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Polymerization and Copolymerization of Phenylhalogenocyclotriphosphazenes[1,2]

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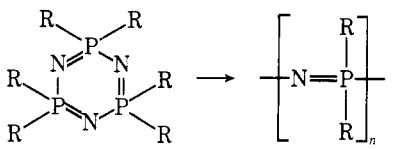
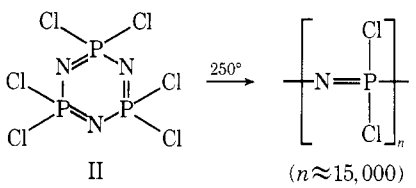
ABSTRACT: $N_3P_3F_5Ph$ (III) homopolymerizes when heated, but gem-$N_3P_3Cl_4Ph_2$ (IV), gem-$N_3P_3F_4Ph_2$ (V), non-gem-$N_3P_3Cl_3Ph_3$ (VI), gem-$N_3P_3Cl_2Ph_4$ (VII), $N_3P_3ClPh_5$ (VIII), and $(NPPh_2)_3$ (IX) do not. However, compounds III, IV, V, and VI copolymerize with $(NPCl_2)_3$ (II), whereas VII, VIII, and IX inhibit the polymerization of II. The polymers were derivatized by placement of halogen with CF_3CH_2O-, or piperidino groups, and the properties of these thermoplastics and elastomers were examined. The mechanistic implications of the results are discussed.

The synthesis of poly(organophosphazenes) by the nucleophilic replacement of chlorine in poly(dichlorophosphazene) by alkoxy, aryloxy, or amino residues is a growing field with a broad potential for both fundamental studies and new applications.[3-13] However, the *direct* formation of poly(organophosphazenes) (I) by the polymerization of



I

fully substituted organocyclotri- or tetraphosphazenes has met with little success. Although halo- or pseudohalocyclophosphazenes, such as $(NPCl_2)_3$, (II), $(NPF_2)_3$, $(NPBr_2)_3$, or $[NP(NCS)_2]_3$, polymerize thermally,[14] hexakisalkoxy, aryloxy, or aminocyclotriphosphazenes do not.

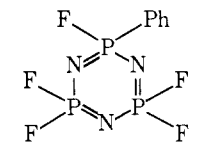


II ($n \approx 15,000$)

In this work we have attempted to clarify this question by an investigation of the polymerization behavior of cyclotriphosphazenes that contain both organic and halogen substituents. The phenyl substituent was chosen as the organic unit because of the high stability of phosphorus–phenyl bonds and the presumed low tendency of phenyl groups to ionize from phosphorus at elevated temperatures. Both chlorine and fluorine were examined as halogen substituents. The objectives of the work were: (1) to establish if any phenylhalocyclotriphosphazenes could be converted directly to linear-type polymers; (2) to determine if any of these phenyl-substituted phosphazenes would copolymerize with chlorocyclophosphazenes, such as $(NPCl_2)_3$; and (3) to utilize the results of these experiments to throw light on the reasons why hexakis-organic-substituted trimers do not polymerize.

Results and Discussion

The phenylhalocyclotriphosphazenes synthesized for this study are depicted in III–VIII. Hexaphenylcyclotriphosphazene (IX) was also prepared. In each case, comparisons were made with the polymerization behavior of hexachlorocyclotriphosphazene (II), and copolymerizations with II were also attempted. A number of attempts were made



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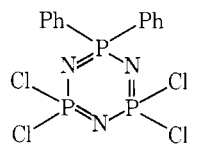

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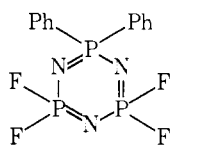

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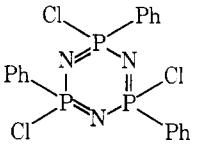
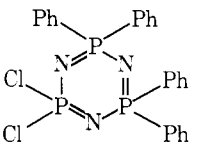


VI



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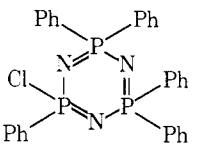
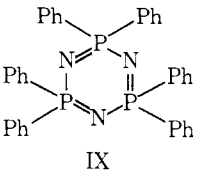


VIII



IX

Ph = C_6H_5

Table I
Summary of Polymerization and Copolymerization Data for Halocyclophosphazenes and Phenylhalocyclophosphazenes[a-c]

Cyclic trimer	Homopolymerization	Homopolymerization[e]	Copolymerization with $(NPCl_2)_3$
$(NPF_2)_3$	+	+	+
$(NPCl_2)_3$[d] (II)	+	+	+
$N_3P_3F_5Ph$ (III)	+	+	+
Gem-$N_3P_3Cl_4Ph_2$ (IV)	−	−	+
Gem-$N_3P_3F_4Ph_2$ (V)	−	−	+
Non-gem-$N_3P_3Cl_3Ph_3$ (VI)	−	−	+
Gem-$N_3P_3Cl_2Ph_4$ (VII)	−	−	−
$N_3P_3ClPh_5$ (VIII)	−	−	−
$(NPPh_2)_3$ (IX)	−	−	−

[a] Ph = C_6H_5. [b] The reaction conditions were 250–300° in evacuated, sealed glass tubes. [c] A plus sign indicates that polymerization occurred, and a minus sign indicates that it did not. [d] See ref 2, 4, 14, 15, 20, 21, and 25. [e] With 1% water present.

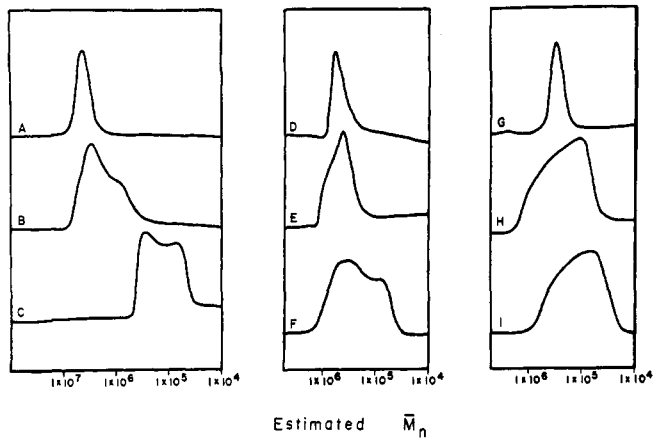


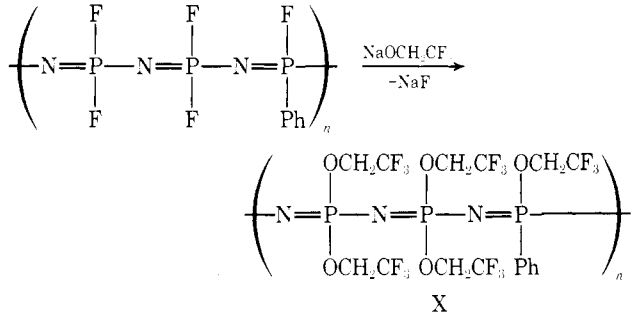
Figure 1. Gel permeation chromatography curves for: A, $[NP(OCH_2CF_3)_2]_2$;[3,4,18] B, $[NP(OPh)_2]_n$; C, polymer XIII; D, polymer XII; E, polymer XIV; F, polymer XV; G, polymer X; H, polymer X synthesized with the use of 1% water present during the polymerization step; I, polymer XI. The data for $[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ constitute calibration curves based on previous work.[2,18,33]

to synthesize $N_3P_3Cl_5Ph$, but these were unsuccessful. The following discussion will be divided into (1) homopolymerization reactions, (2) copolymerizations with $(NPCl_2)_3$, (3) characterization and properties of the polymers, and (4) conclusions and mechanistic implications.

(1) Homopolymerizations. The homopolymerization data are summarized in Table I. In each case the polymerizations were attempted with the trimer sealed in evacuated glass tubes and heated for up to 336 hr at temperatures up to 300°. Of the phenyl-substituted trimers, only $N_3P_3F_5Ph$ (III) could be induced to homopolymerize. This result strikingly illustrates the severe inhibiting effect of phenyl substituent groups on the polymerization. The failure of $N_3P_3Cl_4Ph_2$ and $N_3P_3Cl_2Ph_4$ to homopolymerize suggests that the absence of a PCl_2 unit is not in itself an inhibitory feature. Moreover, the fact that water does not catalyze the thermal homopolymerization of IV–VIII (Table I) suggests that these differences cannot be attributed to the presence or absence of traces of catalytic water or hydroxyphosphazenes.[2] Possible reasons for these differences from the behavior of $(NPCl_2)_3$ are given in a later section. Attempts to induce polymerization of III–IX by exposure to γ rays yielded no polymer, although II polymerized under these conditions.

(2) Copolymerizations. As shown in Table I, all the cyclic trimers could be induced to copolymerize with $(NPCl_2)_3$ except compounds VII, VIII, and IX. Again the pattern is one of inhibition of polymerization with increasing phenylation of the trimer. However, the copolymerization was less sensitive in this respect than the homopolymerization. Curiously, $N_3P_3Cl_3Ph_3$ (VI) copolymerized with $(NPCl_2)_3$, but gem-$N_3P_3Cl_2Ph_4$ (VII) did not, and this is a further indication that the presence of a PCl_2 unit is not a prerequisite for polymerization.

(3) Characterization and Properties of the Polymers. Chloro- and fluorophosphazene high polymers are sensitive to atmospheric moisture.[2,16] For this reason most of the polymers prepared in this study were derivatized by replacement of the halogen atoms with sodium trifluoroethoxide. The derivatization procedure is illustrated by the reaction



X

No evidence was found that derivatization using sodium trifluoroethoxide altered the chain length or phenyl content of the polymers.

Polymers and Copolymers from $(NPF_2)_3$. Hexafluorocyclotriphosphazene was shown previously to polymerize in a high pressure system at 350° to yield an insoluble rubbery elastomer.[16,17] Traces of water do not inhibit this polymerization. The same trimer copolymerized with an equimolar amount of II at 300°, but the elastomeric product was insoluble and could not be characterized.

Polymers from $N_3P_3F_5Ph$ (III). The polymer obtained by homopolymerization of III was a colorless elastomer that was extremely sensitive to atmospheric moisture. It was derivatized with the use of sodium trifluoroethoxide. The derivatized polymer was a white, adhesive thermoplastic that was soluble in tetrahydrofuran or acetone. This polymer was estimated to have an $\bar{M}_n$ molecular weight near 300,000 by gel permeation chromatography analysis (Figure 1). An intrinsic viscosity value of 0.32 dl/g in tetrahydrofuran was found. The infrared spectrum showed peaks at 2988 w (C–H), 1594 w (aryl), 1486 w (aryl), 1453 m (C–H), 1443 m (P–aryl), 1421 s (P–O–C), 1285 s (P=N), 1244 s (P=N), 1167 s (P–O–), 1128 s (P–aryl), 1085 s (C–O), 1032 w (aryl), 1002 w (P–aryl), 966 s (P–O), 877 m (CH_2), 848 m (CH_2), 754 m (aryl), 698 m (aryl), 662 m (CF_3), 565 s cm^{-1}, which provided confirmation for the expected linear or macrocyclic structure. The microanalysis data (see Experimental Section) were consistent with the structure X. The property differences between this polymer and $[NP(OCH_2CF_3)_2]_n$[4,18] can perhaps be ascribed to lower molecular weight and a lower degree of crystallinity.

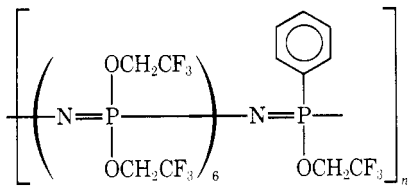
Trimer (III) was also polymerized thermally in the presence of 1 mol % water to yield a clear, amber-colored elastomer. This was derivatized with sodium trifluoroethoxide to yield a film-forming polymer that was of lower molecular

weight than the product discussed above. The $\bar{M}_n$ value (gel permeation chromatography) was approximately 100,000 and the intrinsic viscosity was 0.29 dl/g in tetrahydrofuran. The infrared spectrum was virtually identical with that of the product described above.

Copolymers. The polymers formed by copolymerization of $N_3P_3F_5Ph$ (III), gem-$N_3P_3Cl_4Ph_2$ (IV), gem-$N_3P_3F_4Ph_2$ (V), or non-gem-$N_3P_3Cl_3Ph_3$ (VI) with $(NPCl_2)_3$ (II) in a 1:1 molar ratio at 250° were brown, soluble elastomers. Each copolymer was then derivatized with sodium trifluoroethoxide to yield film-forming thermoplstics. They were less flexible at 25° than films of $[NP(OCH_2CF_3)_2]_n$.

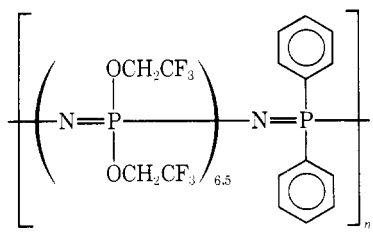
$\bar{M}_n$ value molecular weights were estimated from gel permeation chromatography data. These values and the intrinsic viscosities are listed in Table II.

Infrared spectra of the trifluoroethoxy-substituted polymers closely resembled the spectrum described above for the derivatized polymer from $N_3P_3F_5Ph$. In particular, the presence of both phenyl and trifluoroethoxy side groups was confirmed, and the persistence of the phosphazene skeleton was evident. Microanalyses (see Experimental section) were consistent with a linear (or macrocyclic) structure, with the ratios of the repeating units being consistent with the following formulas (XI–XIV).



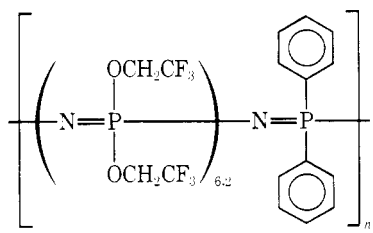
XI

(from $N_3P_3F_5Ph$ and $(NPCl_2)_3$)



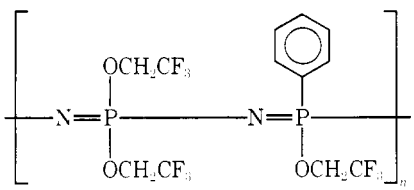
XII

(from gem-$N_3P_3Cl_4Ph_2$ and $(NPCl_2)_3$)



XIII

(from gem-$N_3P_3F_4Ph_2$ and $(NPCl_2)_3$)



XIV

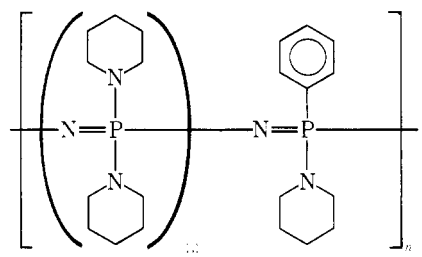
(from non-gem-$N_3P_3Cl_3Ph_3$ and $(NPCl_2)_3$)

A copolymer formed from non-gem-$N_3P_3Cl_3Ph_3$ and $(NPCl_2)_3$ was also derivatized with piperidine. Microanalysis of this polymer indicated the structure shown in XV. Both phenyl and piperidino groups were detected from the infrared spectrum of XV. It is of interest that the $\bar{M}_n$ and intrinsic viscosity values for polymer XV were somewhat lower that those found for polymer XIV, and this is consistent with the observation noted previously[7] that aminolysis of chlorophosphazene chains frequently results in some chain cleavage.

Table II
Estimated $\bar{M}_n$ Values[a] and Intrinsic Viscosities[a] for Derivatized Copolymers of III–VI with $(NPCl_2)_3$[b]

Cotrimer	$\bar{M}_n$	μ, dl/g
$N_3P_3F_5Ph$ (III)	66,000	0.25[c]
Gem-$N_3P_3Cl_4Ph_2$ (IV)	500,000	0.47[c]
Gem-$N_3P_3F_4Ph_2$ (V)	250,000	0.30[c]
Non-gem-$N_3P_3Cl_3Ph_3$ (VI)	400,000	0.39[c]
	300,000	0.31[d]

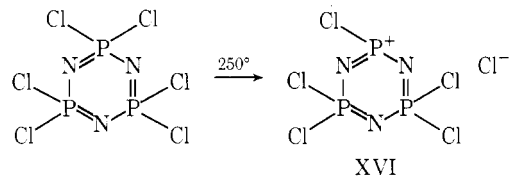
[a] In tetrahydrofuran solution. [b] 1:1 molar mixtures of the polymerization components were used. [c] Derivatized with $NaOCH_2CF_3$. [d] Derivatized with piperidine.



XV

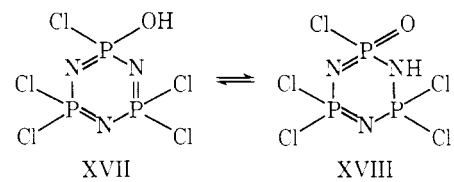
Conclusions and Mechanistic Implications. The results show that the introduction of phenyl groups into a fluoro- or chlorophosphazene trimer reduces the reactivity toward homopolymerization and copolymerization and, at the same time, lowers the molecular weight of the polymers formed. Two explanations can be formulated to explain these observations: first, a mechanistic reason and, second, a thermodynamic one.

The mechanism of polymerization of $(NPCl_2)_3$ has been studied in some detail.[14] This reaction is believed to follow an ionic mechanism,[15,19–21] and to be initiated by ionization of chloride ion from phosphorus[15] (XVI). However, traces



XVI

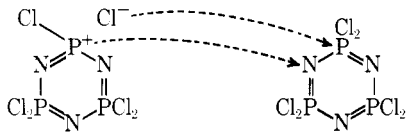
of water function as a polymerization catalyst, and hydroxyphosphazenes (XVII) or oxophosphazanes (XVIII) may



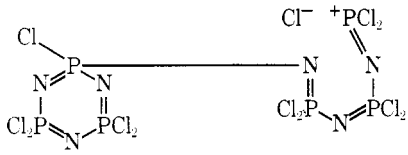
XVII XVIII

also be initiators.[2] Under anhydrous conditions, subsequent steps in the mechanism may involve attack by a phosphazenium cation (XVI) on nitrogen as shown in XIX.

The introduction of phenyl groups in place of chlorine or fluorine could (a) reduce the number of chlorine atoms



XIX



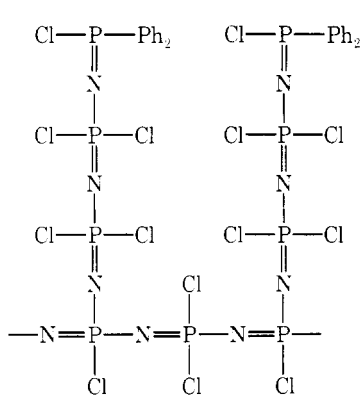
XX

available for ionization, (b) lower the tendency for ionization of chlorine by withdrawal of electrons from phosphorus by a conjugative mechanism,[22] (c) sterically retard attack either by a growing chain end or at the phosphorus atom to which the phenyl group is attached, (d) mechanistically reduce the reactivity of the remaining P–Cl bonds to hydrolysis and hence lower the tendency for formation of species analagous to XVII or XVIII, or (e) protect the trimer physically from attack by atmospheric moisture because of hydrophobic influence of the phenyl groups.

Possibilities (d) and (e) appear unlikely in view of the fact that the deliberate introduction of water into the system had no perceptible accelerating influence. However, possibility (c) seems plausible since, even when PCl_2 units are present in the trimer, the chain ends could consist of PClPh or PPh_2 units. Perhaps even more significant is the observation that compounds VII, VIII, and IX actually inhibited the polymerization of $(NPCl_2)_3$. Presumably, species such as XVI or XX could attack compounds such as VII, VIII, and IX but once these latter units form the chain ends, propagation would be inhibited. This viewpoint is also consistent with the observation that the copolymers formed from $(NPCl_2)_3$ and IV or V are of shorter chain length than those normally obtained by the homopolymerization of $(NPCl_2)_3$.

Phenyl groups could also affect the ring–polymer equilibria that are believed to exist in these systems. The geometries of organophosphazene cyclic trimers are such that intramolecular steric repulsions are lower in trimers than in the linear polymers.[14,23-25] Hence, it is conceivable that ring opening of species such as IV–IX under homopolymerization conditions may occur at elevated temperatures but that recyclization to form a trimer is the preferred subsequent step.

Finally, the prospect must also be considered that the copolymers are not formed by linear copropagation but could be graft copolymers with structures such as, for example, XXI. Two items of evidence suggest that the graft



XXI

structure is not a principal component of the copolymer. First, it is difficult to rationalize the total *inhibition* of $(NPCl_2)_3$ polymerization by gem-$N_3P_3Cl_2Ph_4$ or $N_3P_3ClPh_5$ if graft addition of the comonomer is the principal reaction. Thus, inhibition of retardation of the main chain growth is understandable only if the cotrimer is introduced at the principal propagation site. Second, pyrolysis of polymer XIV at 400° in a helium flow system[18] yielded an oily distillate. Mass spectra of this mixture provided evidence for the presence of cyclic oligomers such as $[NP(OCH_2CF_3)_2]_{3-5}$, but no $[NP(OCH_2CF_3)(Ph)]_3$ was detected. Among the broad range of oligomers found that were derived from *both* $(NPCl_2)_3$ and $(NPClPh)_3$ were oligomeric ions or fragments of formula A_xB_y (where A is $NP(OCH_2CF_3)_2$ and B is $NP(OCH_2CF_3)(Ph)$) including A_2B, A_3B, A_4B, AB_2, A_2B_2, A_3B_2, AB_3, A_2B_3, AB_4, B_4, and B_5. Undoubtedly, the pyrolysis brings about some scrambling of repeating units. However, the oligomeric products detected are those that would be expected from structure XIV rather than XXI.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (El Monte Chemical Co.) was purified by vacuum sublimation at 50° (1×10^{-2} mm) followed by two recrystallizations from *n*-heptane. Sodium fluoride (Baker, Reagent) and aluminum chloride (Fisher Anhydrous) were dried at 110° for 24 hr before use. The following reagents were used as received from the manufacturer: phenyllithium (Alfa Products, 2.4 m in 70:30 benzene:ether), sodium azide (Alfa Products), phosphorus pentachloride (B & A), chlorodiphenylphosphine (Pfaltz and Bauer), dichlorophenylphosphine (Pfaltz and Bauer), ammonium chloride (Fisher, Certified ACS), ammonia (Matheson Gas Products), and chlorine (Matheson Gas Products). Benzene (Mallinckrodt Analytical Reagent) was dried by distillation from calcium hydride and acetonitrile (Baker Reagent) by distillation from P_4O_{10}. Tetrahydrofuran (Fisher, Reagent) was dried by distillation from CaH_2 for synthetic purposes but was used as received for gel permeation chromatography work. The following solvents were also used as received from the manufacturer: diethyl ether (Fisher, Anhydrous Reagent), chlorobenzene (Fisher, Purified), *n*-pentane (Fisher, Technical), and chloroform (Fisher, Certified).

Synthesis of Cyclic Phosphazenes. $(NPF_2)_3$ was synthesized by the interaction of $(NPCl_2)_3$ with sodium fluoride in acetonitrile.[26] A 75% yield of material (bp 50–51°) was obtained. $N_3P_3F_5Ph$ (III) was prepared by the reaction of $(NPF_2)_3$ with phenyllithium in diethyl ether.[27] A 65% yield of III (bp 35° (0.05 mm)) was obtained. Gem-$N_3P_3Cl_4Ph_2$ (IV) was obtained from a Friedel Crafts reaction between $(NPCl_2)_3$ and benzene.[28] The product, mp 93–95° (lit. 95.5°), was obtained in 19% yield after purification by two recrystallizations from *n*-heptane. Non-gem-$N_3P_3Cl_3Ph_3$ (VI) was prepared in 5% yield (mp 152–156°) by the reaction of $PhPCl_5$ with ammonium chloride.[29] Gem-$N_3P_3Cl_2Ph_4$ (VII) was synthesized from $[Ph_2(NH_2)P{=}NP(NH_2)Ph_2]^+Cl^-$[30,31] and phosphorus pentachloride[31] in 36.5% yield, mp 139–141°. $(NPPh_2)_3$ was prepared by the interaction of sodium azide (65 g, 1.0 mol) and diphenylchlorophosphine (220 g, 1.0 mol)[32] to yield $(NPPh_2)_3$ (60 g, 30%) (mp 228°) and $(NPPh_2)_4$ (15 g). The phosphonous azide intermediate *should not* be isolated from this reaction because of a possible detonation hazard.

Gem-$N_3P_3F_4Ph_2$ (V) was prepared by the following procedure. Gem-$N_3P_3Cl_4Ph_2$ (IV) (25.86 g, 0.06 mol) was distilled from P_4O_{10}, and sodium fluoride (45.6 g, 1.09 mol) was added to it. Ten drops of distilled water were added as catalyst and the mixture was heated at reflux for 1 week. The mixture was then filtered hot to remove sodium fluoride and sodium chloride, and the solvent was removed from the filtrate to leave a colorless oil. This solidified when cooled. The solid was extracted with hot *n*-heptane and removal of solvent from the extracts gave white, crystalline 1,1-diphenyl-3,3,5,5-tetrafluorocyclotriphosphazene (V): mp 63–65°, 7.3 g (33.3%); infrared spectra showed peaks at (cm^{-1}) 1585 (w), 1438 (s), 1254 (s), 1217 (s), 1180 (m), 1155 (m), 1122 (s), 1065 (w), 1025 (m), 994 (s), 951 (m), 925 (m), 904 (s), 819 (s), 737 (s), 728 (s), 691 (s), 629 (w), and 588 (s). Anal. Calcd for $C_{12}H_{10}F_4N_3P_3$: C, 39.45; H, 2.74; F, 20.82; N, 11.51; P, 25.48; mol wt 365. Found: C, 39.38; H, 2.79; F, 20.58; N, 11.53; P, 25.42; mol wt 365 (mass spectrum).

$N_3P_3ClPh_5$ (VIII) was prepared from phenyltetrachlorophosphorane and $[Ph_2(NH_2)P{=}NP(NH_2)Ph_2]^+Cl^-$. Phenyldichlorophosphine (8.00 g, 0.0447 mol) was dissolved in dry benzene (250 ml) and chlorine was bubbled through until the solution was bright yellow. Dry nitrogen was then bubbled through the solution until it became colorless. This procedure was designed to avoid the presence of free chlorine and the possibility of NCl_3 formation. This solution was then added dropwise to a refluxing, stirred suspension of $Ph_4P_2N_3H_4Cl$ (20.0 g, 0.0447 mol) in benzene (1200 ml). The addition was completed over a period of 3 hr. After 42 hr at reflux temperature, the reaction mixture was cooled and filtered, and 6.6 g of unreacted $Ph_4P_2N_3H_4Cl$ was recovered. The solvent was then removed on a rotary evaporator to leave a brown oil which did not crystallize on cooling. The oil was dissolved in hot acetonitrile and then cooled to yield a white crystalline solid. This was then filtered off, washed with a hot 1:1 mixture of *n*-pentane:chloroform, and the residue discarded. The solvent was removed on a rotary evaporator to leave a white solid which was recrystallized from acetonitrile to yield $N_3P_3ClPh_5$ (VIII) (mp 149–152°, yield 2.1 g, 8.5%). A number of unsuccessful attempts were made to prepare $N_3P_3Cl_5Ph$. Several reagents were used in an attempt to replace fluorine in $N_3P_3F_5Ph$ by chlorine. These included the use of NaCl in boiling acetonitrile, PCl_5 in refluxing tetrachloroethane, in refluxing (~185°), and $HgCl_2$ in refluxing acetonitrile. Starting materials only were recovered. An attempt was made at direct synthesis by the reaction of phosphorus pentachloride with ammonium chloride followed by addition of phenyltetrachlorophosphrane, but the only product isolated was hexachlorocyclotriphosphazene.

Polymerizations and Copolymerizations. Polymerization and Copolymerization of $(NPF_2)_3$. The polymerization of $(NPF_2)_3$ has been described previously.[16,17] However, it was of interest to examine both the effect of water on this reaction and the prospect that $(NPF_2)_3$ might copolymerize with $(NPCl_2)_3$. Hexafluorocyclotriphosphazene (4.98 g, 0.02 mol) was sealed in an evacuated glass tube together with water vapor (2×10^{-4} mol) (1 mol %) added via a vacuum line. The tube was then heated at 340° inside a nitrogen-pressured autoclave at 3000 psi for 4 hr. The resultant polymer was an amber colored rubbery elastomer that was insoluble in and unswelled by tetrahydrofuran, acetone, or benzene.

Hexafluorocyclotriphosphazene (2.49 g, 0.01 mol) and $(NPCl_2)_3$ (3.48 g, 0.01 mol) were sealed together in an evacuated glass tube. The tube was then heated in an autoclave at 300° and 2600 psi pressure for 6 hr. The product was an amber-colored elastomer which appeared to contain no residual trimer. The polymer hydrolyzed rapidly in contact with the atmosphere. It was insoluble in and unswelled by tetrahydrofuran, acetone, or benzene. It should be noted that pure $(NPF_2)_3$ cannot normally be polymerized thermally at temperatures below ~340°. Thus, the polymerization temperature is lowered by the presence of $(NPCl_2)_3$.

Polymerization of $N_3P_3F_5Ph$ (III). A sample of $N_3P_3F_5Ph$ (0.05 g, 0.00163 mol) was sealed in an evacuated glass tube. The tube was then placed in a thermoregulated oven at 300° for 42 hr. During this time, the mobile liquid was converted to a gel. This polymer was hydrolytically unstable and it was derivatized with sodium trifluoroethoxide for characterization. The polymer was dissolved in dry tetrahydrofuran (50 ml) and the solution was added slowly to a boiling solution of excess sodium trifluoroethoxide in tetrahydrofuran (100 ml). After 24 hr, the solvent was evaporated, the residue was dissolved in a minimum amount of tetrahydrofuran, and the polymer was precipitated twice into water. The polymer was then reprecipitated twice from the tetrahydrofuran into benzene to remove low molecular weight oligomers. The yield was 0.2 g (17% based on $N_3P_3F_5Ph$). Anal. Calcd for $C_{16}H_{15}F_{20}N_3O_5P_3$: C, 27.16; H, 2.12; F, 40.31; N, 5.94; P, 13.15. Found: C, 26.83; H, 2.04; F, 39.13; N, 5.78; P, 12.95. DSC curves suggested a glass transition at −69° and both endothermic and exothermic transitions in the −40 to −50° region. (The T_g value for $[NP(OCH_2CF_3)_2]_n$ is −66°.)

$N_3P_3F_5Ph$ (1.00 g, 3.26×10^{-3} mol) was also polymerized at 300° for 40 hr in the presence of 1 mol % water to yield a polymer similar in appearance and properties to the material formed in the absence of moisture. The yield was 0.46 g (20%). Anal. Calcd for $C_6H_5F_5N_3P_3$: C, 27.16; H, 2.12; F, 40.31; N, 5.94; P, 13.15. Found: C, 26.12; H, 2.00; F, 38.97; N, 5.91; P, 13.28.

Copolymerization of $N_3P_3F_5Ph$ (III) with $(NPCl_2)_3$. $N_3P_3F_5Ph$ (0.92 g, 3×10^{-3} mol) and $(NPCl_2)_3$ (1.04 g, 3×10^{-3} mol) were heated together and sealed in vacuum in a glass tube. The tube was then heated at 250° for 22 hr in a thermoregulated oven. The product was a rubbery elastomer that was sensitive to atmospheric moisture. It was derivatized using sodium trifluoroethoxide by the technique described earlier. The yield was 2.28 g (53%): infrared spectra showed peaks at (cm^{-1}) 2985 w (C–H), 1950 w (aryl), 1484 w (aryl), 1455 m (C–H), 1442 m (P–aryl), 1414 s (P–O–C), 1282 s (P=N), 1237 s (P=N), 1167 s (P–O–), 1123 s (P–aryl), 1082 s (C–O–), 1030 w (aryl), 1001 w (P–Ph), 965 s (P–O–), 870 m (CH_2), 844 m (CH_2), 751 m (aryl), 695 m (aryl), and 656 m (CF_3). Anal. Calcd for 1:1 copolymer ($C_{28}H_{29}F_{33}N_6O_{11}P_6$): C, 23.40; H, 1.88; F, 43.66; N, 5.85; P, 12.95. Calcd for structure XI: C, 22.87; H, 1.85; F, 44.13; N, 5.84; P, 12.92. Found: C, 22.76; H, 1.90; F, 41.80; N, 5.63; P, 12.71. DTA and DSC curves indicated the presence of T_g-like transitions at −53 and +60°.

Copolymerization of Gem-$N_3P_3Cl_4Ph_2$ (IV) with $(NPCl_2)_3$. Gem-$N_3P_3Cl_4Ph_2$ (0.30 g, 7×10^{-4} mol) and $(NPCl_2)_3$ (0.24 g, 7×10^{-4} mol) were melted and sealed together in an evacuated tube. The polymerization temperature was 250°. Reaction times longer than 40 hr yielded cross-linked polymer, but reaction times for 35–40 hr yielded a tetrahydrofuran-soluble polymer. Since the polymer was hydrolytically unstable, it was allowed to react with sodium trifluoroethoxide in tetrahydrofuran. The purification followed the procedure described above. The yield was 3.45 g (53%): the infrared spectrum showed peaks at (cm^{-1}) 2989 w (C–H), 1592 w (aryl), 1484 w (aryl), 1457 m (C–H), 1440 m (P–Ph), 1420 s (P–O–C), 1281 s (P=N), 1236 s (P=N), 1171 s (P–O–), 1121 s (P–Ph), 1083 s (C–O), 1030 w (aryl), 1000 w (P–Ph), 962 s (P–O), 869 m (CH_2), 842 m (CH_2), 753 m (aryl), 696 m (aryl), 660 m (CF_3). Anal. Calcd for 1:1 copolymer ($C_{16}H_{15}F_{15}N_3O_5P_3$): C, 27.16; H, 2.12; F, 40.31; N, 5.94; P, 13.15. Calcd for structure XII: C, 25.64; H, 2.02; F, 41.66; N, 5.9; P, 13.07. Found: C, 26.51; H, 2.01; F, 41.90; N, 5.82; P, 12.78.

Copolymerization of $N_3P_3F_4Ph_2$ (V) with $(NPCl_2)_3$. A copolymerization was carried out between $N_3P_3F_4Ph_2$ (0.60 g, 0.016 mol) and $(NPCl_2)_3$ (0.57 g, 0.016 mol) in an evaculated sealed tube at 250° for 10 hr. The copolymer was hydrolytically unstable and was, therefore, derivatized and purified as described previously. The yield was 0.82 g (36%). Anal. Calcd for 1:1 copolymer ($C_{16}H_{15}F_{15}N_3O_5P_3$): C, 27.16; H, 2.12; F, 40.31; N, 5.94; P, 13.15. Calcd for structure XIII: C, 25.89; H, 2.04; F, 41.44; N, 5.91; P, 13.09. Found: C, 26.38; H, 2.01; F, 41.63; N, 5.83; P, 12.97. The infrared spectrum was almost identical with that obtained from polymer XII.

Copolymerization of Non-gem-$N_3P_3Cl_3Ph_3$ (VI) with $(NPCl_2)_3$. A copolymerization was effected between VI (0.30 g, 6.3×10^{-4} mol) with the use of the same techniques as those described previously. The reaction condition was 250° for 48 hr; longer polymerization times resulted in cross-linking. One sample of this polymer was derivatized with the use of trifluoroethoxide (XIV). The yield was 3.48 g (60%). The other sample was treated with piperidine and triethylamine (48 hr at reflux temperature in tetrahydrofuran solution) to yield XV (1.12 g, 37%)). Polymer XIV was shown by microanalysis to be a 1:1 copolymer: infrared spectra showed peaks at (cm^{-1}) 2970 m (C–H), 1590 w (aryl), 1483 w (aryl), 1454 m (C–H), 1438 m (P–Ph), 1417 m (P–O–C), 1279 s (P=N), 1230 s (P=N), 1166 s (P–O), 1125 m (P–Ph), 1079 s (C–O–), 1028 w (aryl), 998 w (P–Ph), 960 s (P–O–), 869 m (CH_2), 842 m (CH_2), 748 m (aryl), 692 m (aryl), 653 m (CF_3). Anal. Calcd for $C_{12}H_{11}F_9N_2O_3P_2$: C, 31.03; H, 2.37; F, 36.85; N, 6.03; P, 13.36. Found: C, 31.04; H, 2.15; F, 36.58; N, 6.13; P, 13.10. For polymer XV the analytical data were: infrared spectra showed peaks at (cm^{-1}) 2950 s (C–H), 2850 s (C–H), 2760 w (C–H adjacent to N), 1620 w (aryl), 1440 m (P–Ph and C–H), 1380 w, 1350 m, 1330 m (ring stretch), 1295 m and 1240 s (P=N), 1190 s, 1160 m, 1115 s, 1065 (C–N coupled), 1030 m (aryl), 950 s (P=N), 900 w (C–C), 850 w and 835 w (CH_2), 795 w, 715 m, 695 m (aryl). Anal. Calcd for "1:1 copolymer" ($C_{21}H_{35}N_5P_2$): C, 60.14; H, 8.35; N, 16.71; P, 14.80. Calcd for formula XV: C, 59.96; H, 8.40; N, 16.85; P, 14.79. Found: C, 60.34; H, 8.69; N, 16.81; P, 14.60. A glass transition was detected in the −32 to −43° region from DTA and DSC data.

Other Attempted Polymerizations and Copolymerizations. Polymerizations were attempted with gem-$N_3P_3Cl_4Ph_2$, gem-$N_3P_3F_4Ph_2$, non-gem-$N_3P_3Cl_3Ph_3$, gem-$N_3P_3Cl_2Ph_4$, $N_3P_3ClPh_5$, and $N_3P_3Ph_6$ in evacuated, sealed glass tubes. The tubes were heated in thermoregulated ovens at 250 and 300°. The only products isolated were starting materials with decomposition evident at higher temperatures.

Thermal copolymerization of $(NPCl_2)_3$ with gem-$N_3P_3Cl_2Ph_4$, $N_3P_3ClPh_5$, and $N_3P_3Ph_6$ was also attempted, but again only starting materials were isolated.

For attempted γ-ray initiated polymerizations, evacuated, sealed glass tubes were prepared containing 1–4g samples of $(NPCl_2)_3$, $N_3P_3F_5Ph$, $N_3P_3F_4Ph_2$, $N_3P_3Cl_4Ph_2$, $N_3P_3Cl_3Ph_3$,

$N_3P_3Cl_2Ph_4$, and $N_3P_3ClPh_5$. These tubes were then exposed at 30° to γ radiation from a cobalt-60 source for 72 hr at a dose rate of 8.7×10^5 rads/hr for a total dose of 6.26×10^7 rads. After irradiation, the tubes were opened and GPC chromatograms of the products were taken. No polymer was present in any of the samples except in the tube containing $(NPCl_2)_3$.

Analytical Techniques. Gel permeation chromatography measurements were made with the use of a Waters Associates ALC/GPC 501 instrument. The columns used were two $\frac{3}{8}$ in. by 2 ft stainless steel columns which contained Styragel 10^4 packing. Tetrahydrofuran was employed as a solvent at a flow rate of 2.0 ml min, with samples injected at a concentration of 0.5 wt vol %. A refractive index detector was used. Approximate calibration of the columns was accomplished by means of medium molecular weight polystyrene standards obtained from Waters Associates together with the use of $\bar{M}_n$ and viscosity data for other phosphazenes.[12,13,18,33] Infrared spectra were obained with the use of a Perkin-Elmer 621 Grating Infrared Spectrometer. Solution viscosity data were obtained with the use of a Cannon-Ubbelohde dilution viscometer (size 75) at 30°. Solutions were prepared at concentrations of 1.0, 0.5, 0.33, and 0.25 g/100 ml. The DTA and DSC curves were obtained with the use of Perkin-Elmer instruments.[34]

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References and Notes

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A Kinetic Study of Anionic Polymerization of *tert*-Butyl Crotonate

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ABSTRACT: A kinetic study of anionic polymerization of *tert*-butyl crotonate in tetrahydrofuran is presented to confirm that the propagation in that polymerization proceeds via a living mechanism without any side reaction if the temperature is lower than −30°. The propagation rate constant is not affected by initiator species if the same counterion (Li^+) is used. However, the initiation efficiency is found to be low and different with initiator species because of the side reactions occurring in the initiation stage. Moreover, it is found that the ion pairs contribute to the propagation more prominently than the free ions, as in the anionic polymerization of methyl methacrylate. The propagation rate constant of the ion pair is markedly smaller than that for methyl methacrylate, because of the steric hindrance between α and β substituents.

The mechanism of anionic polymerization of α,β-unsaturated carbonyl monomers, especially that of methyl methacrylate (MMA) in polar solvents, is now well clarified.[1-7] Despite the fact that anionic polymerizations, under proper experimental conditions, can give monodisperse samples of poly(methyl methacrylate) (PMMA), it was observed that the deactivation of a part of initiators used always occurs because of various kinds of side reactions such as proton abstraction or addition to the carbonyl group.[1,2] The problems arising from the deactivation may be interesting for the study of the mechanism of polymerization but may be more important if we want to study the physical properties of those samples. Even if a slight amount of side reaction would occur during propagation, the samples obtained could not be suitable for precise measurements. In the anionic polymerization of MMA, it was confirmed by Mita et al.[5] and Löhr et al.[6,7] from their kinetic studies that the side reactions such as carbonyl attack occur only at the initiation stage, and then that the propagation proceeds practically without any side reaction at lower temperatures, producing polymer having a narrow molecular weight distribution.

It was previously reported[8] that another α,β-unsaturated carbonyl compound, *tert*-butyl crotonate (TBC), can be polymerized with 2-methylbutyllithium (2-MeBuLi) in tetrahydrofuran (THF) at −78° on a living mechanism to