It is evident from these results that although the bulk of the reaction is carried by the ion pair, a significant portion of the reaction is carried by the free ion. From these plots it is possible to derive from the intercept that the ion-pair rate is $1.40 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$. From the different dependence on k_p of the two slopes, the dissociation constant of the living end ion pair is 3.7×10^{-6}, and the free-ion rate constant is calculated as $1.0 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}$.

This dissociation constant compares with the 5.4×10^{-6} found for triethyloxonium tetrafluoroborate and 4.4×10^{-6} for the low molecular weight polymer oxonium salt, both found from conductance data in pure methylene chloride. Although the kinetic figure is probably not too reliable, it is evidently close to the expected value and lends credence to the suggestion that the free ions are participating in the reaction.

The calculated free-ion rate is only a factor of 7 greater than that of the ion pair, compared with the factor of 10^3 in the anionic polymerization of hydrocarbon monomers. This factor was found recently to be low also for the polymerization of episulfides[9] and was ascribed to the attack being on the carbon α to the charged atom instead of on the charged atom as in the anionic case. Here also the attack is at the carbon α to the charge. This ratio was also found to be low for the polymerization of ethylene oxide by potassium alkoxides in hexamethylphosphoramide,[10] but in general the kinetic behavior was complex in this system.

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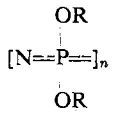
Communications to the Editor

Synthesis of Poly(organophosphazene) Copolymers and Cross-Linked Polymers by Ligand Exchange

High molecular weight poly(alkoxy- and aryloxyphosphazenes) of structure I can be synthesized by the interaction of sodium alkoxides and aryloxides with poly(dichlorophosphazene), $(NPCl_2)_n$.[1,2]



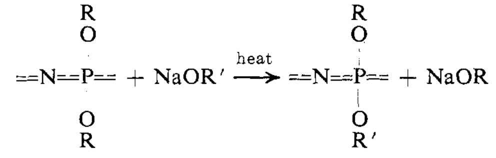
$$[N{=}\overset{OR}{\underset{OR}{P}}{=}]_n$$

I

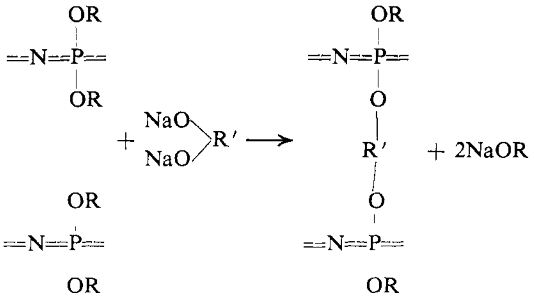
Polymers have been prepared which contain ligands such as OCH_3, OC_2H_5, OCH_2CF_3, $OCH_2C_2F_5$, $OCH_2C_3F_7$, and OC_6H_5, with 15,000 or more repeating units in the chain. With one exception,[3] where two different nucleophiles were allowed to react simultaneously with poly(dichlorophosphazene), the organo-substituted polymers reported to date have been homopolymers. The rubbery or thermoplastic polymers prepared by this route are not cross-linked, a fact which limits their applicability.

We now report a method for the preparation of alkoxyphosphazene copolymers or cross-linked poly(organophosphazenes) by ligand-exchange reactions. The two processes are exemplified by the reactions shown in Schemes I and II.

SCHEME I



SCHEME II



For example, poly[(heptafluorobutoxy)(trifluoroethoxy)-phosphazene], $[NP(OCH_2C_3F_7)(OCH_2CF_3)]_n$, can be prepared by allowing sodium 2,2,3,3,4,4,4-heptafluorobutoxide to react with a solution of poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)]_n$ (II), in dry tetrahydrofuran. The copolymers formed by this method vary from elastomers to gums, depending on the ratio of alkoxide to polymer in the reaction mixture. In a similar manner, poly[(pentafluoropropoxy)(trifluoroethoxy)phosphazene], $[NP(OCH_2C_2F_5)(OCH_2CF_3)]_n$, can be prepared from II and sodium 2,2,3,3,3-pentafluoropropoxide.

II can be cross-linked by reaction with the disodium salt of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol in tetrahydrofuran. The cross-linked polymers formed by this process swell in solvents such as tetrahydrofuran, but, unlike the precursor polymer, they do not dissolve. The degree of cross-linking is enhanced by increases in the ratio of diol salt to poly(organophosphazene), with the degree of swelling being correspondingly reduced. Extensive cross-linking is also accompanied by a change in the polymer properties from those of a flexible thermoplastic to those of a stiff, leathery material. Poly[bis(heptafluorobutoxy)phosphazene], $[NP(OCH_2C_3F_7)_2]_n$, reacts similarly with the hexafluoro-1,5-pentanediol salt in a Freon TA–tetrahydrofuran solvent system.

Copolymer Formation. A solution prepared from 2,2,3,3,-4,4,4-heptafluorobutanol (3.00 g, 0.015 mol) and sodium (0.35 g, 0.015 g-atom) in dry tetrahydrofuran (100 ml) was added to a stirred solution of poly[bis(trifluoroethoxy)phosphazene] (2.43 g, 0.010 mol/monomer unit) in dry tetrahydrofuran (200 ml) at 25°. The mixture was heated to reflux and allowed to react for 4 hr. After cooling, the polymer was precipitated into cold water (2000 ml), washed with water, and reprecipitated from Freon TA into heptane by pressure filtration through a Millipore filter. The resultant polymer was a

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(2) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, 5, 1709 (1966).

(3) S. H. Rose, *Polym. Lett.*, 6, 837 (1968).

rubbery elastomer. *Anal.* Calcd for $C_6H_4O_2F_{10}NP$ (1:1 copolymer): C, 20.99; H, 1.17; F, 55.39; N, 4.08; P, 9.04. Found: C, 20.69; H, 1.55; F, 55.66; N, 4.42; P, 8.32. Treatment of the poly[bis(trifluoroethoxy)phosphazene] with an equimolar amount of sodium heptafluorobutoxide yielded a copolymer which was a gum. A solution of poly[bis(trifluoroethoxy)phosphazene] (5.83 g, 0.024 mol) in dry tetrahydrofuran (200 ml) was treated with a solution prepared from 2,2,3,3,3-pentafluoropropanol (3.62 g, 0.024 mol) and sodium (0.55 g, 0.024 g-atom) in dry tetrahydrofuran (100 ml) in the same manner as described above. The resulting copolymer was a flexible, film-forming material, but it showed no elastomeric properties.

Cross-Linking. To a stirred solution of poly[bis(trifluoroethoxy)phosphazene] (6.4 g, 0.026 mol/monomer unit) in dry tetrahydrofuran (50 ml) at 25° was added a filtered solution prepared from 2,2,3,3,4,4-hexafluoropentanediol (0.28 g, 0.0013 mol) and sodium (0.06 g, 0.0026 g-atom) in tetrahydrofuran (25 ml). A viscosity increase occurred immediately and gelation took place within 10 min. Removal of the solvent yielded a polymer almost indistinguishable in appearance and flexibility from the un-cross-linked form. *Anal.* Calcd for $C_{81}H_{80}O_{40}F_{120}N_{20}P_{20}$ (one cross-link per ten monomer units): C, 19.55; H, 1.64. Found: C, 19.92; H, 1.88. Treatment of the un-cross-linked polymer with ten times the amount of disodium hexafluoropentanedioxide (2.8 g, 0.013 mol) in tetrahydrofuran (30 ml) yielded a rubbery conglomerate. Sodium trifluoroethoxide was extracted by prolonged treatment with tetrahydrofuran, and a leathery material was obtained after exhaustive drying. *Anal.* Calcd for $C_{13}H_{12}O_6F_{18}N_3P_3$ (two cross-links per three monomer units): C, 21.04; H, 1.62. Found: C, 21.05; H, 2.03. In these polymers, fluorine analysis cannot be used for characterization, since the fluorine content is almost independent of the degree of cross-linking.

A solution of poly[bis(heptafluorobutoxy)phosphazene] (1.0 g, 0.0023 mol) in Freon TA solvent (50 ml) was treated with a solution prepared from 2,2,3,3,4,4-hexafluoropentanediol (0.05 g, 0.00023 mol) and sodium (0.01 g, 0.00046 g-atom) in dry tetrahydrofuran (20 ml). Precipitation began almost immediately and gelation and phase separation took place slowly during 3 days. The product was insoluble in Freon TA but was swelled by this solvent. Similar results were obtained when half the concentration of cross-linking agent was employed (5 mol %).

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