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Organophosphazenes. 11. Copolymers Derived from 2-(2-Propenyl)pentafluorocyclotriphosphazene and Vinylbenzyl Chloride or Styrene [1]

John G. DuPont and Christopher W. Allen*

Department of Chemistry, University of Vermont, Burlington, Vermont 05405.
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ABSTRACT: The cyclic phosphazene, 2-(2-propenyl)pentafluorocyclotriphosphazene ($N_3P_3F_5C(CH_3)=CH_2$) readily undergoes radical copolymerization with vinylbenzyl chloride or styrene. This process leads to a range of copolymers with variable (6 to 38%) phosphazene content. Preliminary relative reactivity ratio data for the monomers have been determined. These new copolymers have been characterized by ^1H NMR and IR spectroscopy. Molecular weights of the styrene copolymers decrease with increasing phosphazene content (M_w = 117 000 to 33 000; M_n = 75 000 to 25 000). All copolymers exhibited a fairly low degree of polydispersity. Thermal studies (TGA and LC) show that inclusion of the phosphazene unit does not drastically affect the (thermal) stability of the vinyl polymers. The incorporation of the phosphazene unit imparts flame retardant properties to the copolymers.

The synthesis and characterization of new organophosphazenes has been a topic of interest for many investigators.[2] Work in our laboratories has focused on the perturbation of organic π-electron systems by the phosphazene ring[3-5] and the synthesis of organophosphazenes with exocyclic groups which can serve as sites for various synthetic transformations.[1,6] As part of this program, we have recently prepared a variety of propenylfluorocyclotriphosphazene derivatives. Since these materials contain an olefin attached to a phosphazene ring, there are two potential routes to polymerization. Allcock has shown that thermolysis of monoorganocyclophosphazenes[7] leads to linear phosphazene polymers.[8] In this investigation, we chose to probe the olefinic center as a site for polymerization. Of particular interest to us were the questions of what effect the phosphazene unit would have on the ability of the olefin center to participate in polymerization and copolymerization processes and the effect of the phosphazene unit on the properties of the resulting polymers.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp.) was converted to hexafluorocyclotriphosphazene which in turn was converted to 2-(2-propenyl)pentafluorocyclotriphosphazene[1] by previously reported procedures. Commercial grade vinylbenzyl chloride was kindly provided by Dow Corp. and stored at 0 °C. Prior to use, the monomer was extracted with dilute base in order to remove nitromethane and *tert*-butylcatechol inhibitors. The monomer was then dried over Na_2CO_3. Prior to use, several drops of vinylbenzyl chloride were added to 100 mL of methanol in order to detect any polymer that may be present. If no turbidity was observed, the monomer was assumed to contain no polymeric impurities. High purity styrene (>99%) was purchased from Aldrich Chemical Co. and stored at 0 °C. Upon addition of the monomer to methanol, no turbidity was observed, hence it was assumed that no polymer was present. This assumption was confirmed by ^1H NMR measurements.

Measurements. NMR spectra ($CDCl_3$) were obtained on a JEOL C60-HL spectrophotometer at 60 MHz (^1H). Infrared spectra were obtained on Nujol mulls using a Beckman IR-20A spectrophotometer. Thermal analyses were obtained on a DuPont 900/950 unit with sample in He flow atmosphere (100 mL/min) and a 10 °C/min heating rate. Gel permeation chromatography was performed on a Waters AVC 202 high-pressure liquid chromatograph equipped with Waters 10^3 and 10^4 Å microstyragel columns. The columns were calibrated with polystyrene standards (Waters).[9] Both the copolymers and standards were run as 0.10 to 0.15 wt % solutions in toluene. Weight average molecular weight data were obtained in a sedimentation equilibrium experiment[10] using a Beckman Model E ultracentrifuge with cyclohexane as the solvent. The density of the copolymer was estimated as 1.20 g/cm^3 (by flotation in aqueous K_2CO_3). Membrane osmometric data were obtained from Arro Laboratories, Inc. on a Hewlett Packard 502 instrument using dimethylformamide as the solvent. Data at four concentrations (0.252 to 1.008 g/100 mL) were extrapolated to infinite dilution. Elemental analyses were performed by Robertson and Integral Analytical Laboratories.

Radical Copolymerization of 2-(2-Propenyl)pentafluorocyclotriphosphazene with Vinylbenzyl Chloride. Freshly distilled 2-(2-propenyl)pentafluorocyclotriphosphazene (I) and purified vinyl benzyl chloride (II) were added in various mole ratios to thick walled test tubes containing 0.1% benzoyl peroxide initiator. The tubes were flushed several times with dry nitrogen, stoppered with rubber bulbs, and put into an oil bath heated to 80 ± 5 °C for 36 h. Following polymerization, the pale

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Table I
Analyses of Vinylbenzyl Chloride (II)-Propenylphosphazene (I) Copolymers

run	% C	% H	% N	mole ratio of II/I initial	mole ratio of II/I product	mol % of I	% conversion (wt)
1	64.9	5.49	1.55	9.00	15.7	6.0	6.25
2	55.8	4.94	3.78	3.41	5.50	15.4	5.10
3	51.4	4.67	5.04	1.24	3.60	21.7	4.20
4	43.4	3.98	6.74	0.50	2.20	31.3	9.35
5	39.4	3.78	7.97	0.13	1.60	38.5	10.5

Table II
Analyses of Styrene-Propenylphosphazene (I) Copolymers

run	% C	% H	% N	mole ratio of styrene-I initial	mole ratio of styrene-I product	mol % of I	% conversion (wt)
1	79.40	7.02	2.32	9.00	14.8	6.3	22.0
2	69.67	6.28	4.14	4.00	7.00	12.5	20.7
3	55.60	5.20	6.88	1.38	3.25	23.5	38.0
4	48.05	4.48	8.39	0.66	2.20	31.3	40.4
5	43.90	4.10	9.25	0.25	1.73	36.6	36.7

yellow gels were dissolved in 10–15 mL of acetone and filtered in order to remove any insoluble material. The acetone solution was then added dropwise to methanol in order to precipitate the copolymer. The copolymer was then filtered, dissolved in acetone, and reprecipitated several times. The material was then dried and submitted for analysis in order to determine the phosphazene content of the various copolymers. These results are given in Table I.

^{1}H NMR (ArH) δ 7.0 (broad doublet, CH_2Cl), 4.5 (broad singlet, aliphatic H), 1.5 (broad singlet, CH_3), 0.50 (broad singlet); IR 2900 cm^{-1} (m), 1600 (m, aromatic ring), 1450 (m), 1350 (m), 1260 (s, PN str), 950 (s, PF assym), 840 (s, PF sym), 700 (m).

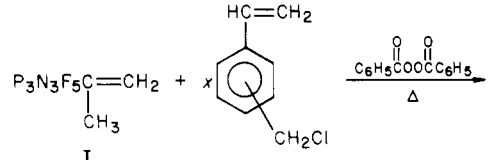
Copolymerization of 2-(2-Propenyl)pentafluorocyclotriphosphazene with Styrene. The procedure for this preparation was identical to that used for the vinylbenzyl chloride–propenylphosphazene copolymer with the exception that styrene was used in place of II and that polymerization time was 4–10 h. The analytical results are summarized in Table II.

^{1}H NMR (ArH) δ 7.5 (broad doublet, aliphatic H), 2.5 (broad singlet, CH_3), 1.6 (broad singlet); IR 2940 cm^{-1} (m), 1600 (m, aromatic ring), 1500 (m), 1450 (m), 1370 (m), 1260 (s, PN str), 1000 (m), 940 (s, PF assym), 820 (s, PF sym), 750 (m), 700 (s).

Attempted Homopolymerization of 2-(2-Propenyl)-pentafluorocyclotriphosphazene. Treatment of 2-(2-propenyl)pentafluorocyclotriphosphazene with benzoyl peroxide for several days under conditions identical to those employed in the copolymerization experiments produced trace quantities of oligomers as indicated by NMR absorptions in the alkane region. However, the bulk of the phosphazene remained unchanged.

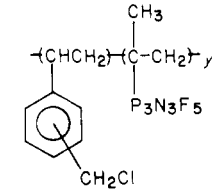
Results and Discussion

The approach to polymer synthesis chosen for this investigation was radical polymerization of an olefinic cyclophosphazene. In this way, we planned to develop a system where the cyclophosphazene unit is appended to the backbone of a traditional organic polymer. Although allylaminocyclophosphazenes have been shown to undergo radical induced polymerization yielding insoluble cross-lined resins,[11] 2-(propenyl)pentafluorocyclotriphosphazene (I) does not undergo significant homopolymerization via benzoyl peroxide activation. However, initial experiments indicated that I could be induced to undergo free radical vinyl copolymerization with styrene derivatives. Therefore, a series of control experiments were carried out, in which the mole ratio of vinylbenzyl chloride (II) to the propenyl phosphazene in the monomer feed was varied. This allows one to produce a range of copolymers with variable phosphazene content. Infrared data indicated that the propenyl phosphazene unit had been incorporated into the copolymer backbone by polymerization through the $-(CH_3)=CH_2$ group, as shown by the disappearance of all olefinic absorptions and the retention of the nearly unperturbed ν_{PNP} and ν_{PF} stretching vibrations. The ^{1}H NMR spectrum also showed the complete absence of peaks in the olefinic region. The elemental analyses and percent conversion data for five vinylbenzyl chloride–propenylphosphazene copolymers may be found in Table I. Since only the phosphazene unit contains nitrogen atoms, the weight percent of nitrogen can be used to calculate the mole ratio of I to II in the copolymers[12] and this result is also included in Table I. Thus, one can represent the polymerization reaction as follows:



I

II, x = 0.11 to 7.69



y = 0.06 to 0.62

The question of orientation of monomer units (head/head vs. head/tail, etc.) cannot be resolved with the limited data available in this investigation. The yields in the synthesis of the vinylbenzyl chloride–propenylphosphazene copolymers were less than 10%, therefore the method of Finemann and Ross[13] was used to calculate approximate reactivity ratio values. The results of these calculations give r_1 (for II) equal to 1.59 and r_2 (for I) equal to 0.014. The low relative reactivity of I toward radicals in this system and the low yields of the copolymer prompted consideration of another organic monomer, styrene, for further investigation.

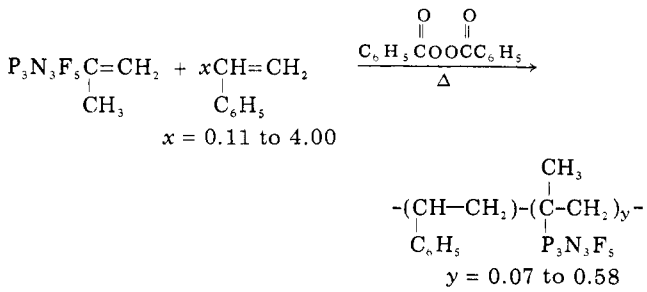
A range of styrene propenylphosphazene copolymers was produced via free radical polymerization. The infrared data showed loss of the olefinic absorptions and retention of unperturbed ν_{PNP} and ν_{PF} absorptions. Similarly, the ^{1}H NMR spectrum indicated the loss of olefinic protons. The elemental analyses, percent conversion, and mole ratio of monomers[12] in each copolymer are found in Table II.

Table III
Molecular Weight Data for Styrene-Propenylphosphazene Copolymers

run no.	mole % I in copolymer	M_w[b]	M_n[b]	M_w/M_n
1	6.3	92K	66K	1.39
2	12.5	75K	60K	1.25
3	23.5	39K	29K	1.34
4	31.2	36K	26K	1.38
5	36.5	33K	25K	1.32
6[a]	20.3	117K	75K	1.56
6	20.3	116K[c]	105K[d]	1.10
7[e]	20.3	101K	60K	1.68

[a] Wt % conversion = 65%. [b] Gel permeation chromatography, 10^3 Å microstyragel columns. [c] Ultracentrifuge (sedimentation equilibrium). [d] Membrane osmometry. [e] Sample 6 heated at 120 °C for 24 h.

The polymerization reaction in this case can be represented as follows:



The weight conversion of the styrene–propenylphosphazene copolymerization reaction was in excess of 10%, therefore the Mayo–Lewis[14] method was used in order to determine approximate reactivity ratio values. The results of these calculations give r_1 (for styrene) equal to 2.20 and r_2 (I) equal to 1.35.

Due to the novelty of the systems and the methods of calculation,[15] the reactivity ratio data for both the vinyl benzyl chloride and styrene system are preliminary results. If, however, one accepts these values as a qualitative measure of the reactivity of the various monomers, we can further probe the nature of the propenylphosphazene by combining the r_1 and r_2 values from the styrene system with the Alfrey–Price equations.[16] For I we obtain a qualitative value of the polarity parameter, e, of 0.18 and the resonance parameter, Q, is 0.21. In a *qualitative* comparison to styrene (Q = 1.00; e = −0.80), one can see that compared to the styrene, the olefinic center in the propenylphosphazene is highly polar but without substantive tendency to resonance stabilization. The high polarity of organic π-electron systems, such as aryl groups, bound to the phosphazene ring has also been deduced from ^1H[3] and ^{13}C[4] NMR data. Aryl group–phosphazene mesomeric interactions are more controversial[4] and evidence has been presented both for[17] and against[5,18] such effects.

The fact that r values for both styrene and the propenylphosphazene are greater than unity is uncommon and corresponds to a tendency to form block copolymers.[19] This is in contrast to the observation of no significant homopolymerization of PPF with benzoyl peroxide activation. While the resolution of this conflict is unclear at this stage, it may be related to the approximate nature[15] of the r values in question.

Molecular weight data for the styrene–propenylphosphazene copolymers may be found in Table III. Data for all copolymers was obtained from gel permeation chromatography and as a check, one of the copolymers was also examined by alternative methods. The agreement between chromatographic and untracentrifuge results for the weight average molecular weight is good. The number average molecular weight values differ somewhat but this may be related to diffusion of low molecular weight species across the membrane and hence a high apparent molecular weight from membrane osmometry. It is interesting and unusual that the copolymers have a fairly low degree of polydispersity (M_w/M_n). Furthermore, the amount of PPF incorporated into the copolymer does not seem to effect M_w/M_n, rather it effects M_w and M_n individually (Figure 1). It appears that increasing the amount of I in the copolymer results in lower molecular weights, hence one might suspect that the propenylphosphazene may have a higher probability of acting as a chain terminating or chain transfer agent.

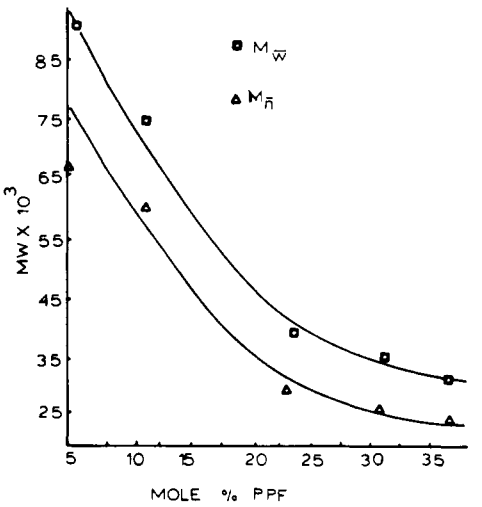


Figure 1. Variation of styrene–propenylphosphazene (PPF) copolymer molecular weight with mol % PPF.

Table IV
$T_{50\%}$ Data for Polymers and Copolymers

polymer	$T_{50\%}$, °C
vinylbenzyl chloride	455
vinylbenzyl chloride–propenylphosphazene	480–485
styrene	425
styrene–propenylphosphazene	440–450

The copolymers appear to be true copolymers as opposed to a mixture of homopolymers. The copolymers are readily soluble in acetone–methanol (1:1), diethyl ether, and low molecular weight hydrocarbon solvents none of which are solvents for the parent organic homopolymers. This was further confirmed by gel permeation chromatography of the copolymers, as only one peak was observed.

The copolymers are stable to dilute acid and base solutions. This is in marked contrast to poly(dichlorophosphazene) which readily undergoes hydrolysis, even in the presence of atmospheric moisture. This resistance to hydrolysis may be a result of shielding of the fluorocyclotriphosphazene moiety by the hydrophobic styrene molecules as well as the greater stability of cyclotriphosphazene phosphorus–fluorine bonds.

Initial data on thermal stability, via thermal gravimetric analysis, for the copolymers are given in Table IV. Note that the incorporation of the propenylphosphazene unit into the copolymer leads to increased thermal stability rather than the destabilization which might be expected due to bulk of the $P_3N_3F_5$ ring. Also note that the molecular weight of the copolymer does not drastically increase or decrease (Table III) when the copolymer is heated at a moderate temperature for a long period of time.

Both of the copolymers were found to be flame retardant under normal atmospheric conditions. Qualitative tests were carried out simply by holding a flame source to the powdered copolymer. Pure vinylbenzyl chloride and styrene polymers readily ignited and sustained a flame, but the copolymers, even when soaked in flammable solvents, would self-extinguish. This behavior can be attributed to the known flame retardency of the phosphazene system.[2,8] Thus we have shown that by copolymerization with a propenylphosphazene with traditional organic monomers, one can produce copolymers with the flame retardent directly attached to the polymer backbone.

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(12) For example, the analysis of a styrene–I copolymer had the following results: C, 55.6; H, 5.20; N, 6.88. Since I is the only monomer containing nitrogen, 42 g of nitrogen (3 N in $P_3N_3F_5$) represent 6.88% of unit molecular weight, which is 612.3 g. Subtracting the weight of I (271 g/mol) from this weight yields the weight due to styrene (612.3–271.0 = 341.3 g of styrene). Dividing this weight by the molecular weight of styrene (104 g/mol) gives the moles of styrene per mole of I (3.27/1).
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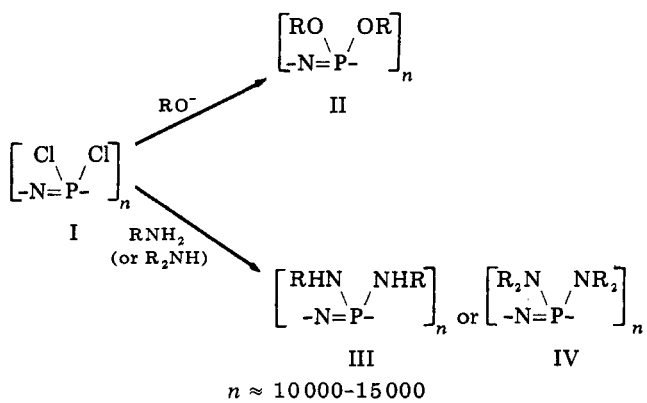
Synthesis of Open-Chain Poly(difluorophosphazene) and Its Reactions with Alkoxides, Aryloxides, and Amines[1]

H. R. Allcock,* D. B. Patterson, and T. L. Evans

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received November 8, 1978*

ABSTRACT: The first synthesis of a soluble form of high molecular weight poly(difluorophosphazene), $(NPF_2)_n$, has been carried out, and the reactions of this polymer with amines, alkoxides, or aryloxides have been examined. Poly(difluorophosphazene) reacted smoothly with sodium trifluoroethoxide to yield high molecular weight $[NP(OCH_2CF_3)_2]_n$. However, reactions with amines, such as methylamine, *n*-butylamine, dimethylamine, or aniline, resulted in some chain cleavage and in the formation of nongeminal, partly substituted products of the general formula $[NPF(NHR)]_n$. The limited chain cleavage was ascribed partly to hydrogen fluoride attack on the polymer backbone and also to subsequent hydrolysis of residual P–F bonds. Comparisons with the chemistry of poly(dichlorophosphazene), $(NPCl_2)_n$, indicate fundamental differences between the substitution chemistry of the fluoro- and chlorophosphazene systems, and explanations for these differences are suggested. From a synthetic viewpoint, the unusual reactivity of $(NPF_2)_n$ provides reaction routes to stable new poly(organophosphazenes), such as $[NP(NHC_4H_9)(OCH_2CF_3)]_n$, that are not accessible through $(NPCl_2)_n$.

Poly(organophosphazenes) are some of the most versatile and unusual synthetic macromolecules yet discovered. The first examples were prepared by Allcock, Kugel, and Valan[2-4] by the interaction of soluble poly(dichlorophosphazene) (I) with alkoxides, aryloxides, or amines, and this reaction route has since been used in our laboratory and elsewhere for the synthesis of at least 80 different stable and, in many cases, useful macromolecules.[5-9] The key feature of this reaction route is the use of a highly reactive polymeric intermediate (I) as a precursor for the formation of chemically stable polymeric products (II–IV). An advantage of this route is the large range of poly(organophosphazenes) that can be prepared with the use of the available alcohols, phenols, or primary and secondary amines, both as homopolymers and as mixed substituent derivatives. Thus, the total number of different polymers (with different properties) that can, in principle, be synthesized by this method is comparable to that of all other synthetic macromolecular systems combined.



However, attempts in our laboratory to extend the scope of this field by the reaction of I with organometallic reagents [with a view to the synthesis of polymers of formula $(NPR_2)_n$] led invariably to cleavage of the

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