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Novel Synthesis of Polyesters by Palladium-Catalyzed Polycondensation of Aromatic Dibromides, Bisphenols, or Aliphatic Diols with Carbon Monoxide

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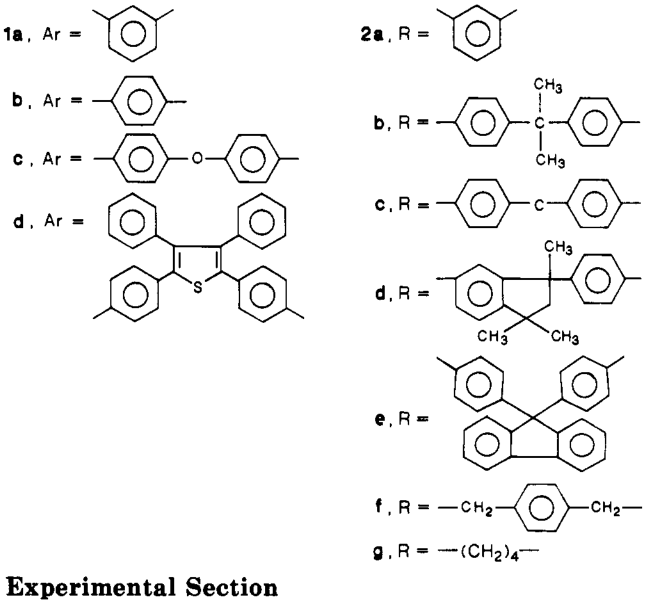
ABSTRACT: A variety of polyesters were successfully synthesized by the palladium-catalyzed carbonylation polymerization of aromatic dibromides and various diols with carbon monoxide under ordinary pressure. Inherent viscosities of the polyesters obtained were between 0.1 and 0.7 dL·g^{-1}. The effects of reaction variables, such as kinds and amounts of bases, catalysts, reaction media, and reaction temperature, were discussed in detail for the reaction of bis(4-bromophenyl) ether and 2,2-bis(4-hydroxyphenyl)propane with carbon monoxide.

Introduction

Recently, organometallic chemistry has progressed rapidly, where transition-metal catalysts have been used in many synthetic reactions.[1,2] In the field of synthetic polymer chemistry, only a few studies on the transition-metal-catalyzed polycondensation have been reported for the synthesis of polymers.[3-6] We reported quite recently a novel synthetic method of polyamides with high molecular weights by the palladium-catalyzed polycondensation of aromatic dibromides, aromatic or aliphatic diamines, and carbon monoxide.[7,8]

Aromatic polyesters are commonly prepared by the polycondensation of bisphenols with aromatic diacid chlorides.[9] It was reported that palladium-catalyzed carbonylation of aromatic bromides with hydroxyl compounds yielded esters under similar mild conditions for amide synthesis.[10,11] Therefore, the ester-forming reaction should be extended to polyester synthesis by using aromatic dibromides, carbon monoxide, and bisphenols or aliphatic diols as nucleophiles in the presence of palladium catalysts and bases. We report herein a novel successful synthesis of wholly aromatic polyesters and aliphatic–aromatic polyesters by the palladium-catalyzed carbonylation polymerization under ordinary pressure (eq 1).

$$\underset{1}{\mathrm{BrArBr}} + \mathrm{CO} + \underset{2}{\mathrm{HOROH}} \xrightarrow[\text{solvent}]{\text{Pd catalyst, base}} \underset{3}{[\!-\!\mathrm{C(O)ArC(O)ORO}\!-\!]_n} \quad (1)$$



Experimental Section

Materials. *p*-Dibromobenzene (**1b**) and bis(4-bromophenyl) ether (**1c**) were recrystallized from ethanol. Resorcinol (**2a**), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) (**2b**), bis(4-hydroxyphenyl) ether (**2c**), and 1,1,3-trimethyl-3-(hydroxyphenyl)-5-indanol (**2d**) were purified by recrystallization from benzene. 9,9-Bis(4-hydroxyphenyl)fluorene (**2e**) was recrystallized from toluene. *p*-Xylene-*α*,*α*′-diol (**2f**) was recrystallized from water. *m*-Dibromobenzene (**1a**), 1,4-butanediol (**2g**), tributylamine, and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were purified by vacuum distillation. 2,5-Bis(4-bromophenyl)-3,4-diphenylthiophene (**1d**) was synthesized according to the method reported in our previous paper.[7] 1,8-Bis(dimethylamino)naphthalene, sodium methoxide, sodium acetate, potassium carbonate, palladium chloride [$PdCl_2$], and palladium acetate [$Pd(OAc)_2$] were used as received. Triphenylphosphine (PPh_3) was recrystallized from hexane.

Dichlorobis(benzonitrile)palladium(II) [$PdCl_2(PhCN)_2$],[12] dichlorobis(triphenylphosphine)palladium(II) [$PdCl_2(PPh_3)_2$],[13] dichloro[1,4-bis(diphenylphosphino)butane]palladium(II) [$PdCl_2$dppb],[14] and dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) [$PdCl_2$dppf][15] were prepared by the reported procedures.

Toluene, tetrahydrofuran (THF), cyclohexanone, and chlorobenzene were purified by distillation. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), 1,3-dimethyl-2-imidazolidone (DMI), and hexamethylphosphoramide (HMPA) were purified by vacuum distillation over calcium hydride.

Polymerization. Polymer 3cb from 1c and 2b. In a three-necked flask equipped with a stirrer, a carbon monoxide inlet, and a reflux condenser were placed 0.8200 g (2.5 mmol) of **1c**, 0.5707 g (2.5 mmol) of **2b**, 0.0702 g (0.1 mmol) of $PdCl_2(PPh_3)_2$, 0.0525 g (0.2 mmol) of PPh_3, and 10 mL of chlorobenzene. The flask was purged several times with carbon monoxide and then heated with stirring at 115 °C in an oil bath. To the mixture, 0.82 mL (5.5 mmol) of DBU was added all at once with a syringe. The reaction mixture was stirred at 115 °C for 1.8 h until the consumption of carbon monoxide stopped. The reaction solution was diluted with 50 mL of chlorobenzene and poured into 450 mL of methanol. The precipitated polymer was filtered, washed thoroughly with hot methanol, and dried at room temperature in vacuo. The yield was 1.1163 g (99%). The inherent viscosity of the polymer in *o*-chlorophenol was 0.51 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} at 30 °C. The infrared (IR) spectrum (KBr) exhibited an absorption at 1740 cm^{-1} (C=O). Anal. Calcd for $(C_{29}H_{22}O_5)_n$: C, 77.30; H, 4.92. Found: C, 77.42; H, 4.84; Br, 1.41.

Other polymers were prepared by analogous procedures.

Measurements. IR spectra were recorded on a Jasco FT/IR-5000 Fourier transform infrared spectrophotometer. The number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$) were determined by means of gel permeation chromatography (GPC) on the basis of a polystyrene calibration on a JASCO HPLC BIP-I apparatus (column, Shodex GPC AD-80M/S polystyrene gel; eluent, DMF containing 0.01 mol·L^{-1} of lithium bromide).

Results and Discussion

The carbonylation polymerization of bis(4-bromophenyl) ether (**1c**) and bisphenol **2b** with carbon monoxide in the

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Table I
Synthesis of Polyester 3cb with Various Bases[a]

base	reactn time, h	polymer yield, %	polymer η_{inh},[b] dL·g^{-1}
tributylamine	24.5	87	0.18
1,8-bis(dimethylamino)-naphthalene	26.2	44	0.08
DBU	3.0	88	0.23
sodium methoxide	5.0	trace	
sodium acetate	8.7	58	0.11
potassium carbonate	1.8	79	0.22

[a] Polymerization was carried out with 2.5 mmol of **1c**, 2.5 mmol of **2b**, 6.0 mmol of the base, 0.15 mmol of $PdCl_2(PPh_3)_2$, and 0.3 mmol of PPh_3 in 5 mL of DMAc at 115 °C under carbon monoxide. [b] Measured at a concentration of 0.5 g·dL^{-1} in *o*-chlorophenol at 30 °C.

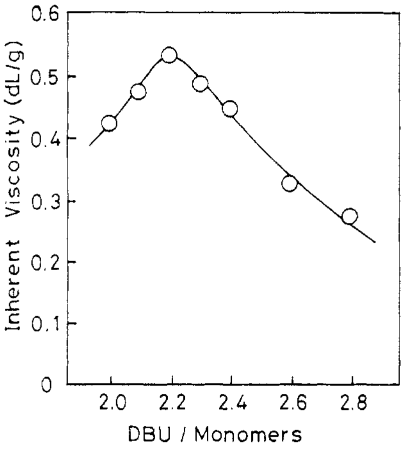

Figure 1. Effect of amount of DBU on inherent viscosity of polyester **3cb** formed by the polycondensation of **1c** with **2b** under carbon monoxide at 115 °C for 0.9–3.1 h. Monomers, 2.5 mmol; $PdCl_2(PPh_3)_2$, 0.15 mmol; PPh_3, 0.3 mmol; chlorobenzene, 10 mL.

presence of a palladium catalyst and a base in an organic solvent giving polyester **3cb** was investigated in detail as a typical polycondensation reaction. The polymerization was carried out by using a conventional catalytic reduction apparatus with a gas burette under ordinary pressure of carbon monoxide until the consumption of carbon monoxide in the gas burette stopped.

In the carbonylation of alcohols with aromatic bromides, a base was required for the acceptor of the hydrogen bromide formed during the reaction.[10,11] The effect of the kind of base on the polymerization was examined first (Table I). Among six bases employed, DBU and potassium carbonate were the most effective, judging from the shorter reaction time and the higher inherent viscosities of the resulting polymer. Since DBU and its hydrobromide dissolved readily in organic solvents and were removed completely from the precipitated polymer, DBU was used as the base for the later polymerizations.

Figure 1 shows the effect of the amount of DBU on the inherent viscosity of the polyester. Although a theoretical amount of the base required for the polymerization was 2 equiv, a slight excess amount of DBU was preferable to obtain the highest inherent viscosity.

The influence of the reaction medium on the inherent viscosity of the polymer is summarized in Table II. Chlorinated aliphatic hydrocarbons, which are often used in the interfacial synthesis of polyesters, could not be used for the present reaction, because this type of solvent reacted with DBU. Five amide-type solvents gave polyesters having inherent viscosities in the range 0.18–0.33 dL·g^{-1}, and the highest viscosity value (0.42 dL·g^{-1}) was obtained when chlorobenzene was employed as the reaction medium. Therefore, future polymerizations were carried out in chlorobenzene.

Table II
Synthesis of Polyester 3cb in Various Solvents[a]

solvent	reactn time, h	polymer yield, %	polymer η_{inh},[b] dL·g^{-1}
toluene	3.1	97	0.34
THF[c]	19.2	24	0.11
cyclohexanone	1.7	89	0.24
chlorobenzene	1.7	100	0.42
DMF	1.1	97	0.33
DMAc	2.5	97	0.26
NMP	2.2	88	0.25
DMI	1.5	86	0.20
HMPA	3.7	79	0.18

[a] Polymerization was carried out with 2.5 mmol of **1c**, 2.5 mmol of **2b**, 6 mmol of DBU, 0.15 mmol of $PdCl_2(PPh_3)_2$, and 0.30 mmol of PPh_3 in 5 mL of the solvent at 115 °C under carbon monoxide. [b] Measured at a concentration of 0.5 g·dL^{-1} in *o*-chlorophenol at 30 °C. [c] At 60 °C.

Table III
Synthesis of Polyester 3cb with Various Palladium Catalysts[a]

catalyst	reactn time, h	polymer yield, %	polymer η_{inh},[b] dL·g^{-1}
$PdCl_2/4PPh_3$	0.9	99	0.48
$Pd(OAc)_2/4PPh_3$	1.3	100	0.41
$Pd(PPh_3)_4$	0.8	89	0.36
$PdCl_2(PhCN)_2/4PPh_3$	0.8	100	0.47
$PdCl_2dppf$	2.1	97	0.40
$PdCl_2dppb$	5.0	76	0.19
$PdCl_2(PPh_3)_2$	1.0	96[c]	0.41
$PdCl_2(PPh_3)_2/PPh_3$	1.5	100	0.50
$PdCl_2(PPh_3)_2/2PPh_3$	1.6	100	0.51
$PdCl_2(PPh_3)_2/3PPh_3$	1.1	99	0.48
$PdCl_2(PPh_3)_2/4PPh_3$	2.7	100	0.51

[a] Polymerization was carried out with 2.5 mmol of **1c**, 2.5 mmol of **2b**, 5.5 mmol of DBU, and 0.15 mmol of the catalyst in 10 mL of chlorobenzene at 115 °C under carbon monoxide. [b] Measured at a concentration of 0.5 g·dL^{-1} in *o*-chlorophenol at 30 °C. [c] Palladium black was precipitated during the polymerization.

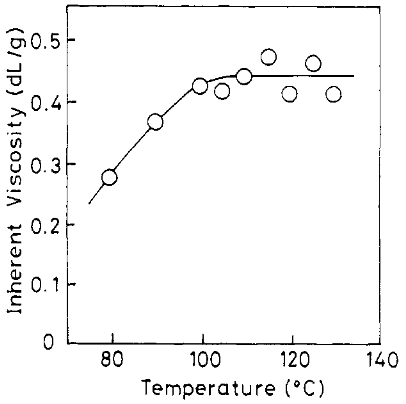

Figure 2. Effect of reaction temperature on inherent viscosity of polyester **3cb** formed by the polycondensation of **1c** with **2b** under carbon monoxide for 1.5–7.0 h. Monomers, 2.5 mmol; DBU, 6 mmol; $PdCl_2(PPh_3)_2$, 0.15 mmol; PPh_3, 0.3 mmol; chlorobenzene, 10 mL.

Figure 2 shows the effect of reaction temperature on the inherent viscosity of the polyester. The polymer with low molecular weight was obtained at a temperature lower than 100 °C. The molecular weight of the polyester tended to increase gradually with increasing reaction temperature, judging from the viscosity values; however, a temperature

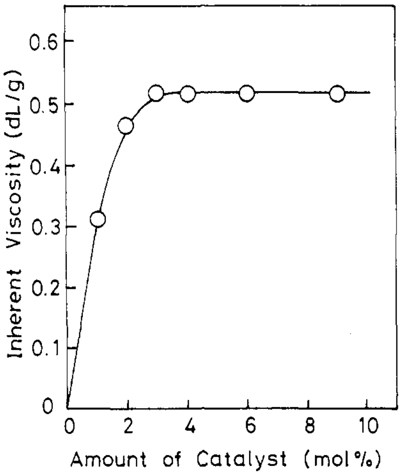

Figure 3. Effect of amount of $PdCl_2(PPh_3)_2$ with 2 equiv of PPh_3 on inherent viscosity of polyester **3cb** formed by the polycondensation of **1c** with **2b** under carbon monoxide at 115 °C for 1.0–17.0 h. Monomers, 2.5 mmol; DBU, 5.5 mmol; chlorobenzene, 10 mL.

above 110 °C was not so effective for increasing the inherent viscosity. The preferable reaction temperature of 115 °C was almost the same as that for polyamide synthesis.[7,8]

Table III summarizes the catalytic effect of palladium compounds on polycondensation. The polymerizations using the palladium catalysts proceeded rapidly and were completed within 3 h except in the case of that using $PdCl_2dppb$. Among the palladium catalysts employed, $PdCl_2$, $PdCl_2(PhCN)_2$, and $PdCl_2(PPh_3)_2$ coupled with PPh_3 gave better results with respect to inherent viscosity of the polymer. The use of a three-fold molar excess of PPh_3 relative to a palladium catalyst was essential to prevent the precipitation of palladium black during the polymerization. Palladium black lacks catalytic activity and even contaminates the polymer. Figure 3 shows the influence of the amount of $PdCl_2(PPh_3)_2$ on the inherent viscosity of the polyester. The polyester having sufficiently high molecular weight was obtained by using more than 3 mol % of the catalyst based on the monomers.

The polymer thus obtained was confirmed to be the corresponding polyester **3cb** by means of IR spectroscopy and elemental analysis. The IR spectrum exhibited a carbonyl absorption at 1740 cm^{-1}, which is the characteristic absorption of ester bond. The elemental analysis values were in good agreement to the calculated values with no trace of metallic ash. The molecular weight of polyester **3cb** having an inherent viscosity of 0.51 $dL \cdot g^{-1}$ was determined by means of GPC. The chromatogram indicated that the $\bar{M}_n$ and $\bar{M}_w$ values were 70 500 and 88 500, respectively, for standard polystyrene, and the ratio $\bar{M}_w/\bar{M}_n$ was 1.3.

A variety of wholly aromatic polyesters **3aa–de** and aliphatic–aromatic polyesters **3af–dg** were prepared from combinations of aromatic dibromides **1a–d** and bisphenols **2a–e** or aliphatic diols **2f,g** under the same reaction conditions as for the polymerization giving polyester **3cb**. Aromatic polyesters **3aa–de** thus obtained had inherent viscosities up to 0.69 $dL \cdot g^{-1}$ (Table IV). Aliphatic–aromatic polyesters **3af–dg** consisting of the aliphatic diols had lower inherent viscosities (0.18–0.36 $dL \cdot g^{-1}$) compared with the aromatic polyesters. Polyesters having a *p*-phenylene unit derived from **1b** were obtained in low inherent viscosities (0.23–0.32 $dL \cdot g^{-1}$) probably due to the low solubility in chlorobenzene and the precipitation of the polymer during the reaction. Tetraphenylthiophene-containing polyesters **3da–dg** had higher inherent viscosities (0.26–0.69 dL/g) and had better solubility in the organic solvent.

Table IV
Inherent Viscosities of Various Polyesters by Palladium-Catalyzed Polycondensation[a]

	dibromide			
diol	**1a**	**1b**	**1c**	**1d**
2a	*b,c*	*b,c*	0.35	0.39
2b	0.20	0.32[b]	0.53	0.50
2c	*b,c*	*b,c*	0.08[b]	0.69
2d	0.19	0.23	0.34	0.34
2e	0.18[b]	0.27[b]	0.42	0.54
2f	0.26	0.24[b]	*c*	0.36
2g	0.18	0.23[b]	0.26	0.26

[a] Polymerization was carried out with 2.5 mmol of the dibromide, 2.5 mmol of the diol, 5.5 mmol of DBU, 0.1 mmol of $PdCl_2(PPh_3)_2$, and 0.2 mmol of PPh_3 in 10 mL of chlorobenzene at 115 °C for 1.5–3.3 h under carbon monoxide. Inherent viscosity was measured at a concentration of 0.5 $g \cdot dL^{-1}$ in *o*-chlorophenol at 30 °C. [b] Polymer precipitation occurred during the polymerization. [c] Polymer obtained was insoluble in *o*-chlorophenol.

Thus, a novel successful approach without use of aromatic diacids and their derivatives has been found for the synthesis of wholly aromatic and aliphatic–aromatic polyesters. This method has some advantages over the conventional route for polyester synthesis using aromatic diacids and their derivatives. Aromatic dibromides are readily prepared by the direct bromination of aromatic compounds, whereas aromatic diacids and their acid chlorides are synthesized by many reaction steps.

Registry No. (**1a**)(**2a**)(CO) (copolymer), 119503-66-1; (**1a**)(**2b**)(CO) (copolymer), 119528-87-9; (**1a**)(**2c**)(CO) (copolymer), 119503-68-3; (**1a**)(**2d**)(CO) (copolymer), 119503-72-9; (**1a**)(**2e**)(CO) (copolymer), 119503-74-1; (**1a**)(**2f**)(CO) (copolymer), 119503-78-5; (**1a**)(**2a**)(CO) (copolymer), 119503-82-1; (**1b**)(**2a**)(CO) (copolymer), 119503-67-2; (**1b**)(**2b**)(CO) (copolymer), 119503-64-9; (**1b**)(**2c**)(CO) (copolymer), 119503-69-4; (**1b**)(**2d**)(CO) (copolymer), 119503-73-0; (**1b**)(**2e**)(CO) (copolymer), 119503-75-2; (**1b**)(**2f**)(CO) (copolymer), 119503-79-6; (**1b**)(**2a**)(CO) (copolymer), 119503-83-2; (**1c**)(**2a**)(CO) (copolymer), 119503-62-7; (**1c**)(**2b**)(CO) (copolymer), 119503-61-6; (**1c**)(**2c**)(CO) (copolymer), 119503-70-7; (**1c**)(**2d**)(CO) (copolymer), 119528-88-0; (**1c**)(**2e**)(CO) (copolymer), 119503-76-3; (**1c**)(**2f**)(CO) (copolymer), 119503-80-9; (**1c**)(**2a**)(CO) (copolymer), 119503-84-3; (**1d**)(**2a**)(CO) (copolymer), 119503-63-8; (**1d**)(**2b**)(CO) (copolymer), 119503-65-0; (**1d**)(**2c**)(CO) (copolymer), 119503-71-8; (**1d**)(**2d**)(CO) (copolymer), 119528-89-1; (**1d**)(**2e**)(CO) (copolymer), 119503-77-4; (**1d**)(**2f**)(CO) (copolymer), 119503-81-0; (**1d**)(**2a**)(CO) (copolymer), 119503-85-4; DBU, 6674-22-2; $PdCl_2(PPh_3)_2$, 13965-03-2; $PdCl_2$, 7647-10-1; PPh_3, 603-35-0; $Pd(OAc)_2$, 3375-31-3; $Pd(PPh_3)_4$, 14221-01-3; $PdCl_2(PhCN)_2$, 14220-64-5; $PdCl_2dppf$, 72287-26-4; $PdCl_2dppb$, 29964-62-3; tributylamine, 102-82-9; naphthalene, 20734-58-1; sodium methoxide, 124-41-4; sodium acetate, 127-09-3; potassium carbonate, 584-08-7.

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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

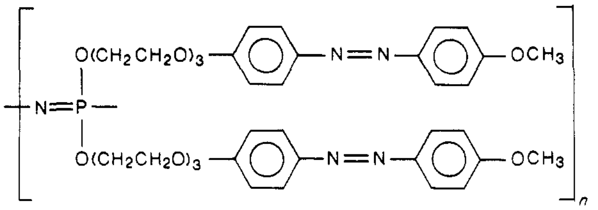
Liquid crystalline polymers are an important subject for fundamental and technological studies because of their unusual anisotropic optical, electrical, and mechanical properties.[1–6] Liquid crystalline polymers fall into two general categories: (1) species with rigid mesogenic groups incorporated into 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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