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anions (such as fluoride) to anions bearing sizable hydrophobic alkyl chains (such as pentanoate). This small dependence implies that the binding is mostly determined by the cation. Nevertheless, some contribution of the anion is evidenced by the differences observed. In particular, under all the conditions employed, SCN^- salts "bind" stronger than chlorides. This result is similar to that obtained from ion-exchange experiments in cationic micellar systems[19] and cationic polysoap monolayers[20] and can be explained in terms of the lower polarizability of the chloride ion.

Comparison of the $K_{binding}$ values for potassium acetate and potassium pentanoate permits an estimation of the importance of hydrophobic interactions in the binding. The data given (Table V) indicate that hydrophobic interactions make only a minor contribution to the binding of pentanoate ion. This suggests that the anions remain mainly outside the polymer coil, such that their interaction with the polymer results in little or no shielding from contact with the solvent. In this regard, it is interesting to note that hydrophobic molecules adsorbed onto PEO remain exposed to a very polar environment.[21]

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Registry No. PEO, 25322-68-3; SCN^-, 333-20-0; LiCl, 7447-41-8; KCl, 7447-40-7; KF, 7789-23-3; NaCl, 7647-14-5; RbCl, 7791-11-9; CsCl, 7647-17-8; NaSCN, 540-72-7; acetate, 127-08-2; pentanoate, 19455-21-1.

Liquid Crystalline Phosphazenes Bearing Biphenyl Mesogenic Groups

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ABSTRACT: New thermotropic liquid crystalline phosphazene cyclic trimers and high polymers have been prepared by the incorporation of biphenyl derivative units connected to the skeleton by oligomeric ethyleneoxy spacer units. The cyclic trimer $[NP\{O(CH_2CH_2O)_2C_6H_4C_6H_4CN\}_2]_3$ showed monotropic nematic schlieren texture between 102 and 59 °C. The phosphazene cyclic trimers and high polymers $[NP\{O(CH_2CH_2O)_3C_6H_4C_6H_4R\}_2]_{3 \text{ and } n}$, where R = OMe, OEt, OPr-*n*, OPr-*i*, and OBu-*n*, have been synthesized. None of these cyclic trimers were liquid crystalline, but all the polymers showed enantiotropic liquid crystallinity.

Introduction

The widespread current interest in liquid crystalline polymers is connected with the possibility that polymeric systems can be prepared with unusual properties, combining the unique characteristics of a small-molecule liquid crystalline system with those of high molecular weight polymers.[1-3] Most of the known side-chain liquid crystalline macromolecular systems are derivatives of carbon-backbone organic polymers or polysiloxanes.[4,5]

Polyphosphazenes with the general formula $[NPR_2]_n$ have a highly flexible phosphorus–nitrogen inorganic backbone, and their properties can be varied by the incorporation of the suitable substituent R.[6-16] Recently,

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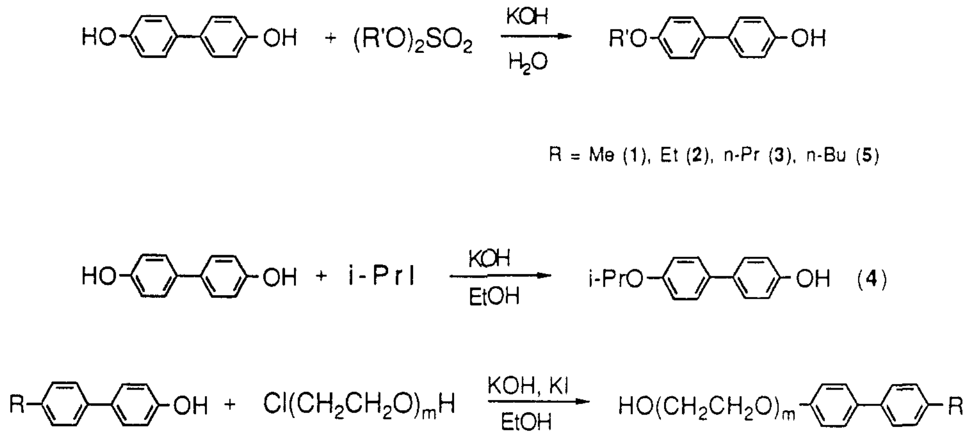
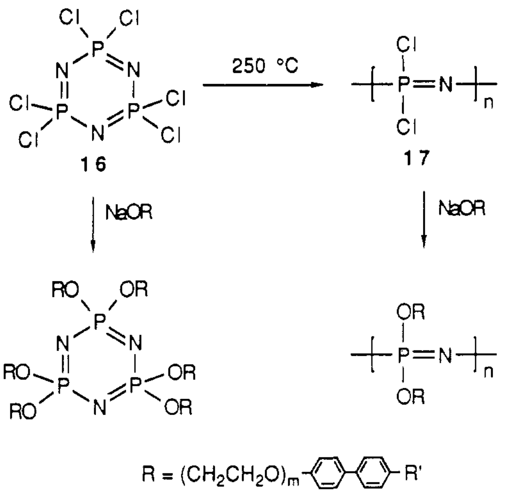
Scheme I



R = Me (1), Et (2), n-Pr (3), n-Bu (5)

R=CN and m=1 (6), 2 (7), 3 (8)
R=OMe and m=2 (9), 3 (10)
R=OEt and m=3 (11)
R=OPr-n and m=3 (12)
R=OPr-i and m=3 (13)
R=OBu-n and m=3 (14)
R=H and m=3 (15)

Scheme II



Cyclic Trimers	High Polymers
R'=CN and m=0 (18), 1 (19), 2 (20), 3 (21)	R'=CN and m=3 (31)
R'=OMe and m=0 (22), 2 (23), 3 (24)	R'=OMe and m=3 (32)
R'=OEt and m=0 (25), 3 (26)	R'=OEt and m=3 (33)
R'=OPr-n and m=3 (27)	R'=OPr-n and m=3 (34)
R'=OPr-i and m=3 (28)	R'=OPr-i and m=3 (35)
R'=OBu-n and m=3 (29)	R'=OBu-n and m=3 (36)
R'=H and m=3 (30)	R'=H and m=3 (37)

we reported the preparation of liquid crystalline poly(organophosphazenes) in which rigid aromatic azo groups were connected to the polyphosphazene chain through flexible oligomeric ethyleneoxy spacer groups to produce a nematic phase system. The cyclic trimeric compounds were used as model systems.[17,18] Singler et al. described similar results from a mixed-substituent polyphosphazene with aromatic azo side groups and trifluoroethoxy cosubstituent units,[19] and Percec et al. reported polyphosphazenes with mesogenic side groups.[20]

In this paper we report the syntheses of liquid crystalline phosphazenes with biphenyl side units, the effect of different substituent groups on the liquid crystallinity, and the observation of smectic liquid crystalline phases from the polyphosphazenes.

Results and Discussion

Synthesis and Characterization. For the preparation of compounds 1–5, a modification of a literature procedure was employed by the use of dialkyl sulfate[21] or isopropyl iodide under basic conditions. The monoalkylation of 4,4′-biphenol and the coupling of the oligomeric ethyleneoxy spacer groups to the biphenyl derivatives (6–15) are illustrated in Scheme I.

Scheme II is a summary of the syntheses of the phosphazene trimers and polymers prepared by reaction of the corresponding sodium alkoxide (or aryl oxide) with hexachlorocyclotriphosphazene (16) or poly(dichlorophosphazene) (17). The linear soluble polymer 17 was prepared by thermal, ring-opening, melt polymerization of the cyclic trimer by the use of standard procedures.[22–24] The preparation of polymer 31 required the use of more forcing reaction conditions (150 °C) within a medium-pressure reaction vessel to overcome the insolubility of the substituted polymer in the boiling solvent at atmospheric pressure.

The structural characterization of the side-group units 1–15 was carried out by ^{1}H NMR and IR spectroscopy, mass spectrometry, and melting behavior (see Table I). The phosphazene cyclic trimers 18–30 and high polymers 31–37 were characterized by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy and by elemental microanalysis (see Tables II and III). The replacement of chlorine atoms by nucleophiles was monitored by ^{31}P NMR spectroscopy and elemental microanalysis. In each case, the ^{31}P NMR spectrum showed a singlet resonance that was indicative of complete chlorine replacement. The chlorine content measured by elemental analysis was <0.04%. Polymer 31, in which biphenyl units are connected to electron-donating alkoxy spacer units and electron-withdrawing cyano groups, was insoluble in all common solvents, probably due to high degree of crystallinity. Therefore, IR

Table I
Characterization Data for Biphenyl Derivatives

					mass spectral data (m/z)	
compd[a]	yield, %	mp, °C	IR (KBr), cm^{-1}	^{1}H NMR,[b] δ	found	calcd
1	28	182–183	3500–3100 (br, OH) 3040 (w, ArCH)	7.61–6.82 (m, ArH, 8 H) 3.84 (s, OCH_3, 3 H)	200	200
2	25	169–170	3500–3100 (br, OH) 3030 (w, ArCH)	7.65–6.89 (m, ArH, 8 H) 4.06 (q, OCH_2, 2 H) 1.43 (t, CH_3, 3 H)	214	214
3	30	166–167	3500–3100 (br, OH) 3040 (w, ArCH)	7.66–6.89 (m, ArH, 8 H) 3.95 (t, OCH_2, 2 H) 1.55 (m, CH_2, 2 H) 1.04 (t, CH_3, 3 H)	228	228
4	32	155–156	3500–3100 (br, OH) 3050 (w, ArCH)	7.62–6.85 (m, ArH, 8 H) 4.72 (m, OCH, 1 H) 1.36 (d, CH_3, 6 H)	228	228
5	33	168–169	3500–3100 (br, OH) 3040 (w, ArCH)	7.59–6.82 (m, ArH, 8 H) 3.99 (t, OCH_2, 2 H) 1.80–1.20 (m, CH_2, 4 H) 0.98 (t, CH_3, 3 H)	242	242
6	73	124–125[c]	3500–3100 (br, OH) 2220 (s, CN)	7.66–6.93 (m, ArH, 8 H) 4.08 (t, CH_2OAr, 2 H) 3.69 (t, OCH_2, 2 H)	239	239
7	62	62–63[d]	3500–3100 (br, OH) 2220 (s, CN)	7.67–6.88 (m, ArH, 8 H) 4.15 (t, CH_2OAr, 2 H) 3.92–3.59 (m, OCH_2, 6 H)	283	283
8	60	59–60	3500–3100 (br, OH) 2220 (s, CN)	7.67–6.96 (m, ArH, 8 H) 4.15 (t, CH_2OAr, 2 H) 3.90–3.58 (m, OCH_2 10 H)	327	327
9	71	135–136	3500–3100 (br, OH)	7.69–6.91 (m, ArH, 8 H) 4.11–3.56 (m, OCH_2, OCH_3, 11 H)	288	288
10	69	102–103	3550–3100 (br, OH)	7.68–6.73 (m, ArH, 8 H) 4.11–3.46 (m, OCH_2, OCH_3, 15 H)	332	332
11	67	115–116	3450–3100 (br, OH)	7.68–6.89 (m, ArH, 8 H) 4.38–3.45 (m, OCH_2, 14 H) 1.43 (t, CH_3, 3 H)	346	346
12	75	106–107	3500–3100 (br, OH)	7.50–6.91 (m, ArH, 8 H) 4.18–3.43 (m, OCH_2, 14 H) 1.59 (m, CH_2, 2 H) 1.04 (t, CH_3, 3 H)	360	360
13	70	71–72	3450–3100 (br, OH)	7.50–6.91 (m, ArH, 8 H) 4.69 (m, OCH, 1 H) 4.18–3.73 (m, OCH_2, 12 H) 1.35 (d, CH_3, 6 H)	360	360
14	71	107–108	3450–3100 (br, OH)	7.51–6.98 (m, ArH, 8 H) 4.17–3.45 (m, OCH_2, 14 H) 1.79–0.98 (m, CH_2, CH_3, 7 H)	374	374
15	69	62–63	3450–3100 (br, OH)	7.52–6.94 (m, ArH, 9 H) 4.13–3.61 (m, OCH_2, 12 H)	302	302

[a] For code, see Scheme I. [b] In $CDCl_3$. [c] On heating, K 120 N 124–125 I; on cooling, I 124 N 112 K. [d] On cooling, I 59 N 32 K.

spectroscopy and elemental analysis were used for the structural characterization.

The molecular weights of polymers **35** and **37** were found by gel permeation chromatography to be in the range $M_n > 10^5$, $M_w > 10^6$, with M_w/M_n values in the range 15–40. Because polymer **31** was insoluble, no GPC or solution viscosity data could be obtained. For polymers **32**–**34** and **36**, viscosities were measured as solutions in warm dimethyl sulfoxide (DMSO) solution.

Properties. Polymers **31**–**37** are white materials. The solubility of the polymers depended on the groups attached to the terminus of the biphenyl moiety. Polymers **35** and **37**, with branched alkoxy (isopropoxy) or hydrogen at the para position, were soluble in common organic solvents such as THF, toluene, dioxane, or chloroform. Polymers **32**–**34** and **36**, with linear alkoxy terminal groups, were soluble in hot DMSO and hot toluene. Polymer **31**, in which the biphenyl group links an electron-donating alkoxy unit (the spacer unit) and the electron-withdrawing cyano group, was insoluble in all common organic media.

Polymer **37** showed a glass transition at 8 °C and a melting transition at 79 °C (see Table III). However, polymers **32**–**36**, with linear alkoxy para substituents, showed higher crystalline melting transitions in the range 106–166 °C (see Table IV). Polymer **35**, with a branched isopropoxy substituent, showed the lowest crystalline melting point, at 106 °C. Glass transitions of polymers **32**–**36** were not clearly detected from DSC studies. Polymer **31**, with a cyano substituent, did not undergo a detectable thermal transition between −100 and +350 °C.

Liquid Crystalline Behavior. The cyanobiphenyl derivatives, **6** and **7**, showed nematic liquid crystallinity (see Table I). The liquid crystalline behavior of the cyclic trimeric phosphazenes is summarized in Table II. Trimer **20**, with a bis(ethyleneoxy) spacer unit, showed monotropic nematic texture between 102 and 59 °C (see Figure 1). Trimer **18** also showed a monotropic nematic phase between 260 and 235 °C on the first cooling cycle, but repeated heating and cooling brought about decomposition, probably due to the high temperature required for the transition. Polymer **31** did not show detectable phase transitions between −100 and +350 °C by DSC studies or optical polarizing microscopy. Trimers **22**–**30**, with unsubstituted or alkoxy-substituted biphenyl groups and the appropriate spacers, did not show liquid crystallinity (enantiotropic or monotropic). However, the polymeric

Table II
Cyclotriphosphazene Characterization Data

compd[a]	yield, %	mp, °C	IR (KBr), cm^{-1}	^{1}H NMR,[b] δ	^{31}P NMR,[b] ppm	elem anal., % found	 calcd
18	81	265[c]	2230 (s, CN) 1250 (s, PN)	7.69–6.94 (m, ArH)	8.6 (s)	C, 72.38 H, 3.41 N, 9.42 Cl, 0.01	C, 72.05 H, 3.72 N, 9.70 Cl, 0
19	83	213–215	2220 (s, CN) 1230 (s, PN)	7.65–6.91 (m, ArH, 8 H) 4.22 (t, OCH_2, 2 H) 4.11 (t, OCH_2, 2 H)	18.0 (s)	C, 69.41 H, 4.29 N, 8.16 Cl, 0.014	C, 69.09 H, 4.64 N, 8.06 Cl, 0
20	79	105[d]	2220 (s, CN) 1240 (s, PN)	7.68–6.99 (m, ArH, 8 H) 4.25–3.61 (m, OCH_2, 8 H)	18.1 (s)	C, 66.64 H, 5.61 N, 7.04 Cl, 0.02	C, 66.99 H, 5.29 N, 6.89 Cl, 0
21	78	*e*	2220 (s, CN) 1250 (s, PN)	7.68–6.99 (m, ArH, 8 H) 4.23–3.64 (m, OCH_2. 12 H)	17.9 (s)	C, 66.02 H, 6.18 N, 5.62 Cl, 0.019	C, 65.60 H, 5.80 N, 5.75 Cl, 0
22	84	259–260	1250 (s, PN)	7.71–6.89 (m, ArH, 8 H) 3.84 (s, OCH_3, 3 H)	9.2 (s)	C, 70.76 H, 5.14 N, 3.01 Cl, 0.009	C, 70.42 H, 5.00 N, 3.16 Cl, 0
23	79	174–176	1250 (s, PN)	7.69–6.91 (m, ArH, 8 H) 4.27–3.65 (m, OCH_2, OCH_3, 11 H)	18.0 (s)	C, 65.57 H, 6.41 N, 2.18 Cl, 0.004	C, 65.90 H, 6.18 N, 2.26 Cl, 0
24	80	145–146	1240 (s, PN)	7.69–6.91 (m, ArH, 8 H) 4.23–3.51 (m, OCH_2, OCH_3, 15 H)	18.1 (s)	C, 64.31 H, 6.34 N, 1.84 Cl, 0.003	C, 64.49 H, 6.55 N, 1.98 Cl, 0
25	75	251–252	1240 (s, PN)	7.67–6.90 (m, ArH, 8 H) 4.10 (q, OCH_2, 2 H) 1.49 (t, CH_3, 3 H)	9.6 (s)	C, 71.21 H, 5.41 N, 3.04 Cl, 0.004	C, 71.33 H, 5.56 N, 2.97 Cl, 0
26	82	154–155	1250 (s, PN)	7.69–6.89 (m, ArH, 8 H) 4.38–3.45 (m, OCH_2, 14 H) 1.47 (t, CH_3, 3 H)	18.1 (s)	C, 65.11 H, 6.59 N, 1.81 Cl, 0.02	C, 65.29 H, 6.85 N, 1.90 Cl, 0
27	78	114–116	1230 (s, PN)	7.68–6.87 (m, ArH, 8 H) 4.26–3.62 (m, OCH_2, 14 H) 1.61 (m, CH_2, 2 H) 1.04 (t, CH_3, 3 H)	18.0 (s)	C, 65.89 H, 7.34 N, 1.71 Cl, 0.017	C, 66.04 H, 7.13 N, 1.83 Cl, 0
28	76	100–102	1230 (s, PN)	7.68–6.88 (m, ArH, 8 H) 4.68 (m, OCH, 1 H) 4.25–3.81 (m, OCH_2, 12 H) 1.35 (d, CH_3, 6 H)	18.1 (s)	C, 66.34 H, 7.45 N, 1.74 Cl, 0.02	C, 66.04 H, 7.13 N, 1.83 Cl, 0
29	81	151–152	1230 (s, PN)	7.61–6.98 (m, ArH, 8 H) 4.24–3.62 (m, OCH_2, 14 H) 1.81–0.98 (m, CH_2, CH_3, 7 H)	18.0 (s)	C, 66.38 H, 7.10 N, 1.64 Cl, 0.034	C, 66.73 H, 7.38 N, 1.77 Cl, 0
30	80	71–72	1240 (s, PN)	7.65–6.91 (m, ArH, 9 H) 4.24–3.61 (m, OCH_2, 12 H)	18.0 (s)	C, 67.42 H, 6.49 N, 1.98 Cl, 0.017	C, 66.97 H, 6.24 N, 2.17 Cl, 0

[a] For code, see Scheme II. [b] In $CDCl_3$. [c] On first cooling, I 260 N 235 K; repeated heating brought about decomposition. [d] On cooling, I 102 N 59 K. [e] Highly viscous product.

analogues **32–36** with alkoxy terminal units revealed an enantiotropic smectic phase. This is an example of the "polymeric effect" in which the liquid crystalline phase is stabilized in the polymeric state. Polymer **37**, with unsubstituted biphenyl groups, showed no detectable liquid crystalline behavior during optical polarizing microscopy or DSC experiments. The transition temperatures and enthalpies measured by DSC for polymers **32–36** are summarized in Table IV. Representative differential scanning calorimetry thermograms for polymers **32** and **33** are shown in Figure 2. For polymer **33**, a transition from the microcrystalline to the liquid crystalline phase occurs at 166 °C. The isotropization occurs over a broad temperature range (>10 °C), with the peak temperature at 183 °C. This relatively broad isotropization temperature range is probably due to the high viscosity and the polydispersity of the polymeric product.[25] The isotropization enthalpy (ΔH_i) on the heating cycle was 0.81 kcal/mru (mru = mole repeat unit). On the cooling cycle, a transition from isotropic to liquid crystalline phase occurs at 170 °C ($\Delta H_i = -1.03$ kcal/mru). Annealing of polymer **33** at 170 °C for several hours and slow cooling of the sample to 155 °C, brought about a well-developed smectic focal-conic fan texture as seen through an optical polarizing microscope.[26] The typical textures for polymers **32** and **33** are presented in Figure 1. The optical textures for polymers **34–36** are similar to those in Figure 1. The other polymers, **32** and **34–36**, showed a similar thermal transition behavior to that of polymer **33**. For polymers **32–36**, the isotropization enthalpies from the smectic to the isotropic phase are in the range 0.43–1.29 kcal/mru, which is expected for a smectic phase.[24,26] The supercooling of isotropization is in the range of 4–13 °C. Therefore, the liquid crystalline phases detected for

Table III
Polyphosphazene Characterization Data

compd[a]	yield, %	IR,[b] cm^{-1}	^{1}H NMR,[c] δ	^{31}P NMR,[c] ppm	mol wt (GPC) M_n	mol wt (GPC) M_w	M_w/M_n	elem anal., % found	elem anal., % calcd
31	92	1220 (s, PN)	*d*	*d*	*d*			C, 63.86 H, 5.91 N, 5.91 Cl, 0.29	C, 65.41 H, 5.78 N, 6.02 Cl, 0
32	72	1230 (s, PN)	7.69–6.90 (m, ArH, 8 H) 4.21–3.54 (m, OCH_2, OCH_3, 15 H)	−8.2 (s)	*e*			C, 64.90 H, 6.81 N, 1.89 Cl, 0.02	C, 64.49 H, 6.55 N, 1.98 Cl, 0
33	81	1240 (s, PN)	7.68–6.91 (m, ArH, 8 H) 4.22–3.52 (m, OCH_2, 14 H) 1.43 (br, CH_3, 3 H)	−7.9 (s)	*f*			C, 64.94 H, 6.99 N, 1.81 Cl, 0.01	C, 65.29 H, 6.85 N, 1.90 Cl, 0
34	79	1240 (s, PN)	7.68–6.84 (m, ArH, 8 H) 4.21–3.59 (m, OCH_2, 14 H) 1.60 (br, CH_2, 2 H) 1.04 (br, CH_3, 3 H)	−8.0 (s)	*g*			C, 66.52 H, 7.40 N, 1.72 Cl, 0.02	C, 66.04 H, 7.13 N, 1.83 Cl, 0
35	74	1240 (s, PN)	7.64–6.87 (m, ArH, 8 H) 4.70 (br, OCH, 1 H) 4.22–3.82 (m, OCH_2, 12 H) 1.36 (d, CH_3, 6 H)	−7.9 (s)[h]	2.2×10^5	3.3×10^5	15	C, 66.41 H, 7.34 N, 1.71 Cl, 0.008	C, 66.04 H, 7.13 N, 1.83 Cl, 0
36	78	1250 (s, PN)	7.64–6.98 (m, ArH, 8 H) 4.23–3.56 (m, OCH_2, 14 H) 1.79–0.98 (m, CH_2, CH_3, 7 H)	−8.4 (s)	*i*			C, 66.99 H, 7.24 N, 1.64 Cl, 0.03	C, 66.73 H, 7.38 N, 1.77 Cl, 0
37[j]	71	1240 (s, PN)	7.60–6.91 (m, ArH, 9 H) 4.22–3.62 (m, OCH_2, 12 H)	−8.0 (s)[h]	1.1×10^5	4.6×10^6	42	C, 66.48 H, 6.52 N, 2.11 Cl, 0.017	C, 66.97 H, 6.24 N, 2.17 Cl, 0

[a] For code, see Scheme I. [b] KBr pellet or thin film cast on KBr. [c] In DMSO-d_6. [d] Insoluble polymer. [e] Inherent viscosity (η_{inh}) was 0.21 dL/g (c = 0.5 g/dL) in DMSO at 50 °C. [f] η_{inh} = 0.16 dL/g (c = 0.5 g/dL) in DMSO at 50 °C. [g] η_{inh} = 0.23 dL/g (c = 0.5 g/dL) in DMSO at 50 °C. [h] In $CDCl_3$. [i] η_{inh} = 0.19 dL/g (c = 0.5 g/dL) in DMSO at 50 °C. [j] T_g = 8 °C, T_m = 79 °C.

Table IV
Thermal Transition Temperatures and Enthalpies for Polymers $[NP\{O(CH_2CH_2O)_3C_6H_4C_6H_4R\}_2]_n$

polymer	R	$T_{k\text{-}lc}$[a]	T_i[b]	ΔH_i[c]
32	OMe	155 (139)[d]	166 (157)[d]	0.43 (−0.71)[d]
33	OEt	166 (139)	183 (170)	0.81 (−1.03)
34	OPr-*n*	153 (143)	159 (150)	0.69 (−0.84)
35	OPr-*i*	106 (101)	125 (121)	1.29 (−1.45)
36	OBu-*n*	158 (151)	177 (173)	1.03 (−1.11)

[a] Transition temperatures from microcrystalline to liquid crystalline phase, in °C. [b] Isotropization temperatures, in °C. [c] Isotropization enthalpies, in kcal/mru (mru = mole repeat unit). [d] Measurements on cooling are recorded in parentheses.

polymers **32–36** are smectic. Furthermore, the spontaneous formation of a focal-conic fan texture by the coalescence of the batonnets directly from the isotropic phase strongly suggests that they are smectic A phases.[27]

The above results together with our previous reports[17,18] clearly show that the liquid crystalline behavior can be controlled by the incorporation of tailored substituents into a phosphazene structure.

Experimental Section

Materials. Tetrahydrofuran (THF), dioxane, and toluene were dried over sodium benzophenone ketyl and were distilled under nitrogen before use. 4-Cyano-4′-hydroxybiphenyl was obtained from Tokyo Kasei and was used as received or was purified by sublimation. Di-*n*-propyl sulfate and di-*n*-butyl sulfate from Tokyo Kasei were used as received. All other reagents (Aldrich) were also used as received. Silica gel (60–200 mesh, Fisher) was used for column chromatography. Hexachlorocyclotriphosphazene (Ethyl Corp.) was purified by recrystallization from *n*-hexane followed by sublimation at 40 °C (0.50 mmHg). Poly(dichlorophosphazene) was prepared by thermal polymerization of $(NPCl_2)_3$ at 250 °C. An average of 25–35% conversion to the linear polymer was obtained.

Instruments. The substitution reaction of $(NPCl_2)_n$ with the sodium salt of **8** was carried out by the use of a pressure reactor apparatus (Buchi Model BEP 280). ^{1}H NMR spectra were recorded with the use of a JEOL FX90Q NMR spectrometer operated at 90 MHz or a Bruker WP-200 spectrometer operated at 200 MHz. Chemical shifts are relative to tetramethylsilane at δ = 0. ^{31}P NMR (^{1}H decoupled) spectra were obtained with a JEOL FX90Q NMR spectrometer operated at 36.2 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. Infrared spectra were obtained with a Perkin-Elmer Model 1710 FT-IR spectrophotometer. Perkin-Elmer-7 thermal equipment was used to obtain the DSC thermograms. Solution viscosities were measured in DMSO at 50.1 °C by using a Cannon-Ubbelohde capillary viscometer. The optical textures were observed on a hot-stage (Thomas) polarizing microscope at a magnification of 150×. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $RC_6H_4C_6H_4OH$, Where R = OMe (1), OEt (2), OPr-*n* (3), OPr-*i* (4), and OBu-*n* (5). The procedures are illustrated in Scheme I. Compound **1** was prepared by a literature procedure.[21] For the preparation of **2** and **3**, the reactions were carried out at room temperature for 3 h. Compound **5** was prepared at 40 °C for 3 h with the same workup procedure as described in the literature. The preparation of compound **4** by the reaction between 4,4′-biphenol and isopropyl iodide was carried out as follows. To a warm ethanolic solution (500 mL) of 4,4′-biphenol (18.62 g, 0.1 mol) and potassium hydroxide (5.61 g, 0.1 mol), was added isopropyl iodide (17.0 g, 0.1 mol) in ethanol (50 mL) over a period of 2 h, and the mixture was refluxed for 6 h. After neutralization with 5% hydrochloric acid, the solvent was evaporated, the residue was redissolved in chloroform (800 mL), and the solution was washed with water. The organic layer was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The product was isolated by column chromatography and was purified by recrystallization from methanol. Yield: 7.30 g, 32%.

Preparation of $HO(CH_2CH_2O)_mC_6H_4C_6H_4CN$, Where *m* = 1 (6), 2 (7), and 3 (8). Compounds **6–8** were prepared by the same standard procedure. A typical procedure for compound **6**

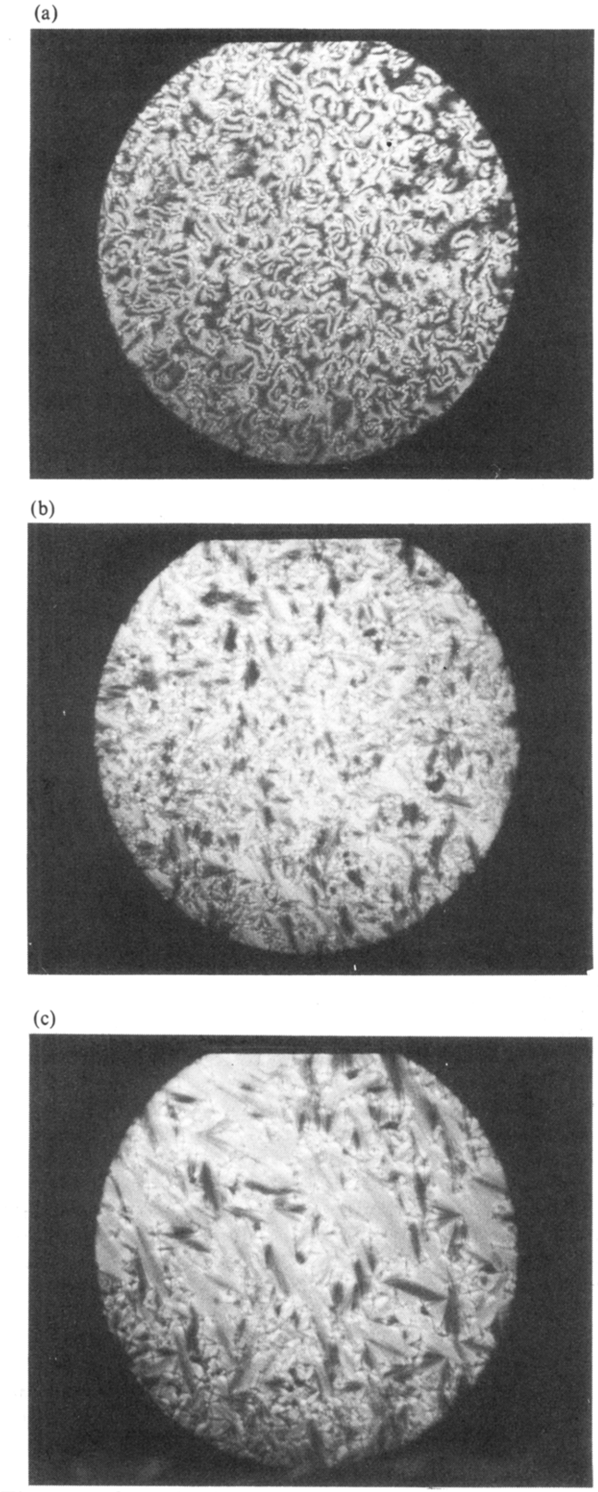


Figure 1. Optical polarizing micrographs of (a) cyclic trimer **20** at 70 °C during a cooling cycle, (b) polymer **32** at 146 °C during a cooling cycle, and (c) polymer **33** at 155 °C during a cooling cycle. (Original magnification = 150×; the micrographs have been reduced to 65% of their original size for printing purposes.)

is as follows. To an ethanolic solution (120 mL) of 4-cyano-4′-hydroxydiphenyl (4.86 g, 24 mmol) and sodium hydroxide (0.96 g, 24 mmol) were added 2-chloroethanol (2.42 g, 30 mmol) and potassium iodide (0.50 g, 3 mmol). After 12 h at reflux, the reaction mixture was neutralized by 5% hydrochloric acid. The solvent was evaporated and the residue was dissolved in chloroform (500 mL). The precipitate was removed by filtration, and the filtrate was washed with water and dried over magnesium sulfate. The product was isolated by column chromatography and was purified by recrystallization from methanol and toluene. Yield: 4.20 g, 73%.

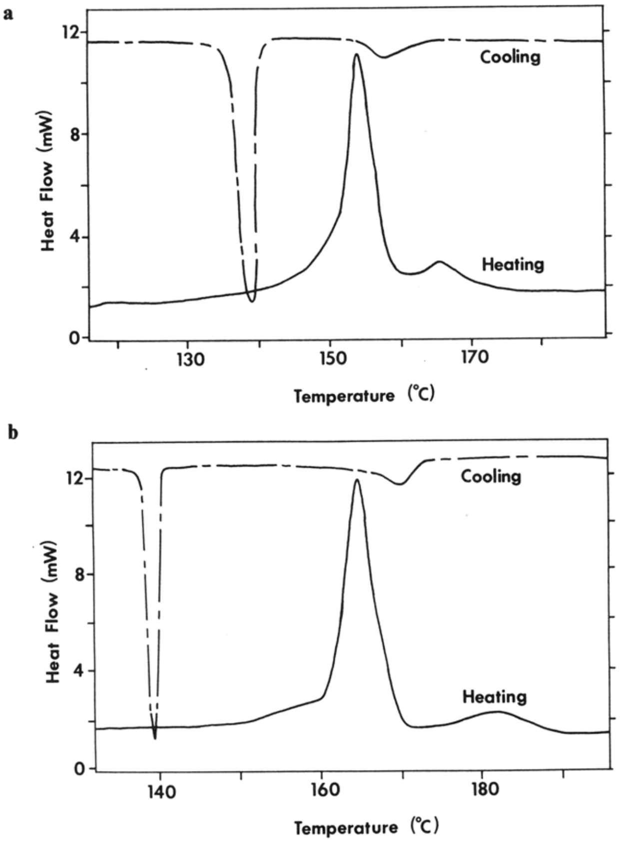


Figure 2. Differential scanning calorimetry thermograms of (a) polymer **32** and (b) polymer **33** (scanning rate = 10 °C).

Preparation of $HO(CH_2CH_2O)_mC_6H_4C_6H_4R$, Where R = OMe and *m* = 2 (9) and 3 (10); R = OEt and *m* = 3 (11); R = OPr-*n* and *m* = 3 (12); R = OPr-*i* and *m* = 3 (13); R = OBu-*n* and *m* = 3 (14); and R = H and *m* = 3 (15). Compounds **9**–**15** were prepared by the same procedure as described for the preparation of compound **6**.

Preparation of $N_3P_3[O(CH_2CH_2O)_mC_6H_4C_6H_4CN]_6$, Where *m* = 0 (18), 1 (19), 2 (20), and 3 (21). The cyclic trimers **18**–**21** were prepared by the same method. Typically, **21** was prepared as follows. A THF solution (5 mL) of hexachlorocyclotriphosphazene (0.10 g, 0.29 mmol) was added to a THF solution (15 mL) of the sodium salt of **8** prepared from **8** (1.08 g, 3.3 mmol) and sodium hydride (0.08 g, 3.3 mmol). After 10 h at reflux, the reaction mixture was filtered through Fuller's earth and silica gel. A highly viscous liquid product was obtained by column chromatography. Yield: 0.47 g, 78%.

Preparation of $N_3P_3[O(CH_2CH_2O)_mC_6H_4C_6H_4R$, Where R = OMe and *m* = 0 (22), 2 (23), 3 (24); R = OEt and *m* = 0 (25) and 3 (26); R = OPr-*n* and *m* = 3 (27); R = OPr-*i* and *m* = 3 (28); R = OBu-*n* and *m* = 3 (29); and R = H and *m* = 3 (30). Trimers **22**–**30** were prepared by the same method as used for **21** except for the use of dioxane/toluene (1:1) as the solvent.

Preparation of $[NP\{O(CH_2CH_2O)_3C_6H_4C_6H_4CN\}_2]_n$ (31). Polymer **31** was prepared in a closed reactor vessel. For the preparation of **31**, a THF solution (30 mL) of poly(dichlorophosphazene) (0.70 g, 6.0 mmol) was injected into a medium-pressure reactor under a dry N_2 atmosphere. Into the reactor were introduced a THF solution (50 mL) of **8** (7.85 g, 24.0 mmol) and sodium (0.55 g, 24.0 mmol) with vigorous stirring. The reaction was carried out at 150 °C (50 psi) for 24 h. The powdery product was purified by Soxhlet extraction with THF and methanol. Yield: 3.60 g, 86%.

Preparation of $[NP\{O(CH_2CH_2O)_3C_6H_4C_6H_4R\}_2]_n$, Where R = OMe (32), OEt (33), OPr-*n* (34), OPr-*i* (35), OBu-*n* (36), and H (37). Polyphosphazenes **32**–**37** were prepared in the same manner. A representative reaction procedure for **32** is as follows. Sodium metal (0.13 g, 5.7 mmol) was dispersed into small spheres in refluxing dioxane/toluene (20 mL, 1:1) by vigorous stirring. After the mixture cooled, a dioxane/toluene (1:1) solution (20 mL) of **10** (1.93 g, 5.8 mmol) was added, and the reaction mixture was refluxed until the sodium spheres had disappeared. To the sodium salt was added a toluene solution (10 mL) of $(NPCl_2)_n$ (0.21 g, 1.8 mmol). After 15 h at reflux, the reaction mixture was cooled and quenched with trimethylsilyl chloride (0.33 g, 3.0 mmol) and was concentrated by evaporation of the solvents. The polymeric product was purified by precipitation from hot toluene into water/acetone (1:1) and ethanol/acetone (1:1). The product was further purified by Soxhlet extraction with methanol. Yield: 0.87 g, 72%.

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Registry No. **1**, 16881-71-3; **2**, 127972-27-4; **3**, 127972-28-5; **4**, 127972-29-6; **5**, 108177-64-6; **6**, 104473-58-7; **7**, 127972-30-9; **8**, 127972-31-0; **9**, 103314-44-9; **10**, 103314-45-0; **11**, 127972-32-1; **12**, 127972-33-2; **13**, 127997-45-9; **14**, 127972-34-3; **15**, 127972-35-4; **16**, 940-71-6; **18**, 127997-47-1; **19**, 127972-39-8; **20**, 127972-41-2; **21**, 127972-43-4; **22**, 127972-45-6; **23**, 127972-47-8; **24**, 127972-49-0; **25**, 127972-51-4; **26**, 127972-53-6; **27**, 127997-49-3; **28**, 127972-55-8; **29**, 127972-57-0; **30**, 127972-59-2; 4,4′-biphenol, 92-88-6; isopropyl iodide, 75-30-9; 4-cyano-4′-hydroxydiphenyl, 19812-93-2; 2-chloroethanol, 940-71-6.

Zinc N-Substituted Porphyrins as Novel Initiators for the Living and Immortal Polymerizations of Episulfide

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ABSTRACT: Zinc N-substituted porphyrins such as zinc *N*-methyl and -phenyl-5,10,15,20-tetraphenylporphyrins carrying the thiolate group as the axial ligand ($R = CH_3$, $X = SCH_2CH_2CH_3$ (**1b**), $R = C_6H_5$, $X = SCH_2CH_2CH_3$ (**2b**)) brought about the living polymerization of 1,2-epithiopropane (propylene sulfide, PS), affording a polymer of very narrow molecular weight distribution. The number-average molecular weight of the polymer could be controlled by the mole ratio of the monomer reacted to the initiator. NMR studies demonstrated that the polymerization is initiated by the attack of the zinc–propylthio group of the initiator onto the monomer, generating a zinc thiolate as the growing species. The polymerization of 1,2-epithiopropane using **1b** as initiator proceeded with an immortal character in the presence of 1-propanethiol, affording a polymer of uniform molecular weight with the number of the polymer molecules exceeding that of the initiator molecules.

Introduction

Living polymerization to give polymers of uniform molecular weight is of fundamental as well as practical importance for the elaborate molecular design of polymer materials. We have so far shown that metalloporphyrins of aluminum are excellent initiators of wide applicability for ring-opening polymerizations of heterocyclic monomers[1] such as epoxides, lactones, and lactide and addition polymerizations of conjugate vinyl monomers such as methacrylic esters,[2] all of which proceed with living character at the aluminum–axial group bond, affording polymers of controlled molecular weight with narrow molecular weight distribution. On the basis of these

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