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ORGANOSUBSTITUTED PHOSPHAZENES. XI. COPOLYMERS DERIVED FROM 2-(--ETC(U).

JUL 78 J G DUPONT, C W ALLEN

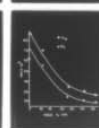
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Organosubstituted Phosphazenes. XI. Copolymers Derived from 2-[2-Propenyl] pentafluorocyclotriphosphazene and Vinyl Benzyl Chloride or Styrene.

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Organophosphazenes: XI. Copolymers Derived from 2-[2-Propenyl]pentafluorocyclotriphosphazene and Vinyl Benzyl Chloride or Styrene¹

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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 vinyl benzyl chloride or styrene. This process leads to a range of copolymers with variable (6 to 38%) phosphazene content. The relative reactivity ratios of 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 HPLC) show that inclusion of the phosphazene unit does not drastically affect the (thermal) stability of the vinyl polymers.

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Introduction

The problem of construction of non-flammable synthetic polymer systems is one of contemporary technological significance.² Traditionally, flame retardents have been simply additives such as antimony oxychloride,^{2,3} phosphate esters^{2,3,4} or cyclophosphazenes.^{3,5} More recent efforts have involved non-flammable polymers such as polyphosphazenes.⁶ There are difficulties associated with each of these approaches. The possibility exists for the additives to leach out overtime and the additives often represent biohazards. Current economic factors do not favor wide utilization of the polyphosphazenes. An alternative approach to those described above is the incorporation of the flame retardent into the polymer backbone.⁷

Recent work in our laboratories^{1,8} has been directed towards the synthesis of organophosphazenes with exocyclic functional groups capable of undergoing various synthetic transformations. As part of this program, we have investigated the radical copolymerization of 2-[2-propenyl]pentafluorocyclotriphosphazene with two vinyl monomers (styrene and vinyl benzyl chloride). The aim of these studies is to develop a method for incorporation of the flame retardent properties of the phosphazenes into traditional synthetic polymers.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Ethyl Corp.) was converted to hexafluorocyclotriphosphazene which in turn was converted to 2-[2-propenyl]-pentafluorocyclotriphosphazene¹ by previously reported procedures. Commercial grade vinyl benzyl 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 t-butyl catechol inhibitors. The monomer was then dried over Na₂CO₃. Prior to use, several drops of vinyl benzyl 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 60MHz (^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 (100ml/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 weight percent solutions in toluene. Weight average molecular weight data was obtained in a sedimentation equilibrium experiment¹⁰ using a Beckman Model E ultracentrifuge with cyclohexane as the solvent. The density of the copolymer was estimated as 1.20g/cm³ (by flotation in aqueous K_2CO_3). Membrane osmometric data was obtained from Arro Laboratories, Inc. on a Hewlett Packard 502 instrument using dimethylformamide as the solvent. Data at four concentrations (.252 to 1.008g/100ml) were extrapolated to infinite dilution. Elemental analyses were performed by Robertson and Integral Analytical Laboratories.

~~Radical Copolymerization of 2-[2-propenyl]pentafluorocyclotriphosphazene with Vinyl Benzyl Chloride.~~ Freshly distilled 2-[2-propenyl]pentafluorocyclotriphosphazene (PPF) and purified vinyl benzyl chloride (VBC) 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 $80^\circ \pm 5^\circ\text{C}$. for 36 hours. Following polymerization, the pale 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.

NMR: ^1H : $\delta(\text{Ar-H})$ 7.0 (broad doublet), $\delta(\text{CH}_2\text{-Cl})$ 4.5 (broad singlet), $\delta(\text{aliph. H})$ 1.5 (broad singlet), $\delta(\text{CH}_3)$.50 (broad singlet). IR: 2900(m), 1700(m, CC str), 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 VBC/PPF copolymer with the exception that styrene was used in place of VBC and that polymerization time was 4-10 hours. The analytical results are summarized in Table II.

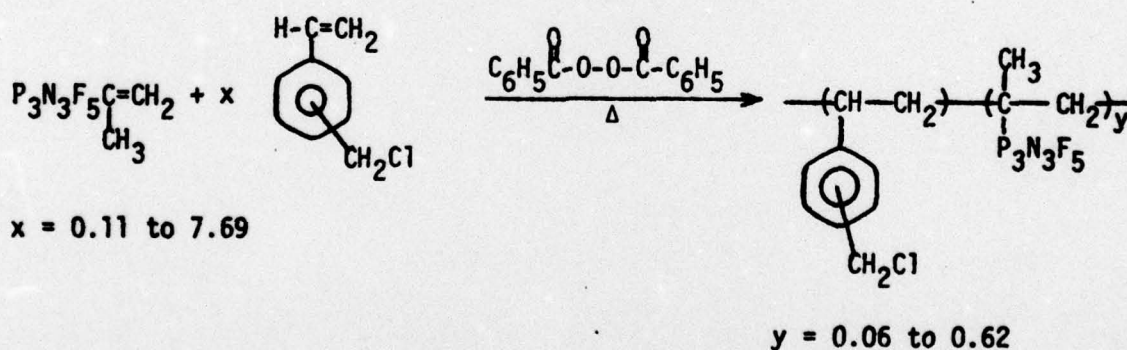
NMR: ^1H : $\delta(\text{Ar-H})$ 7.5 (broad doublet), $\delta(\text{aliph. H})$ 2.5 (broad singlet), $\delta(\text{CH}_3)$ 1.6 (broad singlet). IR: 2940(m), 1600(m, CC str), 1500(m), 1450(m), 1370(m), 1260(s, PN str), 1000(m), 940(s, PF assym), 820(s, PF sym), 750(m), 700(s).

~~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~~

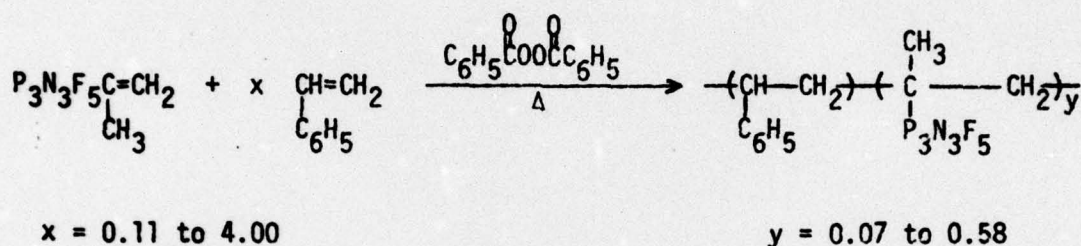
The approach to polymer synthesis chosen for this investigation was radical polymerization of an olefinic cyclophosphazene. In this way, we planned to develop a system where the cyclophosphazene unit is appended to the backbone of a traditional organic polymer. Although allylaminocyclophosphazenes have been shown to undergo radical induced polymerization yielding insoluble cross-linked resins,¹¹ 2-[2-propenyl]pentafluorocyclotriphosphazene (PPF) does not undergo significant homopolymerization via benzoyl peroxide activation. However, initial experiments indicated that PPF 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 vinyl benzyl chloride (VBC) to PPF in the monomer feed was varied. This allows one to produce a range of copolymers with variable phosphazene content. Infrared data indicated that the PPF unit had been incorporated into the copolymer backbone by polymerization through the $-\text{C}(\text{CH}_3)=\text{CH}_2$ group, as shown by the disappearance of all olefinic absorptions and the retention of the nearly unperturbed νPNP and νPF stretching vibrations. The ^1H NMR spectrum also showed the complete absence of peaks in the olefinic region. The elemental analyses and percent conversion data for five VBC/PPF 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 VBC to PPF in the copolymers¹² and this result is also included in Table I. Thus, one can represent the polymerization reaction as follows:



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 VBC/PPF copolymers were less than 10%, therefore the method of Finemann and Ross¹³ was used to calculate the reactivity ratios. The results of these calculations give r_1 (for VBC) equal to 1.59 and r_2 (for PPF) equal to 0.014. The low relative reactivity of PPF towards 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/PPF copolymers were 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 ^1H NMR spectrum indicated the loss of olefinic protons. The elemental analyses, percent conversion, and mole ratio of monomers¹² in each copolymer is found in Table II. The polymerization reaction in this case can be represented as follows:



The weight conversion of the styrene/PPF copolymerization reaction was in excess of 10%, therefore the Mayo-Lewis¹⁴ method was used in order to determine the reactivity ratios. The results of these calculations give r_1 (for styrene) equal to 2.20 and r_2 (for PPF) equal to 1.35. Table III shows the relationship (in terms of reactivity ratios) of PPF to common organic monomers which form copolymers with styrene.

In order to further probe the nature of the PPF monomer in this system, the values of r_1 and r_2 were combined with the Alfrey-Price equations.¹⁵ For PPF, the calculated value of the polarity parameter, e , is 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 the styrene, the olefinic center in PPF 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 ¹⁶ and ^{13}C ¹⁷ nmr data. Aryl group/phosphazene mesomeric interactions are more controversial¹⁷

and evidence has been presented both for¹⁸ and against¹⁹ such effects.

The fact that r values for both styrene and PPF are greater than unity is uncommon and corresponds to a tendency to form block copolymers.²⁰ This is in contrast to the observation of no significant homopolymerization of PPF with benzoyl peroxide activation. The resolution of this conflict is unclear at this stage. One possibility is that in the copolymerization reaction, PPF is activated by a styrene (or styrene oligomer) radical and hence is reactive towards additional PPF units. When activation of PPF is by radicals derived from benzoyl peroxide, the resulting PPF radical may exhibit reduced reactivity due both to the polarity induced by the phosphazene unit and by electron delocalization through the aryl unit.

Molecular weight data for the styrene/PPF copolymers may be found in table IV. 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 ultracentrifuge 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 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 PPF in the copolymer results in lower molecular weights, hence one might suspect that the PPF may have a higher probability of acting as a chain terminating or chain transfer agent.

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 polydichlorophosphazene 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 is given in Table V. Note that the incorporation of the PPF unit into the copolymer does not appear to lead to 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 IV) 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 VBC and styrene polymers readily ignited and sustained a flame, but the copolymers, even when soaked in flammable solvents, would self extinguish. This is not surprising since the copolymers contain substantial amount of phosphorus and nitrogen, which are well known fire retardants.²⁻⁴

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12. For example, the analysis of a styrene/PPF copolymer had the following results:
C = 55.6%; H = 5.20%; N = 6.88%. Since PPF is the only monomer containing nitrogen,
42 grams of nitrogen (3N in $P_3N_3F_6$) represent 6.88% of unit molecular weight,
which is 612.3 grams. Subtracting the weight of PPF (271 grams/mole) from this weight
yields the weight due to styrene (612.3-271.0 = 341.3 grams of styrene). Dividing
this weight by the molecular weight of styrene (104 g./mole) gives the moles styrene
per mole of PPF (3.27/1.).
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Table I
Analyses of VBC/PPF Copolymers

Run	%C	%H	%N	Mole-Ratio-VBC/PPF		% Conversion (wt.)
				Initial	Product	
1	64.9	5.49	1.55	9.00	15.7	6.25
2	55.8	4.94	3.78	3.41	5.50	5.10
3	51.4	4.67	5.04	1.24	3.60	4.20
4	43.4	3.98	6.74	0.50	2.20	9.35
5	39.4	3.78	7.97	0.13	1.60	10.5

Table II
Analyses of Styrene/PPF Copolymers

<u>Run</u>	<u>Mole-Ratio-Styrene/PPF</u>			<u>% Conversion</u>	
	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>Initial</u>	<u>Product</u>
1	79.40	7.02	2.32	9.00	14.8
2	69.67	6.28	4.14	4.00	7.00
3	55.60	5.20	6.88	1.38	3.25
4	48.05	4.48	8.39	0.66	2.20
5	43.90	4.10	9.25	0.25	1.73

Table III
Monomer Reactivity Ratios for Selected
Styrene Copolymers.^a

<u>M₁</u>	<u>M₂</u>	<u>r₁^b</u>	<u>r₂</u>
Styrene	Methyl Methacrylate	1.0	1.9
Styrene	Acrylonitrile	1.0	2.5
Styrene	Vinylidene Chloride	1.0	5.4
Styrene	PPF	1.0	0.45
Styrene	Vinyl Chloride	1.0	0.05
Styrene	Vinyl Acetate	1.0	0.02

^a data from: M.P. Stevens, "Polymer Chemistry An Introduction," Addison-Wesley, Reading, MA (1975).

^b styrene set at 1.00 in order to serve as reference radical

Table IV
Molecular Weight Data for Styrene/PPF Copolymers

Run #	Mole % P.P.C. 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 Weight % conversion = 65%.

^b Gel permeation chromatography, 10^3 Å microstyragel columns.

^c Ultracentrifuge (sedimentation equilibrium).

^d Membrane osmometry

^e Sample 6 heated @ 120°C. for 24 hours.

Table V

T_{50%} Data for Polymers and Copolymers

<u>Polymer</u>	<u>T_{50%}</u>
VBC	455°C.
VBC/PPF	480°-485°C.
Styrene	425°C.
Styrene/PPF	440°-450°C.

Figure 1. Variation of Styrene/PPF
Copolymer Molecular Weight with
Mole % PPF.

