tively. The plot of the left-hand side of the above equation against $R_p/[M]^2$ (Figure 6) gave a positive slope, indicating the absence of a primary radical termination effect.

Deb[13] deduced a suitable expression which was further simplified by Ghosh and Mitra[14] to analyze the degradative chain transfer to initiator:

$$\ln \frac{R_p^2}{[I][M]^2} = \ln \frac{2f_k k_d k_p^2}{k_t} - \frac{k_p^2}{k_t}\frac{k_{rtI}}{k_{iI}k_p}C_I\frac{[I]}{[M]}$$

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.434\frac{k_p^2}{k_t}\frac{k_{rtI}}{k_{iI}k_p}C_I\frac{[I]}{[M]}$$

Here C_I is the initiator transfer constant. It is noticed that the experimental points fall on a straight line with a positive slope on the plot of left-hand side of above equation against [I]/[M] indicating the absence of degradative chain (initiator) transfer (Figure 6).

The system does not follow retardation at high [initiator]; hence the possibility of degradative addition is also ruled out.

Therefore the high initiator exponent at high [β-PCPY] is attributed to active-center deactivation by chain transfer to solvent (CCl_4) as confirmed by molecular weight data above 6.11×10^{-3} mol L^{-1} of [β-PCPY].

The mechanism[3] of dissociation of β-PCPY into radicals via triplet carbene formation has already been established. In conclusion, the experimental data on the polymerization of 4-VP in CCl_4 are all consistent with chain transfer to solvent.

Acknowledgment. We thank Prof. A. K. Vasishtha, Director, and Prof. R. S. Tewari, Head of the Chemistry Department, H.B.T.I., Kanpur, for providing necessary facilities. S.S. acknowledges financial support from the CSIR, New Delhi.

Registry No. β-PCPY, 92592-50-2; 4-VP, 100-43-6; 4-VP (homopolymer), 25232-41-1.

References and Notes

(1) Shukla, A. K.; Saini, S.; Kumar, P.; Srivastava, A. K. *Angew. Makromol. Chem.* **1986**, *141*, 103.
(2) Srivastava, A. K.; Saini, S. *Acta Polym.* **1984**, *35*, 667.
(3) Saini, S.; Shukla, A. K.; Kumar, P.; Srivastava, A. K. *J. Macromol. Sci. Chem.* **1987**, *35*, 1107.
(4) Saini, S.; Shukla, A. K.; Srivastava, A. K. *Polym. J.* **1985**, *17*, 1117.
(5) Shukla, A. K.; Saini, S.; Kumar, P.; Rai, J. S. P.; Srivastava, A. K. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(6) Nigam, S. K.; Saini, S.; Srivastava, A. K. *Indian J. Chem.* **1986**, *25A*, 944.
(7) Nigam, S. K.; Shukla, A. K.; Saini, S.; Kumar, P.; Srivastava, A. K. *Angew. Makromol. Chem.* **1987**, *149*, 139.
(8) Krohnke, F. *Ber. Dtsch. Chem. Ges.* **1933**, *66B*, 604.
(9) Krohnke, F. *Ber. Dtsch. Chem. Ges.* **1935**, *68B*, 604.
(10) Lumb, J. T. *Tetrahedron Lett.* **1970**, 579.
(11) Berkonitz, J. B.; Yamin, M.; Fuoss, R. M. *J. Polym. Sci., A-1* **1958**, *28*, 69.
(12) Deb, P. C.; Meyerhoff, G. *Eur. Polym. J.* **1974**, *10*, 709.
(13) Deb, P. C. *Eur. Polym. J.* **1975**, *11*, 31.
(14) Ghosh, P.; Mitra, P. S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1743.

Thallium in the Synthesis of Phosphazene Derivatives: Donor-Substituted Polyphosphazenes

R. C. Haddon* and S. V. Chichester-Hicks

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received May 13, 1988*

ABSTRACT: Organothallium salts have been used to prepare a series of phenoxy-substituted cyclotriphosphazenes $[-N{=}P(OC_6H_4\text{-}4\text{-}R)_2-]_3$ and polyphosphazenes $[-N{=}P(OC_6H_4\text{-}4\text{-}R)_2-]_x$, with R = Et, ^{t}Bu, OMe, SMe, and NMe_2. Two new donor-substituted polyphosphazenes (R = SMe and R = NMe_2) undergo iodine doping, and the latter polymer is the most highly conducting polyphosphazene yet to be reported (10^{-4} S/cm).

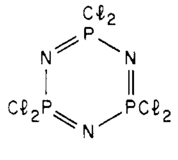
The high level of interest in polyphosphazene chemistry[1] may be attributed, mainly to two factors. First, a wide variety of different phosphazene macromolecules can be prepared by substitution reactions on the parent system, poly(dichlorophosphazene), $[NPCl_2]_x$, according to the Allock procedure[2-5] or by a condensation polymerization.[6] Second, the resultant polyphosphazene derivatives are generally tractable materials with excellent mechanical and chemical stability properties.[2-7]

The nature of the substituents which can be attached to the polyphosphazene backbone via direct substitution reactions is ultimately limited by the properties of the reactive intermediates which are required to effect the appropriate transformation. The largest class of polyphosphazenes is comprised of the aryloxy and alkoxy derivatives and some of these polymers are finding commerical application.[1-5,7] These compounds are usually prepared by the substitution reaction of the sodium salt of the appropriate aryloxide or alkoxide on polydichlorophosphazene.[2,4,5] The sodium salts are prepared as solutions or slurries in an ether solvent by a heterogeneous reaction of the alcohol or phenol with sodium metal or sodium hydride.

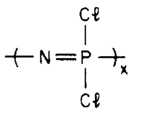
In the present work we report investigations into the utility of thallium alkoxides and aryloxides as reactive intermediates for the synthesis of substituted cyclo- and polyphosphazenes. The study is motivated by the work of Taylor, McKillop, and co-workers, who have pioneered the use of thallium in organic synthesis.[8] In particular, they showed that thallium(I) salts of phenols could be alkylated, acylated, aroylated, or tosylated under mild conditions in quantitative yield by treatment with the appropriate halide precursor. In addition the following was found:[9] "thallium(I) salts of phenols are readily prepared in quantitative yield by the addition of thallium(I) ethoxide to a solution of the phenol in a solvent such as benzene or ethanol. They are crystalline, sharp melting, stable solids which may be conveniently recrystallized from water or aqueous ethanol." On this basis we decided to test the thallium salts as nucleophiles for reaction with

0024-9297/89/2222-1027$01.50/0

hexachlorocyclotriphosphazene (1) and poly(dichlorophosphazene) (2). We also report the synthesis and characterization of two new polyphosphazenes bearing electron-donating substituents. These materials undergo halogen doping with a concommitant enhancement in their electronic conductivity.



1



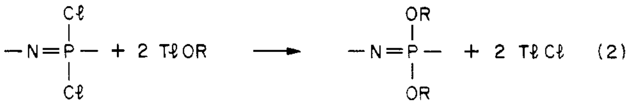
2

Result and Discussion

Thallium Aryloxides. Caution: Thallium compounds are extremely toxic and should be handled with care and all waste must be disposed of properly.[8]

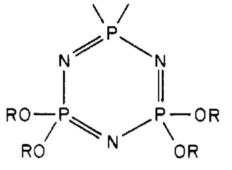
The thallium(I) aryloxides were readily prepared according to the procedure given by Taylor and McKillop.[8,9] The salts were obtained from the reaction of thallium(I) ethoxide with a solution of the appropriate phenol in ethanol, benzene, or tetrahydrofuran (eq 1). In many cases the thallium aryloxides precipitate from solution and may be purified by recrystallization. Alternatively, if the reaction is run in the presence of excess phenol, the volatiles may be removed under high vacuum at the end of the reaction and the resultant solid employed directly in chlorophosphazene reactions. In terms of the outcome of the reaction of the thallium aryloxides to produce organophosphazenes, the two alternative preparations of the thallium salts were equally successful.

$$\mathrm{ROH} + \mathrm{TlOEt} \longrightarrow \mathrm{TlOR} + \mathrm{EtOH} \qquad (1)$$



$$-\mathrm{N}{=}\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{P}}}- + 2\,\mathrm{TlOR} \longrightarrow -\mathrm{N}{=}\underset{\mathrm{OR}}{\overset{\mathrm{OR}}{\mathrm{P}}}- + 2\,\mathrm{TlCl} \qquad (2)$$

Reaction of Thallium Alkoxides and Aryloxides with Hexachlorocyclotriphosphazene (1). The thallium alkoxides and aryloxides are quite soluble in THF, and when added in solid form to a THF solution of hexachlorocyclotriphosphazene, the precipitation of thallium chloride begins immediately (eq 2). Nevertheless we find no evidence for the acceleration of the reaction between aryloxides and 1 as a result of replacing the alkali-metal counterion with thallium(I). The presence of phase-transfer catalysts such as tetrabutylammonium bromide[10] is very effective in accelerating the rates of the reactions of thallium aryloxides with 1 and led to the isolation of the fully substituted cyclic trimers (3–8).



3, R = $-C_6H_4-4-C_2H_5$

4, R = $-C_6H_4-4-t-C_4H_9$

5, R = $-C_6H_4-4-OCH_3$

6, R = $-C_6H_4-4-SCH_3$

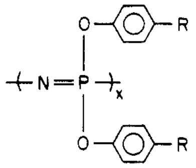
7, R = $-C_6H_4-4-N(CH_3)_2$

8, R = $-CH_2C{\equiv}CH$

The reaction between thallium aryloxides and 1 is a clean process with virtually no discoloration during reaction. Due to its insolubility, thallium chloride is readily removed by filtration at the conclusion of the reaction.

The chief drawbacks of this reaction scheme are the toxicity and expense of thallium compounds.

Reaction of Thallium Aryloxides with Polydichlorophosphazene (2). Allcock has shown that the small-molecule chemistry of hexachlorocyclotriphosphazene often provides a model for the reactivity of polydichlorophosphazene.[2-5] This also proved to be the case with regard to the reactivity of thallium aryloxides toward chlorophosphazenes, and on addition of thallium aryloxide to an ether solution of polymer/trimer mixture the precipitation of thallium chloride was observed to commence immediately (eq 2). The presence of tetrabutylammonium bromide as phase-transfer catalyst[10] both accelerated the reaction and helped to drive it to completion. The resulting polyphosphazenes (9–13) showed a high degree of chlorine replacement.



9, R = C_2H_5

10, R = $t-C_4H_9$

11, R = OCH_3

12, R = SCH_3

13, R = $N(CH_3)_2$

The isolation of soluble polyorganophosphazenes followed the small-molecule procedure with removal of the thallium chloride by filtration, and it is conceivable that this process could be adapted to allow anhydrous isolation of the polymer. The isolation of polyorganophosphazenes which are insoluble in cold solvents is complicated by the presence of thallium chloride. However, it is usually possible to decant a hot solution of the polymer from the thallium chloride as a result of its high density. The traces of thallium chloride remaining with the polymer may be removed by repeated precipitation into (hot) water, in which thallium chloride is sparingly soluble.

Characterization of the High Polymers. The polymers were uncross-linked, as demonstrated by their solubility in organic solvents. The microanalyses confirmed the formulation of the polymers 9–13. The extremely low residual chlorine content (comparable to the levels found in the *cyclo*triphosphazene derivatives) confirms the high efficiency of the substitution reactions.

The ^{31}P NMR spectra are in agreement with a high level of chlorine replacement. The IR spectra exhibited the characteristic polyphosphazene P–N stretching vibration at about 1200 cm^{-1}. The ring breathing mode at about 1500 cm^{-1} was also evident.

The GPC average molecule weights of the polymers soluble in cold organic solvents exhibited a bimodal distribution with values of the order of 10^6 daltons for the high polymer fraction. The solid-phase characterization of the polymers is reported in other publications.[11]

Electrical Conductivities. Unlike most polymers which possess a conjugated backbone, the polyphosphazenes do not exhibit evidence of extended states or electronic conductivity associated with the backbone. Nevertheless, by utilization of the synthetic versatility afforded by the Allcock procedure, it has proved possible to introduce the necessary functionality to provide a conductivity pathway via the side groups of certain poly(organophosphazenes).

The outrigger approach[5] has been utilized by Allcock and co-workers in the synthesis of polyphosphazenes bearing covalently attached copper phthalocyanine side groups.[12] Iodine doping of these polymers led to conductivities in the range 10^{-5}–10^{-8} S/cm. Tetracyanoquinodimethane complexes of quaternized poly(organophosphazenes) exhibited similar conductivities,[13] as did the doped form of poly[bis(pyrrolyl)phosphazene].[14,15]

The availability of donor-substituted poly[bis(phenoxy)phosphazenes] has enabled us to study the effects of this functionality on the electrical conductivity of the doped materials. Allcock and co-workers have already shown that the conductivity of the parent system, poly[bis(phenoxy)phosphazene], is very low ($<10^{-12}$ S/cm, after exposure to iodine).[12] Accordingly, we focused our attention on the materials with superior donor groups present.

Both the 4-SMe- and 4-NMe_2-substituted poly[bis(phenoxy)phosphazenes] (**12** and **13**, respectively) underwent vapor-phase doping with iodine to produce shiny black films. The conductivity of polymer **12** remained below 10^{-7} S/cm but the 4-NMe_2 derivative exhibited conductivities of 10^{-4} S/cm. The doped films were plasticized by iodine and became quite flexible on doping. The mechanical and electrical properties were maintained as long as the films were stored in an inert atmosphere in the presence of iodine.

Experimental Section

Materials. All chemicals were obtained from Aldrich Chemical Co. (except where indicated). Hexachlorocylcotriphosphazene (99%) was purified by recrystallization from heptane (at a temperature below 75 °C), after treatment with charcoal, followed by vacuum sublimation at 60 °C. Tetrahydrofuran and dioxane were obtained in anhydrous grades and distilled from sodium benzophenone ketyl immediately before use. Anisole was obtained in anhydrous grade, distilled from sodium spheres, and stored over 4-Å molecular sieves. 4-Methoxyphenol, 4-(methylthio)phenol, propargyl alcohol, sodium hydride, and thallium ethoxide (Alfa, Strem) were used as received. 4-Ethylphenol was distilled, and 4-*tert*-butylphenol was recrystallized from heptane.

All procedures were carried out under an atmosphere of dry argon in standard Airless Ware or in a helium-filled drybox.

Analytical. The ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4, with positive shifts downfield from the reference. Molecular weights were measured by gel permeation chromatography on a Waters Associates liquid chromatography system using styragel columns. Elemental microanalyses were carried out by Galbraith Laboratories. Electrical conductivities were measured with an in-line four-probe system utilizing pressure contacts. The samples for conductivity studies were solution cast as thin films on a glass substrate.

Polymerization of $(NPCl_2)_3$. The thermal polymerization process of Allcock et al. was followed.[2–5] Samples (80 g) of purified $(NPCl_2)_3$ were loaded into 7.5 × 2.5 cm constricted Pyrex tubes in a drybox. The sample tubes were fitted with Teflon vacuum stopcocks, removed from the drybox and attached to a vacuum line. After they were degassed via the freeze–thaw technique, the tubes were sealed under vacuum. All of the reaction tubes utilized in this study were loaded with material from the same batch of purified trimer. Samples were heated at 250 °C until the contents had become highly viscous which required a heating period of 5–6 days. After cooling, the contents of the sample tubes were removed and stored in a drybox. This mixture of trimer, oligomers, and polymer was utilized without further purification, and yields quoted in this paper are based on starting trimer.[2,3] ^{31}P NMR spectroscopy indicated a 60:40 ratio of trimer to polymer plus oligomers and the absence of cyclic tetramer.

Synthesis of Thallium Aryloxides. The thallium salts were prepared according to the method of Taylor and McKillop.[8,9] Although the salts can be isolated and purified, in most instances it is sufficient to employ an excess of the phenol, remove the volatiles under vacuum, and make direct use of the resulting solid.

Synthesis of (4-Hydroxyphenyl)trimethylammonium Iodide. 4-Aminophenol (67.4 g, 0.62 mol), anhydrous sodium carbonate (65.7 g, 0.62 mol), and 350 mL absolute methanol were placed in a 500-mL, three-necked flask equipped with a mechanical stirrer, reflux condenser, and addition funnel. Iodomethane (154.4 mL, 2.48 mol) was added dropwise at room temperature, the mixture was stirred overnight, and then it was refluxed for an additional day. The reaction was allowed to cool and the resultant off-white crystals were isolated by filtration. The solid was dissolved in hot methanol and filtered, and when the solution cooled, large white needles were formed (115.1 g, 67%): mp 207 °C (lit.[15] mp 195 °C).

Synthesis of 4-(Dimethylamino)phenol. The preparation is based on the procedure of Hünig and Baron,[17] but slight modification was necessary to allow isolation of the product in high yield and purity. The (dimethylamino)phenols rapidly darken and oxidize in the air,[18,19] and we made use of this material immediately after its isolation. The ethanolamine, ether, and water utilized in this reaction were all deoxygenated with nitrogen. (4-Hydroxyphenyl)trimethylammonium iodide (39.1 g, 0.14 mol), ethanolamine (17 mL, 0.28 mol), and a magnetic stirrer were placed in a 250-mL flask fitted with a reflux condenser under a blanket of argon. The flask was immersed in an oil bath preheated to 170 °C. This temperature was maintained for 30 min, during which time the contents of the flask turned into a pale pink viscous liquid. The solution was cooled, poured in 200 mL of water, and extracted with 1 L of ether. The ether was washed with water and dried with sodium sulfate. The solvent was removed and the crystalline white solid evacuated to 0.1 mm (15.8 g, 85%): mp 75.5–76 °C (lit.[19] mp 77.5–78 °C).

Synthesis of $[NP(OC_6H_4\text{-}4\text{-}C_2H_5)_2]_3$ (3). The preparation followed that of compound **4**. The product was obtained as colorless crystals after recrystallization from hexane: mp 78 °C. Anal. Calcd for $C_{48}H_{54}N_3O_6P_3$: C, 66.92; H, 6.32; N, 4.88; P, 10.79; Cl, 0.0. Found: C, 66.96; H, 6.26; N, 5.30; P, 10.75; Cl, 0.004. IR (CsI) 2960 (m, CH_3), 1507 (s, ring) 1180 (vs, br, PN). ^{31}P NMR (C_6D_6) 8.80 (singlet).

Synthesis of $[NP(OC_6H_4\text{-}4\text{-}\textit{tert}\text{-}C_4H_9)_2]_3$ (4). Thallium 4-*tert*-butylphenoxide (white solid, 7 g, 0.02 mol) was added to a solution of $(NPCl_2)_3$ (0.7 g, 0.002 mol) in THF at room temperature. A white precipitate began to form immediately. Tetra-*n*-butylammonium bromide (0.1 g) was added, and the reaction mixture was refluxed overnight. The reaction was allowed to cool and the excess thallium 4-*tert*-butylphenoxide destroyed with concentrated hydrochloric acid (0.8 mL, 0.009 mol). The THF solution was decanted from the thallium chloride and filtered through a coarse porosity frit. Removal of the solvent gave rise to a colorless oil which was dissolved in benzene and washed successively with 1 M sodium hydroxide, 1 M hydrochloric acid, and water. The benzene solution was dried with sodium sulfate, and the solvent was removed to give a colorless oil which crystallized on standing (2.04 g, 99%): mp 132–133 °C. Anal. Calcd for $C_{60}H_{78}N_3O_6P_3$: C, 69.95; H, 7.63; N, 4.08; P, 9.02. Found: C, 70.38; H, 7.80; N, 3.93; P, 8.92. IR (CsI) 2950 (s, CH_3), 1505 (s, ring) 1190 (vs, br, PN) cm^{-1}. ^{31}P NMR (C_6D_6) 8.88 (singlet).

Synthesis of $[NP(OC_6H_4\text{-}4\text{-}OCH_3)_2]_3$ (5). The preparation followed that of compound **7**. The product was obtained as white crystals from heptane: mp 100–102 °C (lit.[20] 103–104 °C). Anal. Calcd for $C_{42}H_{42}N_3O_{12}P_3$: C, 57.74; H, 4.85; N, 4.81; P, 10.63. Found: C, 57.60; H, 4.69; N, 4.73; P, 10.23. IR (CsI) 2830 (w, CH_3), 1505 (s, ring), 1200 (vs, br, PN). ^{31}P NMR ($CDCl_3$) 9.88 (singlet).

Synthesis of $[NP(OC_6H_4\text{-}4\text{-}SCH_3)_2]_3$ (6). The preparation followed that of compound **7**. The product was obtained as colorless crystals by recrystallization from benzene/hexane (56%): mp 103–104 °C. Anal. Calcd for $C_{42}H_{42}N_3O_6P_3S_6$: C, 52.00; H, 4.36; N, 4.33; P, 9.58; S, 19.83; Cl, 0.0. Found: C, 52.14, H, 4.46; N, 4.28; P, 9.85; S, 20.24; Cl, 0.006. IR (CsI) 2910 (w, CH_3), 1491 (s, ring), 1210 (vs, br, PN). ^{31}P NMR ($CDCl_3$) 9.50 (singlet).

Synthesis of $[NP(OC_6H_4\text{-}4\text{-}N(CH_3)_2)_2]_3$ (7). Thallium 4-(dimethylamino)phenoxide (pale green solid, 6.7 g, 0.02 mol) was added to a solution of $(NPCl_2)_3$ (0.7 g, 0.002 mol) in dioxane at room temperature. Tetrabutylammonium bromide (0.1 g) was added and the reaction mixture refluxed overnight. After cooling the reaction, a hydrogen chloride/ether solution (9 mL, 0.009 mol) was added and the mixture filtered. The solvent was removed from the filtration and the resulting solid taken up in toluene, washed with water, and dried over sodium sulfate. Removal of the solvent gave rise to a white crystalline solid which could be recrystallized from benzene/heptane (1.24 g, 65%), mp 187–188 °C. Anal. Calcd for $C_{48}H_{60}N_9O_6P_3$: C, 60.56; H, 6.35; N, 13.24; P, 9.76; Cl, 0.0. Found: C, 60.61; H, 6.25; N, 13.51; P, 10.08; Cl, 0.30. IR (CsI) 2880 (m, br, CH) 1516 (vs, ring), 1185 (vs, br, PN). ^{31}P NMR (C_6D_6) 10.55 (singlet).

Synthesis of $[NP(OCH_2CCH)_2]_3$ (8). Thallium propargyl alkoxide (colorless crystals, 4.66 g, 0.018 mol) was dissolved in THF (20 mL), and a solution of $(NPCl_2)_3$ (0.7 g, 0.002 mol) in THF (20 mL) was added dropwise. The reaction became warm during the addition and there was immediate formation of a white precipitate. The reaction mixture was stirred for 2 days at room temperature. The reaction was quenched with concentrated hydrochloric acid (1 mL, 0.011 mol), and the thallium chloride was removed by filtration through a fine frit. The solvent was removed to give a colorless oil which was taken up in benzene, washed with water, and dried with sodium sulfate. Removal of the solvent gave a colorless oil which eventually crystallized (0.7 g, 75%): mp 31–32.5 °C. Anal. Calcd for $C_{18}H_{18}N_3O_6P_3$: C, 46.47; H, 3.90; N, 9.03; P, 19.97. Found: C, 46.51; H, 3.84; N, 9.03; P, 20.32. ^{1}H NMR ($CDCl_3$) 2.62 (t, 1 H), 4.67 (m, 2 H). ^{13}C NMR ($CDCl_3$) 54.1, 77.2, 77.9. ^{31}P NMR ($CDCl_3$) 17.31 (singlet). Mass spectrum (chemical ionization), *m/e* calcd 465, found 466 [(M + 1)$^+$, 100%].

Synthesis of Poly[bis(4-ethylphenoxy)phosphazene][21,22] **(9).** Thallium 4-ethyl phenoxide (bone solid, 35.73 g, 0.11 mol) was added to a solution of the $(NPCl_2)_3/(NPCl_2)_x$ mixture (3.5 g, 0.03 mol) in THF (250 mL) at room temperature. A white precipitate began to form immediately. Tetrabutylammonium bromide (0.5 g, 0.0015 mol) was added and the reaction refluxed for 2 days. At the end of this time the reaction was cooled, the excess thallium aryloxide quenched with hydrogen chloride/ether solution (55 mL, 0.055 mol), and the thallium chloride allowed to settle at the bottom of the reaction flask. The mixture was filtered, the filtrate volume reduced to about 100 mL, and the polymer precipitated into methanol. The precipitate was collected, dissolved in chloroform and reprecipiated into methanol (0.4 g, 23%). Anal. Calcd for $C_{16}H_{18}NO_2P$: C, 66.92, H, 6.32; N, 4.88; P, 10.79; Cl, 0.0. Found: C, 66.69; H, 6.48; N, 4.91; P, 11.13; Cl, 0.16. IR (film) 2950 (s, C–H), 1507 (m, ring), 1200 (vs, br, PN). ^{31}P NMR (C_6D_6) −19.3 (singlet).

Synthesis of Poly[bis(4-*tert*-butylphenoxy)phosphazene][22] **(10).** The preparation followed that of polymer **11** (2.7 g, 30%). Anal. Calcd for $C_{20}H_{26}NO_2P$: C, 69.95; H, 7.63; N, 4.08; P, 9.02; Cl, 0.0. Found: C, 70.26; H, 7.75; N, 3.92; P, 8.82; Cl, 0.013. IR (film) 2950 (s, br), 1510 (s, ring), 1215 (vs, br, PN). ^{31}P NMR (C_6D_6) −18.68 (singlet).

Synthesis of Poly[bis(4-methoxyphenoxy)phosphazene][21,22] **(11).** Thallium 4-methoxyphenoxide (white solid, 131 g, 0.40 mol) was added to a solution of $(NPCl_2)_3/(NPCl_2)_x$ mixture (13.92 g, 0.12 mol) in THF (100 mL)/dioxane (300 mL) at room temperature. Tetrabutylammonium bromide (2 g, 0.006 mol) was added, the THF removed by distillation, and the reaction refluxed for 2 days. On cooling the reaction mixture the polymer precipitated from solution. Excess thallium reagent was destroyed by the addition of concentrated hydrochloric acid (18 mL, 0.2 mol). The polymer was redissolved by heating the reaction vessel and the supernatant decanted from the thallium chloride. The solvent volume was reduced and the polymer precipitated by pouring the hot dioxane solution into hot water. The polymer was then taken up into hot dioxane and reprecipiated into methanol. The polymer was collected, redissolved in dioxane, hot filtered, and when the solution had cooled, isolated by filtration (8.51 g, 24%). Anal. Calcd for $C_{14}H_{14}NO_4P$: C, 57.74; H, 4.84; N, 4.81; P, 10.64; Cl, 0.0. Found: C, 58.02; H, 4.83; N, 4.80; P, 10.68; Cl, 0.012. IR (film) 3060, 3000, 2950 (m, CH), 2830 (m, CH_3), 1507 (s, ring), 1200 (vs, br, PN). ^{31}P NMR (C_6D_6) −18.93 (singlet).

Synthesis of Poly[bis(4-(methylthio)phenoxy)phosphazene] (12). Thallium 4-(methylthio)phenoxide (white solid, 34 g, 0.10 mol) was added to a solution of the $(NPCl_2)_3/(NPCl_2)_x$ mixture (3.48 g, 0.03 mol) in THF (100 mL)/dioxane (300 mL) at room temperature. Tetrabutylammonium bromide (0.5 g, 0.0015 mol) was added, the THF removed by distillation, and the reaction refluxed for 3 days. On cooling the reaction mixture the polymer precipitated from solution. Excess thallium reagent was destroyed with hydrochloric acid (5 mL, 0.055 mol). The polymer was redissolved by heating the reaction vessel and the supernatant decanted from the thallium chloride. The solvent volume was reduced and the polymer precipitated by pouring the hot dioxane solution into hot water. The polymer was collected, redissolved in dioxane, hot filtered, and precipitated into methanol. The polymer was then hot filtered in dioxane, and when the solution had cooled it was isolated by filtration (2.00 g, 21%). Anal.[23] Calcd for $C_{14}H_{14}NO_2PS_2$: C, 52.00; H, 4.36; N, 4.33; P, 9.58; Cl, 0.0. Found: C, 50.79; H, 4.05; N, 4.15; P, 9.22; Cl, 0.003. IR (film) 2910 (w, CH_3), 1488 (s, ring), 1205 (vs, br, PN). ^{31}P NMR (DMSO, 110 °C) −20.85 (singlet).

Synthesis of Poly[bis(4-(dimethylamino)phenoxy)phosphazene] (13). A solution of $(NPCl_2)_3/(NPCl_2)_x$ mixture (5.8 g, 0.05 mol) in THF (200 mL) was added to a slurry of thallium 4-(dimethylamino)phenoxide (white solid, 50 g, 0.15 mol) in THF (100 mL) at room temperature. Tetrabutylammonium bromide (1 g, 0.003 mol) was added, and the reaction was refluxed overnight. Anisole was added, the THF removed by distillation, and heating (110 °C) continued for 2 more days. On cooling the reaction mixture, the polymer precipitated from solution. Excess thallium reagent was destroyed by the addition of hydrochloric acid (5 mL, 0.055 mol). The polymer was redissolved by heating and the supernatant decanted from the thallium chloride. The supernantant was allowed to cool and the solid collected and washed with a large excess of water. The polymer was successively taken up in hot pyridine and precipitated into water, methanol, and water (3.87 g, 24%). Anal. Calcd for $C_{16}H_{20}N_3O_2P$: C, 60.56; H, 6.35; N, 13.24; P, 9.76; Cl, 0.0. Found: C, 60.48; H, 6.28; N, 12.97; P, 9.90; Cl, 0.008. IR (film) 2850 (m, br, C–H), 1513 (s, ring), 1200 (vs, br, PN). ^{31}P NMR (C_6D_5Cl, 100 °C) −19.02 (singlet).

Acknowledgment. We are grateful to M. Y. Hellman for the molecular weight determinations.

Registry No. **3**, 117371-31-0; **4**, 74799-72-7; **5**, 1184-42-5; **6**, 117371-32-1; **7**, 60160-20-5; **8**, 108112-49-8; $(NPCl_2)_3$, 940-71-6; iodine, 7553-56-2; (4-hydroxyphenyl)trimethylammonium iodide, 6545-97-7; 4-aminophenol, 123-30-8; iodomethane, 74-88-4; 4-(dimethylamino)phenol, 619-60-3; ethanolamine, 141-43-5; thallium 4-*tert*-butylphenoxide, 117371-33-2; thallium 4-(dimethylamino)phenoxide, 117371-34-3; thallium propargyl oxide, 117371-35-4.

References and Notes

(1) *ACS Symp. Ser.* **1988**, *No. 360*, 250–312.
(2) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(3) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
(4) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.
(5) Allcock, H. R. *Chem. Eng. News* **1985**, *63*(11), 22.
(6) (a) Neilson, R. H.; Ford, R. R.; Hani, R.; Roy, A. K.; Scheide, G. M.; Wettermark, U. G.; Wisian-Neilson, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 442. (b) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910. (c) Neilson, R. H.; Hani, R.; Scheide, G. M.; Wettermark, U. G.; Wisian-Neilson, P.; Ford, R. R.; Roy, A. K. In Reference 1, p 283. (d) Neilson, R. H.; Wisian-Nelson, P. *Chem. Rev.* **1988**, *88*, 541.
(7) Schneider, N. S.; Desper, C. R.; Beres, J. J. In *Liquid Crystalline Order in Polymers*; Blumstein, A., Ed.; Academic Press: New York, 1978; Chapter 9.
(8) Taylor, E. C.; McKillop, A. *Acc. Chem. Res.* **1970**, *3*, 338.
(9) Taylor, E. C.; McLay, G. W.; McKillop, A. *J. Am. Chem. Soc.* **1968**, *90*, 2422.
(10) Austin, P. E.; Riding, G. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.
(11) Tanaka, H.; Gomez, M. A.; Tonelli, A. E.; Chichester-Hicks, S. V.; Haddon, R. C. *Macromolecules* **1988**, *21*, 2301. Tanaka, H.; Gomez, M. A.; Tonelli, A. E.; Chichester-Hicks, S. V.; Haddon, R. C. *Macromolecules*, in press.
(12) Allcock, H. R.; Neenan, T. X. *Macromolecules* **1986**, *19*, 1495.
(13) Alcock, H. R.; Levin, M. L.; Austin, P. E. *Inorg. Chem.* **1986**, *25*, 2281.

(14) Haddon, R. C.; Stein, S. M.; Chichester-Hicks, S. V.; Marshall, J. H.; Kaplan, M. L.; Hellman, M. Y. *Mater. Res. Bull.* **1987**, *22*, 117.
(15) Haddon, R. C.; Chichester, S. V.; Bowmer, T. N. In Reference 1, p 296.
(16) Oae, S.; Price, C. C. *J. Am. Chem. Soc.* **1958**, *80*, 3425.
(17) Hünig, S.; Baron, W. *Chem. Ber.* **1957**, *90*, 395.
(18) Crossley, M. L.; Dreisbach, P. F.; Hofmann, C. M.; Parker, R. P. *J. Am. Chem. Soc.* **1952**, *74*, 573.
(19) Bordwell, F. G.; Boutan, P. J. *J. Am. Chem. Soc.* **1956**, *78*, 87.
(20) Fitzsimmons, B. W., Shaw, R. A. *J. Chem. Soc.* **1964**, 1735.
(21) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; Laliberte, B. R.; Sacher, R. E.; Matton, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 433.
(22) Dieck, R. L.; Goldfarb, L. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 361.
(23) The microanalytical discrepancy for **12** may result from incomplete combustion of the sample. See ref 13 and 24.
(24) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980**, *13*, 1325.

Studies of the Phase Transitions in Poly[bis(4-ethylphenoxy)phosphazene] and Poly[bis(4-*tert*-butylphenoxy)phosphazene]. 1. ^{31}P NMR Study

Hajime Tanaka,[†] M. A. Gomez,[‡] A. E. Tonelli,* S. V. Chichester-Hicks, and R. C. Haddon

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received May 13, 1988; Revised Manuscript Received July 25, 1988*

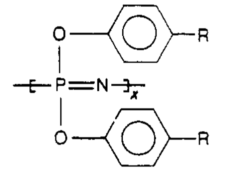
ABSTRACT: The solid–liquid crystalline phase transition of poly[bis(4-ethylphenoxy)phosphazene] has been studied by solid-state ^{31}P NMR. The glass transition of poly[bis(4-*tert*-butylphenoxy)phosphazene] has also been studied. There are a number of transitions in poly[bis(4-ethylphenoxy)phosphazene] which strongly depend on thermal history. The highest premelt transition $T(1)$ around 110 °C is assigned to the solid to liquid crystalline transition from the abrupt change in the mobility of the poly[bis(4-ethylphenoxy)phosphazene] backbone observed by ^{31}P NMR. Three resonances having different chemical shifts are observed at room temperature (below $T(1)$) in poly[bis(4-ethylphenoxy)phosphazene] and assigned to the crystalline, interfacial, and amorphous phases. Poly[bis(4-*tert*-butylphenoxy)phosphazene] has a much higher T_g than poly[bis(4-ethylphenoxy)phosphazene], shows little evidence of crystallinity, and appears to be liquid crystalline both above and below T_g.

Introduction

Recently[1] we have reported preliminary results of a multinuclear NMR study of poly[bis(4-ethylphenoxy)phosphazene]. Polyphosphazenes are unusual among synthetic polymers in that they have an inorganic backbone consisting of alternating N and P atoms. This results in various unique properties,[2–17] such as unusual mechanical and thermal properties and biocompatibility. A wide variety of side groups may be attached to the backbone P atoms leading to a large number of chemically unique polyphosphazenes. It is well-known[18] that most semicrystalline polyphosphazenes have three transitions: T_g, the thermotropic transition from crystalline to mesophase, and the melting transition. Among these transitions, the thermotropic transition is unique and interesting. Furthermore, recently[19–21] it has been found that some polyphosphazenes, whose substituents have the structures $-OC_6H_4X$, have multiple crystalline forms below $T(1)$, the crystal–liquid crystal transition, and their occurrence depends on the crystallization conditions.

These crystalline modifications and the mesophase have been studied mainly by X-ray diffraction, electron diffraction, and thermal analysis. Only a few studies[8,22,23] have been concerned with the dynamic properties of polyphosphazenes. High-resolution solid-state NMR is one of the most powerful methods available for the study of the dynamics and conformations of solid polymers. However, to our knowledge there are no reported studies of the phase transitions in polyphosphazenes by high-resolution solid-state NMR. Generally polyphosphazenes have two kinds of nuclei, ^{31}P and ^{13}C, which are readily observed[23] by NMR. ^{31}P, which is an abundant spin, gives information concerning the mobility and conformation of the backbone, while ^{13}C NMR gives information on the conformation, packing, and mobility of the side groups. Together ^{31}P and ^{13}C NMR provide comprehensive information with which we may begin to understand the physical properties of the polyphosphazenes. Information concerning the backbone mobility and conformation may shed light on the nature of the crystalline and liquid crystalline states in polyphosphazenes.

Poly[bis(4-ethylphenoxy)phosphazene] and poly[bis(4-*tert*-butylphenoxy)phosphazene] are typical polyphosphazenes; however they have not been widely studied.[24,25]



R = CH_2CH_3 or $C(CH_3)_3$

Here we focus our attention on the motional and conformational states of these two polyphosphazenes. We mainly report on the crystal–liquid crystal transition in poly[bis(4-ethylphenoxy)phosphazene] and the glass transition in poly[bis(4-*tert*-butylphenoxy)phosphazene]. Comparison of the results observed for poly[bis(4-ethylphenoxy)phosphazene] and poly[bis(4-*tert*-butylphenoxy)phosphazene] permits a discussion of the effects of side-chain bulkiness on the formation of crystal and liquid crystalline phases. The results of solid-state ^{13}C NMR and

---

[†] Permanent address: Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

[‡] Permanent address: Instituto de Plasticos y Caucho, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain.

0024-9297/89/2222-1031$01.50/0