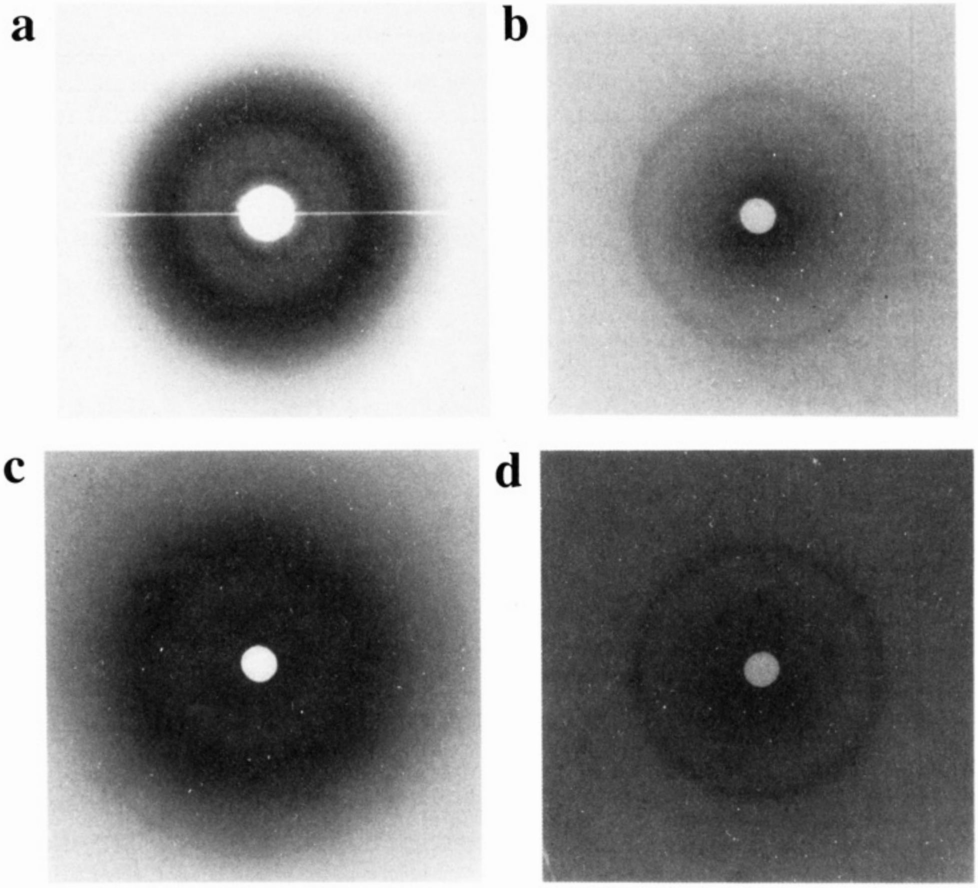


Figure 1. X-ray diffraction diagrams of polymers **16** (a, WAXD; b, SAXD) and **18** (c, WAXD; d, SAXS).

measured by the use of a Perkin-Elmer 241 polarimeter. A Perkin-Elmer DSC 7 with TAC 7 controller was used to obtain DSC thermograms. Gel permeation chromatography was carried out with the use of a Hewlett-Packard HP1090 liquid chromatograph with an HP1037A refractive index detector. THF with 3% tetra-*n*-butylammonium bromide was used as the eluent. The column was PL gel, 10 μm (Polymer Laboratories), calibrated with standard polystyrene. The X-ray experiments with unoriented samples were carried out with Cu Kα radiation by the use of a flat-plate camera. The system was evacuated during the measurements. The Sybil molecular graphics program was used to obtain the estimated length of side groups. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $HOC_6H_4N(O)NC_6H_4OR$ Where R = 2-Octoxy (5), 2-Butoxy (6), or 2-Methyl-1-butoxy (7). For the preparation of compounds **5**–**7**, monoetherifications of 4,4′-dihydroxyazoxybenzene with (*R*)-(−)-2-octanol, (*R*)-(−)-2-butanol, and (*S*)-(−)-2-methyl-1-butanol were carried out by the use of the Mitsunobu reaction. A typical reaction procedure is described for the preparation of compound **5** as follows: Into a THF (400 mL) solution of 4,4′-dihydroxyazoxybenzene (12.00 g, 52 mmol) were added triphenylphosphine (13.64 g, 52 mmol) and diethyl azodicarboxylate (9.06 g, 52 mmol) with stirring. A THF (50 mL) solution of (*R*)-(−)-2-octanol was then slowly added to the reaction mixture. The reaction mixture was stirred for 30 h at room temperature under a nitrogen atmosphere. The product was isolated by column chromatography to give compound **5**, which was further purified by recrystallization from methylene chloride and *n*-hexane (R_f = 0.43, diethyl ether/*n*-hexane, 1/1). For **6** and **7**, R_f values were 0.36 and 0.39, respectively. The average yield from the reactions was in the range of 25–30%.

Characterization data for **5**: mp 59–61 °C; ^{1}H NMR ($CDCl_3$) δ 8.20 (m, ArH, 4 H), 6.90 (m, ArH, 4 H), 4.41 (m, OCH, 1 H), 1.72 (m, CH_2, 1 H), 1.60 (m, CH_2, 1 H), 1.50–1.20 (m, CH_2, CH_3, 11 H), 0.87 (t, CH_3, 3 H); IR (KBr) 3350–3000 (br), 2930, 1596, 1500, 1466, 1252, 1156, 838 cm^{-1}; MS *m*/*z* calcd 342, found 342; $[\alpha]^{24} = -4.5°$ (*c* = 2.5 g/100 mL, THF).

Characterization data for **6**: mp 77–79 °C; ^{1}H NMR ($CDCl_3$) δ 8.20 (m, ArH, 4 H), 6.91 (m, ArH, 4 H), 4.39 (m, OCH, 1 H),

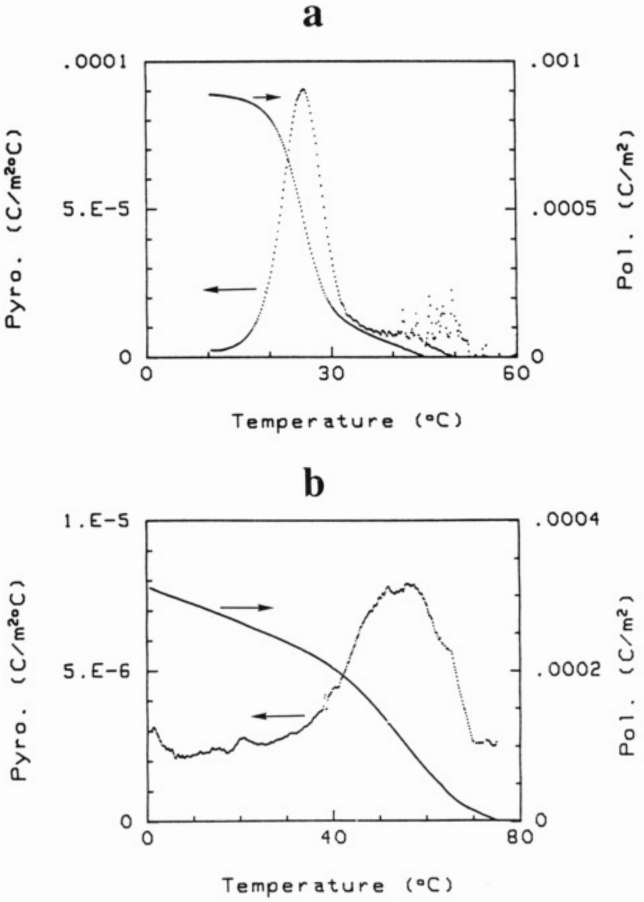


Figure 2. Pyroelectric coefficients and spontaneous polarization (a) for polymer **17** and (b) for **18**. In each case the curve containing the peak represents the pyroelectric coefficient.

1.76 (m, $\mathrm{C}H_2$, 1 H), 1.62 (m, $\mathrm{C}H_2$, 1 H), 1.32 (d, $\mathrm{CH_3}$, 3 H), 0.98 (dd, $\mathrm{CH_3}$, 3 H); IR (KBr) 3350–3000 (br), 2960, 1596, 1500, 1466, 1255, 1158, 836 cm^{-1}; MS m/z calcd 286, found 286; $[\alpha]^{24} = +9.6°$ (c = 1.5 g/100 mL, THF).

Characterization data for 7: mp 84–86 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.25 (m, ArH, 4 H), 6.92 (m, ArH, 4 H), 3.86 (m, $\mathrm{OC}H_2$, 1 H), 3.77 (m, $\mathrm{OC}H_2$, 1 H), 1.89 (m, CH, 1 H), 1.58 (m, $\mathrm{C}H_2$, 1 H), 1.28 (m, $\mathrm{C}H_2$, 1 H), 1.01 (d, $\mathrm{CH_3}$, 3 H), 0.94 (dd, $\mathrm{CH_3}$, 3 H); IR (KBr) 3350–3000, 2960, 1596, 1500, 1468, 1255, 1158, 836 cm^{-1}; MS m/z calcd 300, found 300; $[\alpha]^{24} = +8.9°$ (c = 0.33 g/100 mL, THF).

Preparation of $\mathrm{HO(CH_2CH_2O)_mC_6H_4N(O)NC_6H_4OR}$ Where R = 2-Octoxy and *m* = 3 (8); R = 2-Butoxy and *m* = 1 (9), *m* = 2 (10); and R = 2-Methyl-1-butoxy and *m* = 1 (11), *m* = 3 (12). Compounds 8–12 were prepared by similar procedures. As an example, compound 8 was prepared as follows: Into an ethanol (100 mL) solution of compound 5 (5.60 g, 16 mmol) and potassium hydroxide (1.12 g, 20 mmol) was added 2-[2-(2-chloroethoxy)ethoxy]ethanol (3.37 g, 20 mmol). The reaction mixture was refluxed for 20 h. The solvent was evaporated and the residue was dissolved in chloroform. The precipitate was washed with water and dried over magnesium sulfate. The product was isolated by column chromatography to yield a highly viscous liquid (yield 5.0 g, 66%). An average yield for 9–12 was 60–70%. For compounds 9–12, further purification was performed by recrystallization from methylene chloride/*n*-hexane.

Characterization data for 8: ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.21 (m, ArH, 4 H), 6.92 (m, ArH, 4 H), 4.40 (m, OCH, 1 H), 4.19 (t, $\mathrm{OCH_2}$, 2 H), 3.95–3.59 (m, $\mathrm{OCH_2}$, 10 H), 1.72 (m, $\mathrm{C}H_2$, 1 H), 1.60 (m, $\mathrm{C}H_2$, 1 H), 1.50–1.19 (m, $\mathrm{CH_2}$, $\mathrm{CH_3}$, 11 H), 0.87 (t, $\mathrm{CH_3}$, 3 H); IR (KBr) 3350–3000 (br), 2960, 1596, 1501, 1468, 1250, 1158, 836 cm^{-1}; MS m/z calcd 474, found 474; $[\alpha]^{24} = -3.3°$ (c = 0.4 g/100 mL, THF).

Characterization data for 9: mp 64–66 °C; ^{1}H NMR ($\mathrm{CDCl_3}$), δ 8.22 (m, ArH, 4 H), 6.91 (m, ArH, 4 H), 4.39 (m, OCH, 1 H), 4.19 (t, $\mathrm{OCH_2}$, 2 H), 3.89 (t, $\mathrm{OCH_2}$, 2 H), 1.76 (m, $\mathrm{C}H_2$, 1 H), 1.63 (m, $\mathrm{C}H_2$, 1 H), 1.32 (d, $\mathrm{CH_3}$, 3 H), 0.98 (dd, $\mathrm{CH_3}$, 3 H); IR (KBr) 3300–3000 (br) 2965, 1596, 1500, 1466, 1250, 1158, 838 cm^{-1}; MS m/z calcd 330, found 330; $[\alpha]^{24} = +8.5°$ (c = 1.5 g/100 mL, THF).

Characterization data for 10: mp 50–52° C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.20 (m, ArH, 4 H), 6.92 (m, ArH, 4 H), 4.38 (m, OCH, 1 H), 4.20 (t, $\mathrm{OCH_2}$, 2 H), 3.92–3.60 (m, $\mathrm{OCH_2}$, 6 H), 1.75 (m, $\mathrm{C}H_2$, 1 H), 1.62 (m, $\mathrm{C}H_2$, 1 H), 1.31 (d, $\mathrm{CH_3}$, 3 H), 0.97 (dd, $\mathrm{CH_3}$, 3 H); IR (KBr) 3350–3000 (br), 2970, 1596, 1499, 1462, 1251, 1158, 838 cm^{-1}; MS m/z calcd 374, found 374; $[\alpha]^{24} = +13.3°$ (c = 1.0 g/100 mL, THF).

Characterization data for 11: mp 74–76 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.23 (m, ArH, 4 H), 6.93 (m, ArH, 4 H), 4.20 (t, $\mathrm{OCH_2}$, 2 H), 3.92–3.75 (m, $\mathrm{OCH_2}$, 4 H), 1.89 (m, CH, 1 H), 1.56 (m, $\mathrm{C}H_2$, 1 H), 1.28 (m, $\mathrm{C}H_2$, 1 H), 1.01 (d, $\mathrm{CH_3}$, 3 H), 0.94 (dd, $\mathrm{CH_3}$, 3 H); IR (KBr) 3350–3000 (br), 2972, 1598, 1500, 1466, 1250, 1159, 836 cm^{-1}; MS m/z calcd 344, found 344; $[\alpha]^{24} = +6.9°$ (c = 1.5 g/100 mL, THF).

Characterization data for 12: mp 53–55 °C; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.21 (m, ArH, 4 H), 6.92 (m, ArH, 4 H), 4.21 (t, $\mathrm{OCH_2}$, 2 H), 3.94–3.57 (m, $\mathrm{OCH_2}$, 10 H), 1.88 (m, CH, 1 H), 1.55 (m, $\mathrm{C}H_2$, 1 H), 1.29 (m, $\mathrm{C}H_2$, 1 H), 1.02 (d, $\mathrm{CH_3}$, 3 H), 0.95 (dd, $\mathrm{CH_3}$, 3 H); IR (KBr) 3350–3000 (br), 2970, 1600, 1500, 1465, 1250, 1158, 838 cm^{-1}; MS m/z calcd, 432 found 432; $[\alpha]^{24} = +7.1°$ (c = 1.5 g/100 mL, THF).

Preparation of 15–19. Polymers 15–19 were prepared by following similar procedures. As a representative example, the preparation of 15 is described. A THF (15 mL) solution of poly(dichlorophosphazene) (0.35 g, 3.0 mmol) was added to a THF suspension (50 mL) of the sodium salt of 8 prepared with 8 (4.36 g, 9.2 mmol) and sodium hydride (0.22 g, 9.2 mmol). The reaction mixture was refluxed for 12 h. After evaporation of the solvent to obtain a viscous mixture, the product was isolated by precipitation into water. Repeated precipitation from THF into water was performed for further purification. The reddish, adhesive polymeric product was obtained (2.1 g, 70%). The average yield for 15–19 was 60–75%. Structural characterizations are summarized in Table I. Optical rotation was measured in THF. For 15, $[\alpha]^{24} = -4.1°$ (c = 2 g/100 mL); for 16, $[\alpha]^{24} = +6.4°$ (c = 1 g/100 mL); for 17, $[\alpha]^{24} = +9.3°$ (c = 1 g/100 mL); for 18, $[\alpha]^{24} = +4.3°$ (c = 1 g/100 mL); for 19, $[\alpha]^{24} = +5.1°$ (c = 1 g/100 mL).

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Registry No. 2, 5978-70-1; 3, 14898-79-4; 4, 616-16-0; 5, 133164-75-7; 6, 133164-71-3; 7, 133164-72-4; $\mathrm{HOC_6H_4}$-*p*-N=$\mathrm{NC_6H_4}$-*p*-OH, 15596-57-3.