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Liquid Crystalline Phosphazenes. High Polymeric and Cyclic Trimeric Systems with Aromatic Azo Side Groups

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ABSTRACT: A new class of thermotropic liquid crystalline polymers and cyclic trimers has been prepared by the linkage of aromatic azo mesogenic units to the phosphorus atoms of cyclic and polymeric phosphazenes through flexible oligomeric ethyleneoxy spacer units. The single-substituent polymers, of formula $[NP\{O(CH_2CH_2O)_mC_6H_4N{=}NC_6H_4OCH_3\}_2]_n$ where $m = 2$ or 3, showed thermotropic liquid crystallinity. The cyclic trimer, $[NP\{O(CH_2CH_2O)_2C_6H_4N{=}NC_6H_4OCH_3\}_2]_3$, showed typical nematic schlieren texture between 192 and 166 °C on the cooling cycle (monotropic). The influence of a terminal para substituent on the mesogen, the length of the spacer unit, and the cyclic or long-chain polymeric character of the phosphazene on the liquid crystallinity were investigated.

Introduction

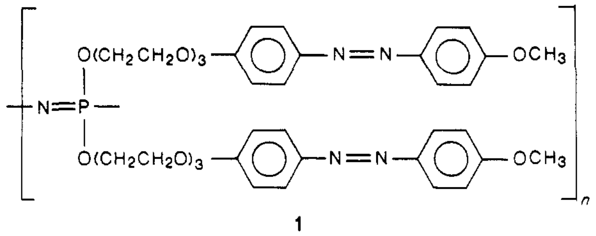
Liquid crystalline polymers are an important subject for fundamental and technological studies because of their unusual anisotropic optical, electrical, and mechanical properties.[1-6] Liquid crystalline polymers fall into two general categories: (1) species with rigid mesogenic groups incorporated into the backbone structure (main-chain liquid crystalline polymers); (2) polymers with mesogenic units in the side-group structure. This present work deals with polymers of the second type.

Side-chain liquid crystallinity generally requires a molecular structure in which a flexible polymer chain, or flexible connector group between the mesogen and backbone, provides sufficient conformational freedom to allow the rigid mesogenic units to form stacks or organized domains. Liquid crystallinity has been detected when mesogenic side groups are linked to highly flexible polysiloxane chains.[7,8] The phenomenon also becomes manifest when the carrier macromolecule is a less flexible chain such as a polymethacrylate or polyacrylate system, provided the spacer group is sufficiently long and flexible.

Polyphosphazenes comprise a broad class of macromolecules with the general formula $(NPR_2)_n$.[9-12] The physical properties of polyphosphazenes can be understood in terms of a highly flexible backbone[13,14] with specific physical or chemical properties imposed by the side group structure. Thus, increasing size and rigidity of the side groups generally reduces the overall molecular flexibility as side group–side group interactions become increasingly severe. This influence by different types of side groups has been the subject of a number of earlier papers from our laboratory.[13-21] Specifically, the role played by flexible alkyl or alkyl ether side groups,[15] organosilyl or siloxy units,[16] substituted aryloxy structures,[17] steroidoxy units,[18] phthalocyanine groups,[19] ionically bound tetracyanoquinodimethane units,[20] and various organometallic side groups[21] has been considered.

Definite liquid crystallinity was not detected in any of these earlier systems. However, evidence did exist, based mainly on the work of Allen,[22] Schneider, Singler, and their co-workers,[23] that specific polyphosphazenes, particularly those with fluoroalkoxy or simple aryloxy side groups, are capable of an unusual mesophase-like behavior,[24,25] a phenomenon that is still not fully understood. On the basis of this accumulated information, we concluded that the most likely molecular structures for the generation of liquid crystalline behavior in polyphosphazenes were those in which known mesogenic moieties, such as aromatic azo groups, were connected to the polyphosphazene chain via a flexible spacer group.

The first polymer of this type prepared by us that displayed liquid crystallinity is shown as structure 1. A brief communication on that work has appeared.[26] At the same time, Singler et al. reported similar results from a mixed-substituent polyphosphazene that bore both aromatic azo mesogenic side groups and trifluoroethoxy cosubstituent units.[27]



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In this paper we develop the concept of liquid crystallinity in single-substituent aromatic azo phosphazene polymers with particular emphasis on (1) the effect of a para methoxy or hydrogen substituent at the terminus of the aromatic azo unit, (2) liquid crystalline behavior as a function of the length of the ethyleneoxy spacer unit, and (3) the influence of different phosphazene skeletal structures on liquid crystallinity by comparisons of the behavior

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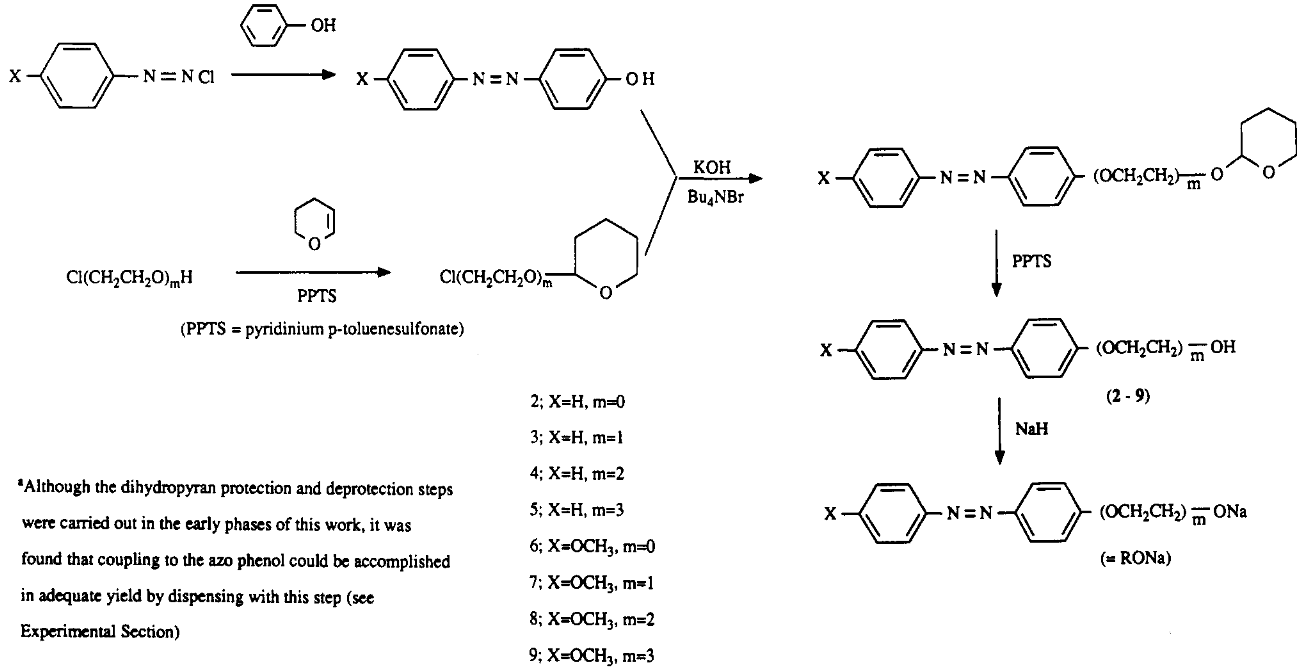
Scheme I
Synthesis of Mesogen/Spacer Unit[a]



2; X=H, m=0
3; X=H, m=1
4; X=H, m=2
5; X=H, m=3
6; X=OCH$_3$, m=0
7; X=OCH$_3$, m=1
8; X=OCH$_3$, m=2
9; X=OCH$_3$, m=3

[a] Although the dihydropyran protection and deprotection steps were carried out in the early phases of this work, it was found that coupling to the azo phenol could be accomplished in adequate yield by dispensing with this step (see Experimental Section)

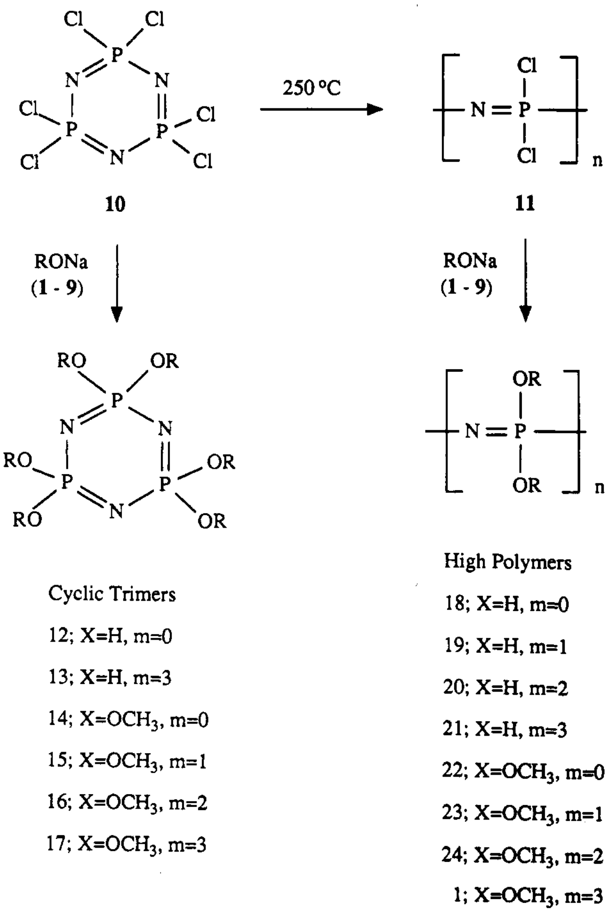
of cyclic trimeric and high polymeric phosphazenes that bear the same mesogenic and spacer units. Studies of cyclic trimeric systems are also valuable for the information they provide as small molecule reaction models for the high polymers.[28]

Results and Discussion

Synthetic Approach. The aromatic azo units were first linked to the ethyleneoxy spacer groups by the reactions illustrated in Scheme I. The alcohol (or phenol) function of each side group was then converted to its sodium salt by treatment with sodium hydride, and this nucleophile was allowed to react with the cyclic trimer, $(NPCl_2)_3$ (**10**), or with the high polymer, $(NPCl_2)_n$ (**11**). The latter species was prepared from $(NPCl_2)_3$ by a thermally induced, ring-opening, melt polymerization, as described in earlier papers.[9-11] Steric hindrance effects retarded the rate of reaction when no ethyleneoxy spacer groups were present (reagents **2** and **6**, Scheme I). Such reactions were, therefore, carried out under more forcing conditions at higher temperatures in a sealed reaction vessel (see Experimental Section).

The 14 compounds synthesized are identified in Scheme II as **12–17** (cyclic trimers) and **1**, **18–24** (high polymers). The molecular structural effects explored in these series are as follows. First, two different terminal groups (X), hydrogen and methoxy, were examined as para substituents attached to the terminal aromatic ring. (Analogues were also prepared with a cyano or nitro unit as the terminal group, but these compounds proved to be too insoluble to allow effective purification.) Second, the flexible spacer unit was varied over the range of zero through three ethyleneoxy units. Finally, the effect on liquid crystalline behavior of the replacement of a (rigid) cyclic trimeric ring by a linear high polymeric skeleton was examined. The details of the synthetic procedures are given in the Experimental Section.

Scheme II
Linkage of Mesogen/Spacer to Phosphazene Skeleton



Cyclic Trimers
12; X=H, m=0
13; X=H, m=3
14; X=OCH$_3$, m=0
15; X=OCH$_3$, m=1
16; X=OCH$_3$, m=2
17; X=OCH$_3$, m=3

High Polymers
18; X=H, m=0
19; X=H, m=1
20; X=H, m=2
21; X=H, m=3
22; X=OCH$_3$, m=0
23; X=OCH$_3$, m=1
24; X=OCH$_3$, m=2
1; X=OCH$_3$, m=3

Proof of Molecular Structure. Structure proof was obtained at various stages in the syntheses. For example, the structure and purity of the free mesogen, *p*-[(4-methoxyphenyl)azo]phenol, was confirmed by ^{1}H NMR and IR spectroscopy, mass spectrometry, and melting point. Second, each of the spacer group–mesogen combinations 2–9 was subjected to ^{1}H NMR, infrared, and mass spectrometric analysis (see Table I). Finally, cyclic trimers **12–17** and high polymers **1**, **19**, **20**, **21**, **23**, and **24** were examined by ^{1}H and ^{31}P NMR spectroscopy, infrared spectrometry, and elemental microanalysis. The ^{31}P NMR and elemental microanalysis data were critical for moni-

Table I
Characterization Data for Spacer Group-Mesogen Combinations

					mass spectral data	
compd[a]	yield, %	mp, °C	IR (KBr), cm^{-1}	^1H NMR, δ[b]	found	calcd
2	*c*	151–153	3500–3000 (br, OH)	7.93–6.95 (m, Ar H)	198	198
3	72	97–98	3500–3100 (br, OH)	7.92–6.94 (m, Ar H, 9 H), 4.09 (t, OCH_2, 2 H), 3.69 (t, OCH_2, 2 H)	242	242
4	69	62–64	3500–3150 (br, OH)	7.91–6.96 (m, Ar H, 9 H), 4.25–3.69 (m, OCH_2, 8 H)	286	286
5	63	55–56	3500–3150 (br, OH)	7.93–7.00 (m, Ar H, 9 H), 4.20–3.70 (m, OCH_2, 12 H)	330	330
6	68	140–141	3500–3050 (br, OH)	7.92–6.84 (m, Ar H, 8 H), 3.87 (s, OCH_3, 3 H)	228	228
7	74	154–155	3500–3100 (br, OH), 1420 (w, N=N)	7.91–6.96 (m, Ar H, 8 H), 4.26–3.68 (m, OCH_2, OCH_3, 7 H)	272	272
8	70	116–117	3500–3100 (br, OH), 1420 (w, N=N)	7.94–6.95 (m, Ar H, 8 H), 4.28–3.68 (m, OCH_2, OCH_3, 11 H)	316	316
9	73	112–113	3500–3100 (br, OH), 1420 (w, N=N)	7.92–6.96 (m, Ar H, 8 H), 4.26–3.67 (m, OCH_2, OCH_3, 15 H)	360	360

[a] For structures, see Scheme I. [b] In $CDCl_3$. [c] Commercial product.

Table II
Cyclophosphazene Characterization Data

						elem anal.	
compd[a]	yield, %	mp, °C	IR (KBr), cm^{-1}	^1H NMR, δ[b]	^{31}P NMR, ppm	found	calcd
12	69	179–180	1250 (s, PN)	7.92–6.98 (m, Ar H)[b]	18.5[b]	C, 65.38; H, 4.19; N, 16.12; Cl, 0.03	C, 65.62; H, 4.10; N, 15.95; Cl, 0
13	70	*c*	1240 (s, PN)	7.93–7.00 (m, Ar H, 9 H)[b], 4.20–3.70 (m, OCH_2, 12 H)	18.0[b]	C, 61.79; H, 5.87; N, 9.84; Cl, 0.084	C, 61.44, H, 6.02; N, 9.95; Cl, 0
14	72	240–241	3020 (w, Ar CH), 1420 (w, N=N), 1240 (s, PN)	7.92–6.84 (m, Ar H, 8 H),[d] 3.87 (s, OCH_3, 3 H)	18.6[d]	C, 62.71; H, 4,48; N, 13.87; Cl, 0.09	C, 62.52; H, 4.44; N, 14.02; Cl, 0
15	74	234–236	1250 (s, PN)	7.88–6.94 (m, Ar H, 8 H),[d] 4.11–3.65 (m, OCH_2, OCH_3, 7 H)	17.9[d]	C, 61.54; H, 5.39; N, 11.67; Cl, 0.07	C, 61.33; H, 5.15; N, 11.92; Cl, 0
16	67	197 (on heating), I 192 N 166 K (on cooling)	1250 (s, PN)	7.91–6.95 (m, Ar H, 8 H),[d] 4.11–3.68 (m, OCH_2, OCH_3, 11 H)	18.0[d]	C, 60.79; H, 6.01; N, 10.09; Cl, 0.03	C, 60.44; H, 5.67; N, 10.36; Cl, 0
17	67	111–112	1240 (s, PN)	7.89–6.92 (m, Ar H, 8 H),[b] 4.10–3.66 (m, OCH_2, OCH_3, 15 H)	18.5[b]	C, 59.98; H, 6.38; N, 8.94; Cl, 0.01	C, 59.76; H, 6.07; N, 9.17; Cl, 0

[a] For structures, see Scheme II. [b] In $CDCl_3$. [c] Liquid at 25 °C. [d] In DMSO-d_6.

toring the degree to which the chlorine atoms in **10** or **11** had been replaced by the organic side groups. In each case, a singlet ^{31}P NMR spectrum was indicative of complete halogen replacement. Elemental microanalysis revealed that less than 0.01% of chlorine remained after the substitution reactions.

Those polymers that lacked an ethyleneoxy spacer group (**18** and **22**) were insoluble in all common media due to their high degree of microcrystallinity. Hence, solution state NMR spectra could not be obtained, and infrared spectroscopy coupled with elemental microanalysis were the main methods used for structure proof. High polymers **23** and **24** were also insoluble in a wide range of organic solvents at room temperature. However, they were sufficiently soluble at elevated temperatures that ^1H and ^{31}P NMR spectra could be obtained. The characterization data are summarized in Tables II and III.

The molecular weights of polymers **1**, **19**, **20**, and **21** were estimated by gel permeation chromatography to be in the range $M_n = 1.0 \times 10^5$ to 5×10^5, $M_w > 4 \times 10^6$, with M_w/M_n values in the region 9–40. Because polymers **18** and **22** were insoluble, no GPC or solution viscosity molecular weight data could be obtained. Species **23** and **24** were examined by solution viscosity studies because they were soluble only in hot solvents.

General Properties. The colors of all the phosphazenes synthesized in this work corresponded to the colors of the aromatic azo/spacer units employed. Thus, those phosphazenes with phenylazophenoxy mesogenic units were yellow-red, while those with (*p*-methoxyphenyl)azophenoxy units were yellow. The color was not affected by the length of the spacer group or by the change in phosphazene skeleton from cyclic trimer to high polymer. Thus, no significant electronic interactions were detected between the mesogenic unit and the phosphazene skeleton, even in the absence of the spacer group.

Although all the cyclic trimers were soluble in warm organic media, the solubility of the polymers depended markedly on the length of the spacer group. For example, those polymers with no alkylene ether spacer unit were only sparingly soluble in solvents such as dimethyl sulfoxide (DMSO). Species **22** was slightly soluble in boiling DMSO, but precipitated when the solution was cooled. Species **18** was insoluble in all common solvents. Polymers **23** and **24** dissolved in hot DMSO above 130 and 100 °C, respectively, but precipitated slowly when cooled to 50 °C. Species **1** was soluble in tetrahydrofuran (THF), dioxane, or chloroform at room temperature.

Glass transition temperatures (T_g) and melting points are listed in Table III. In general, the presence of the *p*-methoxy substituent on the mesogen enhances the polymer crystallinity.

Liquid Crystallinity. Only one of the cyclic trimers showed evidence of liquid crystallinity. This was trimer **16**, with a bis(ethyleneoxy) spacer group and a para methoxy substituent. For this compound, on the cooling cycle from the melt, a transition from isotropic liquid to nematic liquid crystalline phase occurred at 192 °C and from nematic to crystalline at 166 °C. The optical texture of the liquid crystalline phase is shown in Figure 2a. It corresponds to a typical nematic schlieren texture. Presumably trimers **14** and **15** were not liquid crystalline

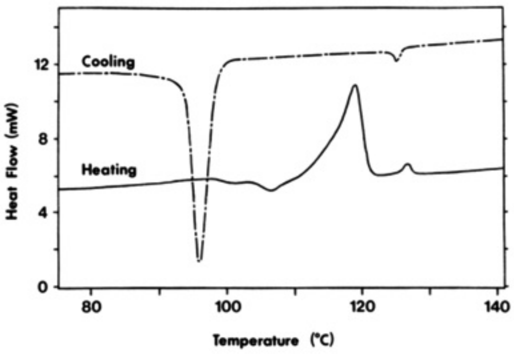


Figure 1. Differential scanning calorimetry thermograms of polymer 1 (scanning rate = 10 °C/min).

because the spacer units are too short to allow co-orientation of the mesogens. Trimer **17**, with a tris(ethyleneoxy) spacer unit, appeared to form a particularly stable crystal system that precluded formation of a liquid crystalline phase. This provides an interesting comparison with the analogous high polymer (**1**) where the flexibility of the macromolecular chain tips the balance in favor of liquid crystalline character. These differences are also evident from the fact that trimer **16** shows monotropic liquid crystalline behavior (on the cooling cycle only) but polymer **24** shows enantiotropic liquid crystallinity. Those cyclic trimers with a hydrogen atom as a terminal unit showed no evidence of liquid crystallinity, and this illustrates the important role played by the terminal group.

For the high polymers also, the nature of the terminal group exerted a strong influence on the presence or absence of a liquid crystalline phase. Polymer **21**, with a tris(ethyleneoxy) spacer and a terminal hydrogen atom, was not liquid crystalline, but its analogue with a terminal methoxy group (**1**) generated a liquid crystalline phase during both the heating and cooling cycles (enantiotropic). The behavior of **1** is illustrated by the differential scanning calorimetry thermogram shown in Figure 1. During the heating cycle, a transition from microcrystalline to liquid crystalline occurs at 118 °C, and this phase melts to form an isotropic liquid at 127 °C. On the cooling cycle, the transition from isotropic liquid to liquid crystalline occurs at 126 °C. However, significant supercooling (24 °C) was evident for the liquid crystalline to microcrystalline transition, which occurred at 94 °C. A polarized optical micrograph of the liquid crystalline phase of **1** is shown in Figure 2b. This appears to be a nematic phase because (a) the melting transition is reversible within a 1 °C temperature range, (b) the isotropization enthalpy is small (0.10 kcal/mru; mru, mole repeat unit), and (c) the overall texture observed in the polarizing microscope is a typical nematic pattern.

Polymer **24**, with a bis(ethyleneoxy) spacer and a terminal methoxy unit shows a more complex behavior (Figure 3). When heated, the polymer undergoes a microcrystalline to liquid crystalline transition at 145 °C (detected at 125 °C on the cooling cycle), an intermediate transition at 165 °C (155 °C on cooling), and a liquid crystalline to melt transition at 168 °C (165 °C on cooling). The exotherms on the cooling cycle (second to fifth cycle) corresponded to ΔH values of −0.15 (165 °C), −0.66 (155 °C), and −4.28 kcal/mru (125 °C). The phase detected between 165 and 168 °C (155 and 165 °C on cooling) appeared to be a nematic system, on the basis of the same arguments as used for polymer **1**. The mesophase found for **24** in the region 145–165 °C (125–155 °C on cooling) is probably a smectic form, on the basis of the temperature sequence of the liquid crystalline transitions, but a definitive assignment is not available at this time. An added source of complexity in this system was the appearance of a new transition at 158 °C beginning in the third heating cycle. This may correspond to the formation of oligomeric depolymerization species formed at the higher temperatures during the preceding cycles.

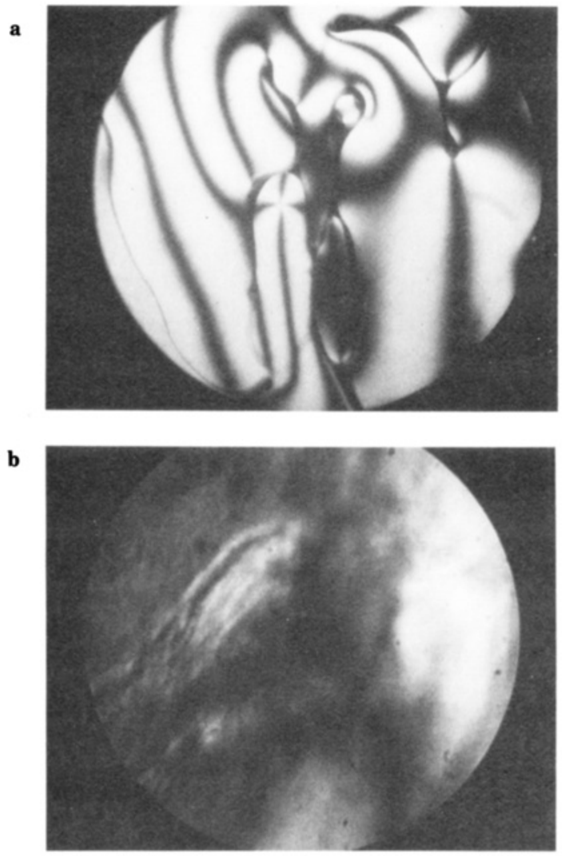


Figure 2. Optical polarization micrographs of (a) cyclic trimer **16** at 182 °C on a cooling cycle and (b) polymer **1** at 121 °C also on a cooling cycle (magnification = 150×).

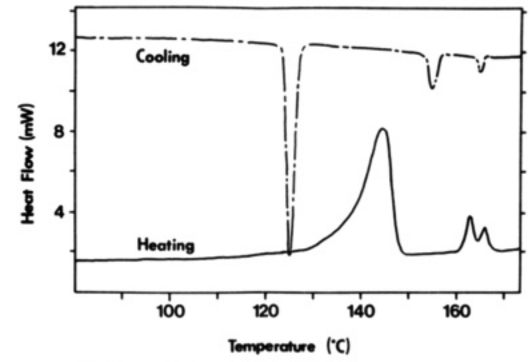


Figure 3. Differential scanning calorimetry thermograms of polymer **24** (scanning rate = 10 °C/min).

Polymers **22** and **23**, with the same mesogenic unit but shorter spacer linkages, showed no liquid crystalline character. Polymer **22** showed no phase transitions at all (by either DSC or polarized microscope examination) between −100 and 350 °C. Polymer **23** is a microcrystalline material with a crystallite melting temperature of 217 °C. The lack of liquid crystalline behavior for these polymers is attributed to the inability of the spacer linkages to decouple the chain motions from those of the side groups.

None of the polymers in which the terminal unit is hydrogen showed any liquid crystalline character. Polymer **18** was microcrystalline, but with a melting temperature above 300 °C. Polymers **19**–**21** were amorphous.

Table III
Polyphosphazene Characterization Data

compd[a]	yield, %	T_g, °C	T_m, °C	IR,[b] cm^{-1}	^{1}H NMR, δ[b]	^{31}P NMR, ppm	mol wt (GPC)			elem anal.	
							M_n	M_w	M_w/M_n	found	calcd
18	86		>300	3020 (w, Ar CH), 1240 (s, PN)	*h*	*h*		*h*		C, 64.39; H, 4.62; N, 16.60; Cl, 0.06	C, 65.62; H, 4.10; N, 15.95; Cl, 0
19	75	53		3010 (w, ArCH), 1420 (w, N=N), 1250 (s, PN)	7.94–6.98 (m, Ar H, 9 H),[c] 4.08 (t, OCH_2, 2 H), 3.7 (t, OCH_2, 2 H)	−7.9[c]	5.1×10^5	4.7×10^6	9	C, 62.43; H, 4.86; N, 13.65; Cl, 0.05	C, 63.75; H, 4.97; N, 13.28; Cl, 0
20	73	28		3020 (w, Ar CH), 1410 (w, N=N), 1250 (s, PN)	7.93–6.93 (m, Ar H, 9 H),[c] 4.21–3.94 (m, OCH_2, 8 H)	−8.1[c]	2.6×10^5	2.6×10^6	10	C, 61.73; H, 5.57; N, 11.49; Cl, <0.01	C, 62.43; H, 5.57; N, 11.37; Cl, 0
21	71	6		1240 (s, PN)	7.90–7.00 (m, Ar H, 9 H),[c] 4.29–3.70 (m, OCH_2, 12 H)	−8.4[c]	1.0×10^5	4.0×10^6	40	C, 60.55; H, 5.97; N, 9.75; Cl, 0.017	C, 61.44; H, 6.02; N, 9.95; Cl, 0
22	82		*i*	3020 (w, ArCH); 2960 (w, CH); 1420 (w, N=N); 1250 (s, PN)	*h*	*h*	*h*			C, 62.24; H, 4.60; N, 13.93; P, 6.23; Cl, 0.06	C, 62.52; H, 4.44; N, 14.02; P, 6.20; Cl, 0
23	65		217	3020 (w, Ar CH); 2940 (w, CH); 1250 (s, PN)	7.92–6.89 (m, Ar H, 8 H),[d] 4.14–3.61 (m, OCH_2, OCH_3, 7 H)	−7.5[d]	*e*			C, 61.12; H, 5.28; N, 11.44; Cl, 0.21	C, 61.33; H, 5.15; N, 11.92; Cl, 0
24	72		145–168[j]	3010 (w, Ar CH); 1410 (w, N=N); 1240 (s, PN)	7.93–6.92 (m, Ar H, 8 H),[f] 4.18–3.68 (m, OCH_2, OCH_3, 11 H)	−7.7[f]	*g*			C, 59.50; H, 5.83; N, 10.19; Cl, 0.07	C, 60.44; H, 5.67; N, 10.36; Cl, 0
1	79		118–127[j]	1410 (w, N=N), 1250 (s, PN)	7.92–6.96 (m, Ar H, 8 H),[c] 4.26–3.67 (m, OCH_2, OCH_3, 15 H)	−8.3[c]	3.3×10^5	6.8×10^6	21	C, 59.22; H, 6.01; N, 9.00; Cl, 0.004	C, 59.76; H, 6.07; N, 9.17; Cl, 0

[a] For structures, see Scheme II. [b] KBr Pellet or thin film cast on KBr. [c] In $CDCl_3$. [d] In DMSO-d_6 at 150 °C. [e] The polymer was soluble only in warm DMSO, in which the inherent viscosity at 60 °C (0.5 g/dL) was 0.17 dL/g. [f] In DMSO-d_6 at 115 °C. [g] η(inh) in DMSO (0.5 g/dL) at 70 °C was 0.15 dL/g. [h] Polymers 18 and 22 were not sufficiently soluble to allow these data to be obtained. [i] Melting transition was not detected below 350 °C. [j] See text for description of liquid crystalline behavior.

Thus, the overall pattern in these systems is one in which the length and flexibility of the spacer unit, the flexibility of the inorganic skeleton, and the nature of the terminal group on the mesogen are critical for the appearance of liquid crystalline behavior. A favorable combination of these factors appears in polymers **1** and **24**. In subsequent publications we will examine the effect of changes brought about by the replacement of the arylazophenoxy groups by other rigid or planar structures.

Experimental Section

Equipment. The halogen substitution reactions between $(NPCl_2)_n$ and **3–5** and **7–9** were carried out in the boiling solvent at atmospheric pressure in standard glassware. However, the reactions with **2** and **6** required the use of a Büchi pressure reactor apparatus. ^{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. ^{1}H NMR spectra were recorded with the use of a Bruker SP-200 spectrometer operated at 200 MHz or a JEOL FX90Q spectrometer operated at 90 MHz. All spectra were referenced to internal or external (high-temperature operation) tetramethylsilane at 0 ppm. Infrared spectra were obtained with the use of a Perkin-Elmer 283B grating spectrophotometer. Gel permeation chromatography was carried out with a Hewlett-Packard HP-1090 liquid chromatograph fitted with an HP-1037A refractive index detector and a Polymer Laboratories gel 10μ column. Tetrahydrofuran (THF) with 0.1% tetra-*n*-butylammonium bromide was used as the eluent. The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of $[NP(OCH_2CF_3)_2]_n$ provided by Drs. R. Singler and G. Hagnauer of the Army Materials Laboratory, Watertown, MA. Solution viscosities were measured in DMSO solvent at 60 ± 1 °C with a Cannon-Ubbelohde capilliary viscometer. Perkin-Elmer-7 thermal analysis equipment was used for the DSC thermograms, with a heating rate of 10 °C/min under a nitrogen atmosphere. The optical textures were observed on a hot stage (Thomas) polarizing microscope at a magnification of 150×. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Materials. Hexachlorocyclotriphosphazene (**10**) (Ethyl Corp.) was purified by recrystallization from n-hexane followed by sublimation at 40 °C (0.05 Torr). Poly(dichlorophosphazene) (**11**) was prepared by the ring-opening polymerization of **10** at 250 °C.[10] Tetrahydrofuran (THF) and toluene were dried over sodium benzophenone ketyl and were distilled in an atmosphere of dry nitrogen before use. All the other reagents (Aldrich) were used as received. Reactions that involved the use of chlorophosphazenes were carried out in an atmosphere of dry nitrogen.

Synthesis of Side Group Units. The diazo coupling reaction between p-anisidine and phenol was used for the preparation of 4-[(4-methoxyphenyl)azo]phenol.[30] The compound was recrystallized from methylene chloride to give the product, mp 140–141 °C, in 68% yield: ^{1}H NMR ($CDCl_3$) δ 7.92–6.84 (m, Ar H, 8 H), 3.87 (s, OCH_3, 3 H).

Coupling of the spacer groups to the two arylazophenols was accomplished in two ways. At the early stage of this work, the reaction pathways in Scheme I were employed.[26,29] In later experiments a direct coupling was carried out in the manner illustrated by the following typical example. A solution of 2-[2-(2-chloroethoxy)ethoxy]ethanol (14.95 g, 0.12 mol) in ethanol (50 mL) was added to an ethanol solution (300 mL) in which potassium hydroxide (5.61 g, 0.10 mol) and 4-[(4-methoxyphenyl)azo]phenol (22.80 g, 0.10 mol) were dissolved along with a catalytic amount of potassium iodide. The reaction mixture was refluxed for 16 h, cooled, and neutralized with dilute hydrochloric acid. After evaporation of the solvent, the crude mixture was redissolved in chloroform, and the solution was washed with water and dried over anhydrous magnesium sulfate. After evaporation of the chloroform, the crude product **8** was column chromatographed on silica gel to isolate the product, which was further purified by recrystallization from methanol (yield 22.17 g, 70%).

Preparation of $N_3P_3(OC_6H_4N{=}NC_6H_5)_6$ (12). A solution of hexachlorocyclotriphosphazene (1.39 g, 4.0 mmol) in THF (10 mL) was added to a THF solution (20 mL) of (4-phenylazo)phenol (7.14 g, 36 mmol), sodium hydride (0.86 g, 36 mmol), and tetra-*n*-butylammonium bromide (1.16 g, 36 mmol). After 20 h at reflux, the reaction mixture was filtered through Fuller's earth and silica gel. The product was isolated by column chromatography and was purified further by recrystallization from methylene chloride (yield 3.64 g, 69%).

Preparation of $N_3P_3[O(CH_2CH_2O)_3C_6H_4N{=}NC_6H_5]_6$ (13). To a THF solution (20 mL) of **2** (2.10 g, 6.4 mmol), sodium hydride (0.15 g, 6.4 mmol), and tetra-*n*-butylammonium bromide (0.20 g, 0.64 mmol) was added a THF solution (10 mL) of hexachlorocyclotriphosphazene (0.27 g, 0.82 mmol). After 16 h at reflux, the reaction mixture was filtered through Fuller's earth and silica gel. Evaporation of the solvent was followed by column chromatography with diethyl ether and tetrahydrofuran. The product was a deep red, viscous liquid (yield 1.21 g, 70%).

Preparation of $N_3P_3(OC_6H_4N{=}NC_6H_4OCH_3)_6$ (14). Compound **14** was prepared from the reaction of hexachlorocyclotriphosphazene (0.25 g, 0.72 mmol) with 4-[(4-methoxyphenyl)azo]phenol by the same procedure used for **13**. After 24 h at reflux, the reaction mixture was cooled and filtered. The product was washed with acetone and water, and the crude product was recrystallized from diglyme (yield 0.72 g, 72%).

Preparation of $N_3P_3[OCH_2CH_2OC_6H_4N{=}NC_6H_4OCH_3]_6$ (15). A solution (5 mL) of hexachlorocyclotriphosphazene (0.25 g, 0.72 mmol) in toluene/dioxane (3/1 v/v) was added to a suspension of the sodium salt of **7**, which was prepared from compound **7** (2.34 g, 8.6 mmol) and sodium hydride (0.20 g, 8.3 mmol) in 20 mL of toluene/dioxane (3/1 v/v). After 20 h at reflux, the cooled reaction mixture was filtered and washed with acetone and water. The product was purified by recrystallization from methylene chloride (yield 0.94 g, 74%).

Preparation of $N_3P_3[O(CH_2CH_2O)_2C_6H_4N{=}NC_6H_4OCH_3]_6$ (16). Into a suspension of **8** (2.72 g, 8.6 mmol) and sodium hydride (0.20 g, 8.3 mmol) in THF (20 mL) was added a THF solution (5 mL) of hexachlorocyclotriphosphazene (0.25 g, 0.72 mmol). The reaction mixture was cooled to ambient temperature after 20 h at reflux, filtered, and washed with acetone and water. The product was recrystallized from methylene chloride (yield 0.98 g, 67%).

Preparation of $N_3P_3[O(CH_2CH_2O)_3C_6H_4N{=}NC_6H_4OCH_3]_6$ (17). A THF solution (5 mL) of hexachlorocyclotriphosphazene (0.25 g, 0.72 mmol) was added to a suspension of **9** (2.34 g, 6.5 mmol) and sodium hydride (0.15 g, 6.4 mmol) in THF (20 mL). After 12 h at reflux, the reaction mixture was filtered through Fuller's earth and silica gel. The product was isolated by column chromatography and was further purified by recrystallization from methylene chloride and *n*-hexane (yield 1.11 g, 67%).

Preparation of $[NP(OC_6H_4N{=}NC_6H_5)_2]_n$ (18). A dioxane solution (80 mL) of sodium 4-(phenylazo)phenoxide prepared from 4-(phenylazo)phenol (8.52 g, 43 mmol), sodium (0.99 g, 43 mmol), and tetra-*n*-butylammonium bromide (1.39 g, 4.3 mmol) was transferred to the 250-mL pressure reaction vessel (Büchi Model BEP 280) under a dry nitrogen atmosphere. A dioxane solution (15 mL) of poly(dichlorophosphazene) (1.00 g, 8.6 mmol) was added and the mixture was maintained at 150 °C (50 psi) for 24 h with stirring. The reddish yellow powdery product was purified by Soxhlet extraction with THF and methanol (yield 3.25 g, 86%).

Preparation of $[NP\{O(CH_2CH_2O)_mC_6H_4N{=}NC_6H_5\}_2]_n$; $m = 1$ (19), $m = 2$ (20). Polymers **19** and **20** were prepared following the same procedure. The procedure for polymer **19** is as follows. A dioxane solution (10 mL) of poly(dichlorophosphazene) (0.28 g, 2.5 mmol) was added slowly to a dioxane solution (30 mL) of the sodium salt of **3**, prepared from the reaction of **3** (2.18 g, 9.0 mmol) and sodium (0.20 g, 9.0 mmol). After 24 h at reflux, the solvent was removed to obtain a viscous solution, which was then precipitated into water. The product was purified by repeated precipitation from THF into water, methanol, and acetone/*n*-hexane (1:1 v/v) (yield 0.82 g, 75%; yield for **20** 0.88 g, 73%).

Preparation of $[NP\{O(CH_2CH_2O)_3C_6H_4N{=}NC_6H_5\}_2]_n$ (21). Into a THF solution (50 mL) of poly(dichlorophosphazene) (0.58 g, 5.0 mmol) was added a THF solution (50 mL) of the sodium salt of **5**, prepared from **5** (5.29 g, 16 mmol) and sodium hydride (0.12 g, 5.0 mmol). After 24 h at reflux, the reaction mixture was concentrated by evaporation of the solvent to give a viscous solution. The product was isolated by two precipitations each from THF into water, methanol, and acetone/*n*-hexane (1:1 v/v). The product was a reddish yellow elastomeric material which was soluble in THF, dioxane, toluene, and DMSO (yield 2.51 g, 71%).

Preparation of $[NP(OC_6H_4N{=}NC_6H_4OCH_3)_2]_n$ (22). A dioxane solution (80 mL) of the sodium salt prepared from 4-[(4-methoxyphenyl)azo]phenol (9.85 g, 43 mmol), sodium hydride (1.03 g, 43 mmol), and tetra-*n*-butylammonium bromide (1.39 g, 4.3 mmol) was transferred to the 250-mL vessel of a Büchi autoclave (Model BEP 280) under a dry nitrogen atmosphere. A dioxane solution (15 mL) of poly(dichlorophosphazene) (1.00 g, 8.6 mmol) was added, and the mixture was heated to 150 °C (50 psi) for 24 h with vigorous stirring. The product was a reddish yellow powdery material which was soluble in boiling DMSO. The product was purified by Soxhlet extraction with THF and methanol each for 72 h (yield 3.55 g, 82%).

Preparation of $[NP(OCH_2CH_2OC_6H_4N{=}NC_6H_4OCH_3)_2]_n$ (23). A THF solution (5 mL) of poly(dichlorophosphazene) (0.20 g, 1.7 mmol) was added to a suspension of **7** (3.16 g, 0.01 mol) and sodium hydride (0.24 g, 0.01 mol) in the presence of tetra-*n*-butylammonium bromide (0.20 g, 0.62 mmol) in THF (20 mL). After 16 h at 50 °C, the reaction mixture was precipitated into water to yield a yellow powdery material. The crude product was purified by repeated precipitation from hot DMSO into water, methanol, and acetone/*n*-hexane (1:1 v/v) and by Soxhlet extraction by THF and methanol each for 48 h (yield 0.75 g, 65%).

Preparation of $[NP\{O(CH_2CH_2O)_mC_6H_4N{=}NC_6H_4OCH_3\}_2]_n$; $m = 2$ (24), $m = 3$ (1). Polymer **24** was prepared by the reaction of poly(dichlorophosphazene) with the sodium salt of **4** by means of an identical procedure to that used for **23** (yield 76%). Polymer **1** was prepared in a different manner. A THF solution (10 mL) of poly(dichlorophosphazene) (0.34 g, 2.9 mmol) was added to a THF solution (40 mL) of **9** (5.40 g, 15 mmol) and sodium hydride (0.36 g, 15 mmol). After 6 h at reflux, the reaction mixture was concentrated by the evaporation of THF under reduced pressure. The product was isolated and purified by repeated precipitation from warm tetrahydrofuran into water, ethanol, and 50 vol % acetone in *n*-hexane (yield 1.59 g, 72%).

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Polymerization of Monomers Containing Functional Silyl Groups. 7. Porous Membranes with Controlled Microstructures

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ABSTRACT: Porous membranes have been prepared from the films of the block copolymers that were synthesized through the anionic living polymerization of (4-vinylphenyl)dimethyl-2-propoxysilane (1) and isoprene, by cross-linking the segregated poly(1) domain and by decomposing the polyisoprene block with ozone. The characterizations of the porous membranes produced were carried out by IR measurement, elemental and gravimetric analyses, scanning electron micrographic (SEM) observation, and BET measurement. The pore widths of the membranes produced from the five block copolymers are estimated to be 28, 27, 17, and 7 nm by SEM observation, corresponding to the widths of polyisoprene domain, and 30, 31, 21, and 11 nm for the respective block copolymers. Thus, the microstructure of the porous membrane could be controlled by block lengths of the original copolymer. Large surface area and nitrogen permeability of the membranes indicate that the hollow domain is continuous through the membrane.

Introduction

Porous membranes were produced by various methods using spinodal decomposition, annealing under tension, and sintering processes.[1] Control of pore size and the size distribution have been emphasized in each case to obtain selective permeable membranes. However, precise regulation of pore size of the membrane is not easy because even slight fluctuation of the processing conditions might cause a broad size distribution. In our previous studies,[2] a new attempt was presented to make a microporous membrane from the film of the block copolymer, which was synthesized through the anionic living polymerization of (4-vinylphenyl)dimethyl-2-propoxysilane (1) and isoprene, by cross-linking the poly(1) domain and by ozonolysis of polyisoprene block. The TEM and SEM observations of the block copolymer and the resulting porous membrane revealed that the lamellar structure of the original block copolymer film directly reflected in the shape and size of the micropores. Accordingly, it is thought that the microstructure of the porous membrane can be controlled chiefly by the morphology of the segregated microphase depending on architecture of block copolymer and casting conditions of the film. Narrow molecular weight distributions of the block lengths of the copolymer cause uniform micropores. Furthermore, the SEM of the cross section of the membrane shows the continuous structure of micropores through the membrane. A large surface area estimated by BET measurement also substantiates the penetrating structure. On the surface of the micropore, formyl and acetyl groups attached to the polymer chain are formed by the oxidative cleavage of the carbon–carbon double bond of polyisoprene.

In this paper, the elaboration is fully described on the control of microstructure of porous membrane prepared from the block copolymers of 1 and isoprene with different block lengths.

Experimental Section

(4-Vinylphenyl)dimethyl-2-propoxysilane, 1. According to our prevous method, 1 was prepared.[3] A solution of (4-vinylphenyl)magnesium chloride was prepared from 4-vinylphenyl chloride (12.4 g, 89 mmol) and magnesium (4.4 g, 180 mmol) in dry tetrahydrofuran (THF, 120 mL). The resulting Grignard reagent was added dropwise over 1-h period to a solution of (2-propoxy)dimethylchlorosilane (13.7 g, 89 mmol) in dry THF (80 mL). The temperature was maintained at 10 °C during the addition. The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. After removal of the THF, the crude product obtained by direct distillation was purified by fractional distillation at 75–78 °C (1 mmHg) (11.1 g, 56.4%). The resulting monomer, 1, was again distilled from a mixture of 1 and phenylmagnesium bromide in THF through a vacuum line into a glass tube equipped with a breakseal for use in the anionic living polymerization.

Block Copolymerization. The anionic living polymer of isoprene (28.0 mmol) was prepared with oligo(α-methylstyryl)dipotassium (0.045 mmol) in dry THF (28 mL) at −78 °C for 3 h in a sealed glass tube equipped with breakable seals. For the characterization of the central segment, an aliquot of the reaction mixture (10 mL) was withdrawn. To the residual THF solution (18 mL) of the anionic living polyisoprene was added a second monomer, 1 (6.94 mmol) in THF (6.8 mL) at −78 °C and it was kept for 5 min at the same temperature to complete the polymerization. The living polyisoprene and the block copolymer (II) were quenched with methanol. The polymers were precipitated by pouring them into a large excess of methanol. The polymers collected were purified by reprecipitation and freeze-drying.

Preparation of Film. The resulting block copolymer dissolved in methyl isobutyl ketone (MIBK) was poured onto an Afron film, and the solvent was allowed to evaporate gradually at 25 °C for 12 h. The as-cast films were about 15–25 μm thick and somewhat brittle to tender corresponding to the content of polyisoprene block.

Cross-Linking. To immobilize the microdomain of poly(1) block, an as-cast film (140 mg, 8.0 cm × 8.0 cm × 20 μm) of the block copolymer from MIBK was immersed in a 2 N HCl aqueous solution (100 mL) at room temperature for 2 days, rinsed with water repeatedly, and dried in vacuo. Progress of the cross-linking reaction was traced by IR measurement.

Ozonolysis. A dichloromethane solution of ozone (5.0 mmol/L) was prepared by passing a stream of oxygen containing about 1.5 mol % of ozone generated by a discharge apparatus. The concentration of ozone was determined by iodometric titration with a neutral 2% solution of potassium iodide and 0.1 N sodium

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