

Synthesis, Characterization, and Modification of 2-Allylphenoxyorganocyclotriphosphazene Copolymers

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SYNOPSIS

The monomer 2-allylphenoxyorganocyclotriphosphazene **I** with phenoxy (or 2,2,2-trifluoroethoxy) side group was synthesized on reacting hexachlorocyclotriphosphazene with phenol (or 2,2,2-trifluoroethanol) and 2-allylphenol with phase-transfer catalysis in a dichloromethane/alkaline solution. The synthesis had a large yield (>80%) and narrow product distribution and proceeded under mild condition. The radical copolymerization of **I** with **II** (styrene, methyl methacrylate, and vinylbenzyl chloride) using azobis(isobutyronitrile) (AIBN) as an initiator was investigated. Reactivity ratios and Alfrey-Price parameters for copolymers were obtained. Organophosphazene monomer **I** was less reactive than **II**. The thermal stability of the copolymer with phenoxy side group was greater than that with 2,2,2-trifluoroethoxy side group. The incorporation of organophosphazene units into an organic polymer backbone decreased the glass transition temperature and increased the thermal stability of the copolymers. Tensile measurement showed that Young's modulus tended to decrease and the polymer became softer and ductile when the incorporated amount of **I** increases. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The organic chemistry of phosphazene has greatly expanded so that organophosphazenes are applied in medicinal chemistry,¹ organometallic chemistry,^{2,3} and polymer chemistry.⁴⁻⁸ The perturbation of organic π -electron systems by the phosphazene ring and syntheses of organophosphazenes with exocyclic groups were discussed.⁹⁻¹¹ Polyorganophosphazenes prepared in this manner have organic substituents bound to phosphorus through an oxygen link. The strongly electron-withdrawing effect of the phosphazene ring on the allyl phenoxy moiety is decreased due to insulation by an oxygen atom.¹² The substituent results in no influence on the electron density of the allyl group. The synthetic procedure is valuable in the sense that a wide variety of substituents and mixed substituents are attached to the polymer backbone. A polymeric material may form, including both in-

organic and organic moieties. The varied ratio of composition of inorganic material to organic material affects the physical properties.

Considerable interest exists to prepare and examine copolymers that contain both organophosphazene and organic compound units. The incorporation of organophosphazene units into an organic polymer backbone might decrease the glass transition temperature and increase the thermal stability and flame retardation of the copolymer. The chloride atom of the phosphazene unit is unstable. 2,2,2-Trifluoroethoxy and phenoxy groups replaced the chloride atom and altered the properties of phosphazenes. In this work, organofunctional phosphazene monomers with both 2,2,2-trifluoroethoxy and phenoxy side groups reacted with styrene, methyl methacrylate, and vinylbenzyl chloride to form the copolymers. The purposes of this work were to investigate the preparation of organophosphazenes that contain side-group unsaturation and that are used as precursors to prepare copolymers with styrene, methyl methacrylate, and vinylbenzyl chloride and, to understand the characterization and modification of the copolymers.

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EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (Aldrich), tetrahydrofuran (THF) (TEDIA) styrene (>99%) (Janssen), methyl methacrylate (Janssen), vinyl benzyl chloride (TCI) azobis(isobutyronitrile) (AIBN) (TCI), 2,2,2-trifluoroethanol (Merck), and phenol (Merck) were obtained from the indicated suppliers; other chemicals were all of reagent grade.

Analytical Equipment

Gel-permeation chromatography analysis was conducted with an instrument (Shimadzu Model LC-6A) equipped with a refractive-index detector (Shimadzu, RDI-6A). The measurement was performed in a polymer/THF solution (5–7 mg/10 mL) by means of two styragel columns—G2000H and G3000H—at a flow rate 1.0 mL/min at 40°C. Approximate calibration of the columns was accomplished with polystyrene standards of narrow range of molecular weight (Waters Associates) and data of other polyphosphazenes. Thermal analysis was measured at 10°C/min, 100 mL N₂/min for the thermogravimetric system (Du Pont 910), and at 20°C/min, 100 mL N₂/min for a differential scanning calorimeter (Du Pont 951).

Elemental analysis was made for C, H, and N (EA, Perkin-Elmer 2400). Mass spectra were measured on a mass spectrometer (JEOL SX-102A). NMR spectra of samples in deuterated chloroform were measured with an FT-NMR spectrometer (JEOL, 300 MHz). Tensile tests (INSTRON 1125) were carried out under room temperatures and at a deformation rate of 1 mm/min. A typical specimen was 20 mm in length, 5 mm in width, and 0.2 mm in thickness. The incorporated content of **I** in the copolymer was determined from the mass fraction of nitrogen. Reactivity ratios and Alfrey-Price parameters for systems according to the terminal model were calculated.

Synthesis of 2-Allylphenoxyphenoxycyclotriphosphazene (**Ia**)

An aqueous solution (50 mL) of sodium hydroxide (6 g, 0.15 mol), phenol (7 g, 0.074 mol), and tetra-*n*-butylammonium bromide (1 g, 3 mmol) was prepared and introduced into the reactor (250 mL, three-necked flask, 35 ± 0.02°C). Phosphazene reactant, (NPCl₂)₃ (5 g, 144 mmol), and dichloromethane (50 mL), which were also at the desired

temperature, were then added to the reactor. The reaction mixture was agitated for 3 h.

After reaction, the oil phase, which was separated from the aqueous phase, was washed with water several times and dried with MgSO₄. Most solvent from the organic phase was removed with an aspirator. A yellowish oillike product was obtained. The products were separated on a pressurized column chromatography and with freezing crystallization.¹³ The analytical results of chloropentaphenoxycyclotriphosphazene are ³¹P-NMR, δ 23.6 ppm (triplet) and 7.7 ppm (double +); EA, C 56.6%, H 3.94%, N 6.7%; *m/e* = 635; mp = 53°C.

An aqueous solution (50 mL) of sodium hydroxide (4 g, 0.1 mol), 2-allylphenol (6.5 g, 0.047 mol), and tetra-*n*-butylammonium bromide (4 g, 12 mmol) was prepared and introduced into the reactor (250 mL, three-necked flask, 35 ± 0.02°C). Chloropentaphenoxycyclotriphosphazene, N₃P₃Cl(OC₆H₄CH₂CHCH₂)₅ (10 g, 157 mmol), and dichloromethane (50 mL) were added to the reactor. The reaction mixture was agitated for 8 h. After reaction, the oil phase, which was separated from the aqueous phase, was washed with water several times and dried with MgSO₄. Most solvent from the organic phase was removed with an aspirator. A yellowish oillike product was obtained. The products were separated on a pressurized column chromatography and with freezing crystallization.¹³ Thin-layer chromatography indicated the presence of product. A portion (4 g) of the crude oil was chromatographed on silica gel (70 g) and eluted with hexane/chloroform (88/12) (10–15 mL/min) to give **Ia** (³¹P-NMR, δ 20.85 ppm; EA, C 63.8%, H 4.6%, N 5.7%; *m/e*, 733).

Synthesis of 2-allylphenoxy-penta(2,2,2-trifluoroethoxy)cyclotriphosphazene (**Ib**)

This procedure was identical to that of **Ia**, except that phenol was used in place of 2,2,2-trifluoroethanol. The analytical results of chloropenta(2,2,2-trifluoroethoxy)cyclotriphosphazene are ³¹P-NMR, δ 26 ppm and 13.9 ppm; EA, C 18.3%, H 3.0%, N 6.4%; *m/e*, 655; those of **Ib** are ³¹P-NMR, δ 16.94 ppm; EA, C 29.9%, H 2.5%, N 5.5%; *m/e*, 763.

Copolymerization of 2-allylphenoxyorgano-cyclotriphosphazene (**I**) with **II** (Styrene [STY], Methyl Methacrylate [MMA], or Vinyl Benzyl Chloride [VBC])

I (1.1 mmol), **II** (5.5 mmol), and AIBN (2 wt %) (or *n*-BuLi [10 wt %]) were added to thick-walled

test tubes. The tubes were flushed several times with dry nitrogen in an ice bath, stoppered with rubber serum cap, and put into an oven heated to $60 \pm 0.5^\circ\text{C}$ for 36 h. After reaction, the gels were dissolved in dichloromethane (10–15 mL) and filtered to remove insoluble material. The solution was added dropwise to methanol to precipitate the copolymer. The copolymer was filtered, dissolved in dichloromethane, and reprecipitated several times. The material was dried and submitted for analysis to determine the phosphazene content of the various copolymers.

Ultraviolet irradiation experiments were carried out in a reactor (Spectro Linker, XL-1000 UV). The lamp produced radiation at 254 and 365 nm. Reaction conditions were the same as those above. Samples were placed 16 cm from the radiation source and were exposed for 48 h.

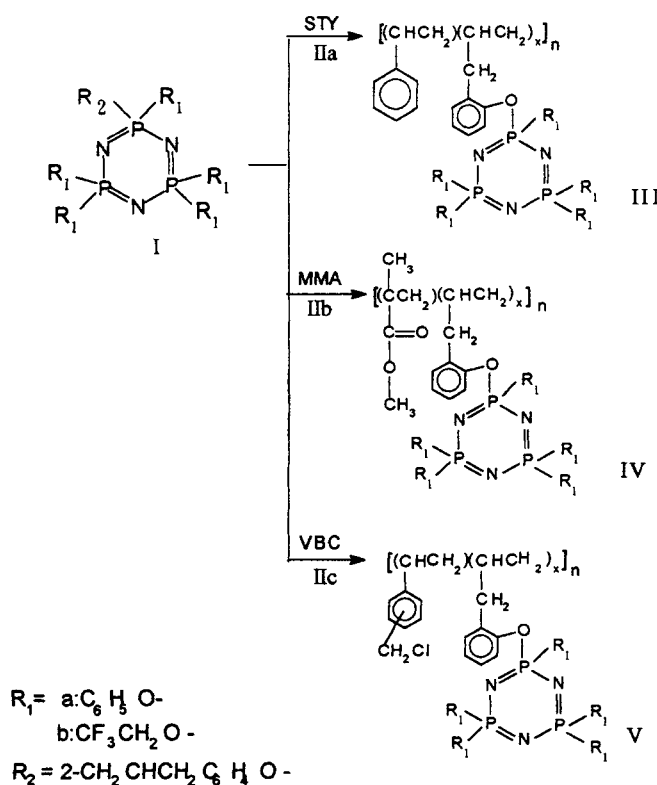
RESULTS AND DISCUSSION

It is known that alkoxy- and (aryloxy) cyclotriphosphazenes can be synthesized by conventional nucleophilic substitution. In this method, the sodium salt of the corresponding alcohol is used. Because of the small solubility of the salt in the solvent and hydrolysis, elevated temperature, prolong

reaction duration, and an inert atmosphere are generally required.¹⁴ Phase-transfer catalysis is applied in the field of synthesis of organophosphazene.^{15,16}

Chloropentaphenoxycyclotriphosphazene $\text{N}_3\text{P}_3\text{Cl}(\text{OC}_6\text{H}_5)_5$ and chloropenta(2,2,2-trifluoroethoxy)cyclotriphosphazene $\text{N}_3\text{P}_3\text{Cl}(\text{OCH}_2\text{CF}_3)_5$ were synthesized from the reaction of hexachlorocyclotriphosphazene $(\text{NPCl}_2)_3$ with phenol and 2,2,2-trifluoroethanol, respectively, with phase-transfer catalysis in a dichloromethane/alkaline solution. **Ia** and **Ib** were synthesized from the reaction of 2-allylphenol with chloropentaphenoxycyclotriphosphazene and chloropenta(2,2,2-trifluoroethoxy)cyclotriphosphazene, respectively, with phase-transfer catalysis. The synthetic procedure had a large yield (>80%), a narrow product distribution, and proceeded under mild reaction conditions. However, if hexachlorocyclotriphosphazene reacted first with 2-allylphenol and then reacted with phenol or 2,2,2-trifluoroethanol, the yield had low (<10%), and hydrolysis must be considered.

Copolymerization reactions are free-radical reactions of 2-allylphenoxyorganocyclotriphosphazenes with phenoxy and 2,2,2-trifluoroethoxy group reacting with STY, MMA, and VBC, respectively. The reactions are expressed as follows.



Type of the Copolymerization

In this work, syntheses of four types (thermal, free-radical, anionic, and with ultraviolet irradiation) of the copolymerization were conducted to prepare and characterize the copolymer. Thermal copolymerization without an initiator was tested in the range of 40–120°C. No copolymer was obtained. Hence, synthesis of this type cannot be used to stimulate the C=C bond to undergo free radical polymerization. When the initiator was AIBN, all copolymerizations occurred (Table I). The advantages of synthesis of this type are the easily controlled reaction condition and the large degree of polymerization. When BuLi served as initiator, the yield of copolymer was small. Two copolymers (IVa and Va) were formed (Table I). The electron-withdrawing effect of the phosphazene ring decreased the reactivity of allyl phenoxy moiety. This procedure is unsatisfactory to synthesize a copolymer of this kind. In ultraviolet irradiation's experiment, the yield at a short wave length (254 nm) was greater than that at 365 nm. However, the yield was smaller than that with AIBN, and copolymers are poorly soluble in general organic solvents to form a transparent gel. The utility is limited.

In Table I, when the weight loss of the copolymer is half, the temperature is expressed as T_{50} in thermogravimetric experiment. T_{50} , T_g , and char yields

with AIBN as initiator were greater than those with *n*-BuLi and ultraviolet irradiation.

Effect of Monomer Ia (or Ib) Concentration

Although the strongly electron-withdrawing effect of the phosphazene ring on the allyl phenoxy moiety is decreased due to insulation by an oxygen atom,¹² 2-allylphenoxyorganocyclotriphosphazene (I) does not undergo significant homopolymerization by way of AIBN activation. We concentrated on copolymerization reactions with STY, MMA, and VBC. A series of control experiments were carried out. Ia (or Ib) at varied concentrations of in the feed influenced the composition of the copolymers and revealed the varied characterization of the copolymers. Figure 1 is a plot of content of I in the copolymer versus the molar fraction of I in the feed. The content of I in the copolymer increased when the molar fraction of I in the feed increased. When the phosphazene unit reacted with VBC, the contents of I in the copolymer greatly increased. Figures 2 and 3 show that the weight conversion of copolymerization and the molecular weight of the copolymers decreased when the concentration of I in the feed increased. The weight conversion of the copolymerization with phenoxy side group was greater than that with a 2,2,2-trifluoroethoxy side group. The or-

Table I Characterization of the Copolymer on Different Initiator

Initiator	Copolymer	Mol % of I in Copolymer	M_n	T_{50}	T_g	Char Yield
AIBN ^a	IIIa	3.16	41,193	421	99	0
	IVa	3.87	38,101	400	120	0
	Va	11.06	28,512	538	65	52.1
	IIIb	4.85	41,574	435	103	0
	IVb	4.95	30,104	398	118	0
	Vb	7.48	33,776	542	68	50
<i>n</i> -BuLi ^b	IVa	3.8	41,783	391	119	8.3
	Va	3.04	35,491	493	54	43.4
Ultraviolet	IIIa ^c	4.25	17,308	430	78	1.9
	^d	2.76	18,524	402	76	0
	Va ^c	6.17	78,851	528	59	47.8
	^d	1.00	67,809	373	52	28.2
	IIIb ^c	3.02	7,246	352	74	1.2
	^d	3.98	10,489	361	71	0
	Vb ^c	7.824	69,188	532	60	48.0
^d	3.14	70,301	488	53	39.8	

Reaction condition: mol ratio of II/I = 5.

^a 60°C, 36 h, AIBN = 2 wt %.

^b 60°C, 36 h, *n*-BuLi = 10 wt %.

^c Room temp, 48 h, λ = 254 nm.

^d Room temp, 48 h, λ = 365 nm.

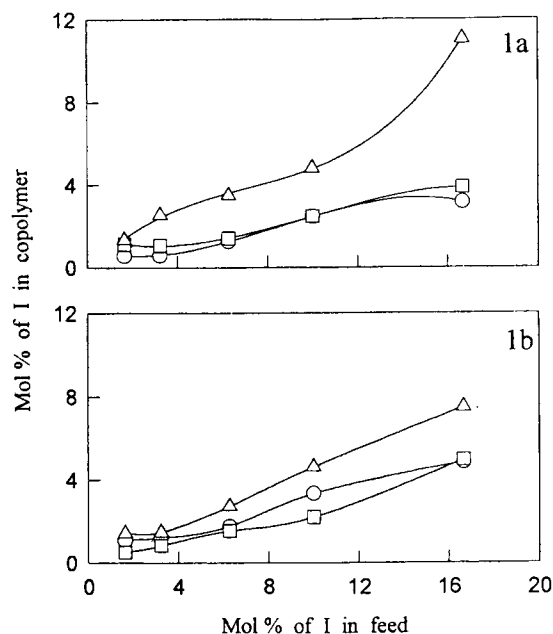


Figure 1 Effect of the concentration of **I** in the feed on the content of **I** in the copolymer (1a) **I** = **Ia**, (1b) **I** = **Ib**: 60°C, 36 h, AIBN = 2 wt %, (O) STY, (□) MMA, (Δ) VBC.

der of molecular weights of the copolymers is **III** > **V** \approx **IV**. According to Figures 1–3, reaction conditions of copolymerization of phosphazene with phenoxy side group were more favorable than those with 2,2,2-trifluoroethoxy group. The amount of **I** incorporated into the copolymer seemed not to affect the degree of polydispersity (M_w/M_n), rather it affected M_w and M_n individually (Fig. 4). The average values of M_w/M_n for **III**, **IV**, and **V** were about 2.1, 4.0, and 1.4, respectively. The distribution of molecular size of **IV** from reacting MMA with 2-allylphenoxyorganocyclotriphosphazene was random and broad. From Figure 3, increasing the proportion of **I** in the feed resulted in smaller molecular weights. Hence, 2-allylphenoxyorganocyclotriphosphazene may have a greater probability of acting as a chain-terminating or chain-transfer agent.

Reactivity Ratio and Alfrey–Price Parameter

The method of Fineman and Ross¹⁷ was used to calculate approximate values of the reactivity ratio. The nature of **Ia** (or **Ib**) was obtained by combining r_1 and r_2 from the copolymerization system with the Alfrey–Price equation.¹⁸ The results of these calculations appear in Table II. According to experimental data, the reactivity ratio for **II**, r_1 , was much larger than that for **I**, r_2 ; hence, the rate of con-

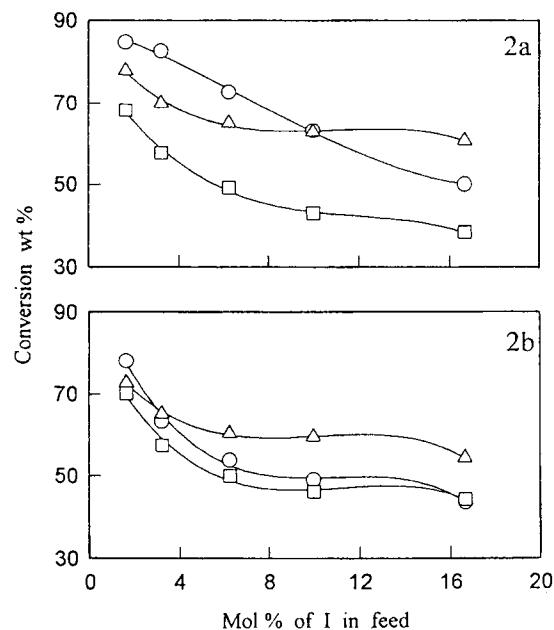


Figure 2 Effect of the concentration of **I** in the feed on the conversion of the reaction (1a) **I** = **Ia**, (1b) **I** = **Ib**: 60°C, 36 h, AIBN = 2 wt %, (O) STY, (□) MMA, (Δ) VBC.

sumption of **II** exceeded that of **I**. The values of $r_1 \cdot r_2$ were located among 0 and 1. These copolymerizations formed a block polymer and preferred

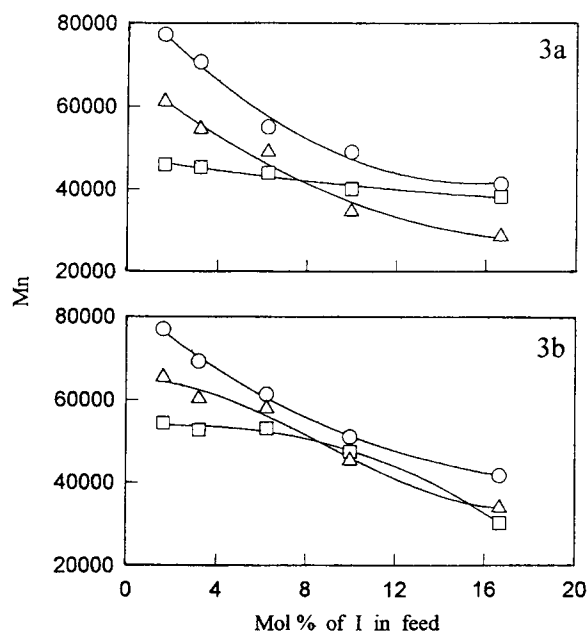


Figure 3 Effect of the concentration of **I** in the feed on the molecular weight of the copolymer (1a) **I** = **Ia**, (1b) **I** = **Ib**: 60°C, 36 h, AIBN = 2 wt %, (O) STY, (□) MMA, (Δ) VBC.

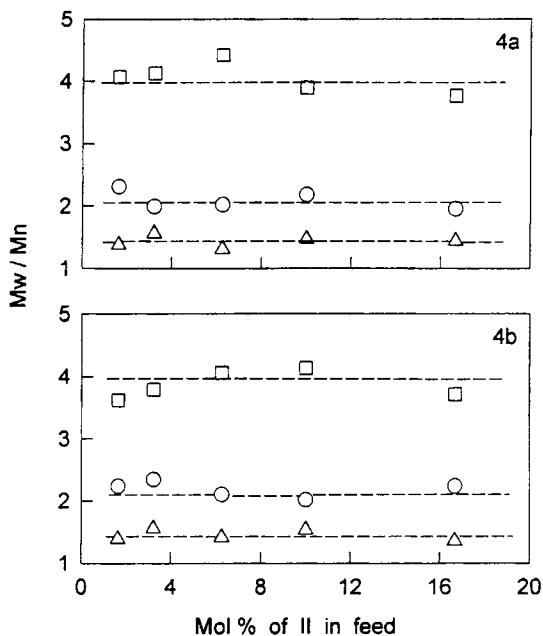


Figure 4 Effect of the concentration of **I** in the feed on the degree of polydispersity (1a): **I** = **Ia**, (1b) **I** = **Ib**: 60°C, 36 h, AIBN = 2 wt %, (O) STY, (□) MMA, (Δ) VBC.

to cross-propagate. The steric crowding of **I** would tend to decrease the incorporated probability of another molecule of **I**. The reactivity of the phosphazene unit with a phenoxy side group (**Ia**) was more than that of **Ib** on reaction with **IIa** or **IIb**. The reactivity ratios (r_1) of **II** were more than one. The addition of a **II** monomer to the growing chain end was favored over the addition of an **I** monomer. The radical of **II** was stable than that of **I**.

The chloride group and acetate group
 $\begin{array}{c} \text{O} \\ || \\ \text{---CC---} \end{array}$ were electronic-withdrawing. The self-

reactivity order of **II** was STY > MMA > VBC. However, the reactivity order of **Ia** with **II** was **Va** > **IVa** > **IIIa**. The reactivity order of **Ib** with **II** was **Vb** > **IIIb** > **IVb**. Alfrey et al.¹⁸ worked out predictive relationships that allow the estimation of r_1 and r_2 from parameters associated with the individual monomers. Each monomer can be characterized by the general reactivity Q , which describes the resonance factor and the polarity interactions of radical and molecule e . The Alfrey-Price Q and e parameters are expected to be identical for **I** with varied copolymerization. However, the Q and e parameters of **I** vary with copolymerization (Table II). The Q parameter was less than one. The e parameter was more than zero. The olefinic center in **I** is highly polar but without substantive tendency to resonance

stabilization, compared with styrene. It is consistent with the reported of DuPont and Allen.¹⁰ The tendency toward alternation is greatest for comonomers having the same Q values with high e values of opposite sign in future work.

Thermal Analysis

Data for thermal decomposition of copolymers are listed in Table III. The reports of Allen and colleagues^{6,10} described decomposition of alkenyl-cyclotriphosphazene copolymers as a two-step process. Although it is tempting to partition the two stages to two distinctive monomer units, the correlation between phosphazene content and weight loss in the first step was qualitative. In this work, the copolymers formed in a two-stage process. The average onset temperatures of **IIIa**, **IVa**, and **Va** were 255, 226, and 244°C, respectively, and that of **IIIb**, **IVb**, and **Vb** were 172, 222, and 240°C, respectively. Hence, the thermal stabilities of copolymers for organic monomers were STY > VBC > MMA (with phenoxy group) and VBC > MMA > STY (with 2,2,2-trifluoroethoxy group). The thermal stability of the phosphazene unit with a phenoxy side group was greater than that with a 2,2,2-trifluoroethoxy side group. The T_{50} values of PSTY, PMMA, and PVBC were 365, 330, and 480°C, respectively. T_{50} values of the copolymers (Table III) all exceeded those above: the order is **V** > **III** > **IV**. Incorporation of the **I** unit into the copolymer increased the thermal stability. The T_{50} value greatly increased on increasing the incorporated proportion of **I** unit in the **V** copolymer. Therefore, the incorporation of **I** unit can increase the thermal stability of the polymer backbone. Char yield represents the residual amount of copolymer at 600°C. As shown in Table III, the char yields of

Table II Reactivity Data for 2-Allylphenoxyorganocyclotriphosphazene Copolymers

Copolymer	r_1	r_2	Q	e
IIIa	5.54	0.02	0.06	0.63
IVa	4.57	0.11	0.23	1.25
Va	1.83	0.27		
IIIb	3.58	0.002	0.047	1.42
IVb	4.32	0.07	0.27	1.49
Vb	2.35	0.36		

Reaction condition: AIBN = 2 wt %, 60°C, 36 h, **I** = 1.1 mmol, **II** = 5.5 mmol. STY: $Q = 1$, $e = -0.8$. MMA: $Q = 0.74$, $e = 0.4$. r_2 , Q , and e for **I**.

Table III Thermal Analysis Data for 2-Allylphenoxyorganocyclotriphosphazene Copolymers

Copolymer	Mol % of Ia		Wt % Loss (1st step)	Wt Loss Range (°C)	T_{50} (°C)	T_g (°C)	Char Yield ^a (%)
	In Feed	In Copolymer					
IIIa	16.7	3.16	19.2	255-360	421	99	0
	10.0	2.48	17.9	250-360	414		0
	7.1	1.25	17.4	260-380	497		0
	3.2	0.60	^b	^b	389		0
	1.6	0.56	^b	^b	379		0
IVa	16.7	3.89	8.8	230-320	400	119	0
	10.0	2.48	18.2	220-335	392		0
	7.1	1.40	8.4	220-315	381		0
	3.2	1.07	7.1	220-325	379		0
	1.6	1.12	29.62	240-340	371		0
Va	16.7	11.06	19.6	250-430	550	65	50.0
	10.0	4.83	18.9	240-440	531		48.6
	7.1	3.51	17.84	245-440	528		48.1
	3.2	2.56	17.1	245-440	527		48.2
	1.6	1.34	16.6	240-440	524		47.3
IIIb	16.7	4.85	8.1	205-275	435	103	0
	10.0	3.33	12.21	220-275	418		0
	7.1	1.75	11.34	185-275	383		0
	3.2	1.20	3.32	100-160	395		0
	1.6	1.09	2.60	150-175	380		0
IVb	16.7	4.95	10.5	215-320	398	118	0
	10.0	2.19	7.9	220-280	390		0
	7.1	1.53	7.8	220-260	369		0
	3.2	0.82	7.53	230-260	374		0
	1.6	0.49	6.67	225-250	361		0
Vb	16.7	7.48	28.4	135-420	542	68	49
	10.0	4.61	26.1	225-420	532		47.3
	7.1	2.72	29.2	280-420	516		46.3
	3.2	1.42	12.2	275-440	496		44.1
	1.6	1.47	26.8	285-425	490		42.4

Reaction condition: 60°C, 36 h, AIBN = 2 wt %.

^a Char yield: the amount of residues at 600°C.

^b The 1st step loss was not obvious.

III and IV were zero, but the char yield of V was more than 40 wt %. Hence, the thermal stability of V is much greater than those of III and IV. The thermal stability of the copolymer with phenoxy side group was greater than that with a 2,2,2-trifluoroethoxy side group.

Glass transition temperatures measured with a differential scanning calorimeter appear in Table III. According to the results, T_g for PSTY, PMMA, and PVBC are 100, 130, and 70°C, respectively. T_g varies with the reagent STY, MMA, or VBC in synthesis of the copolymer. The incorporation of the I unit decreased T_g of the copolymers. The results are similar to the results of Allen et al.⁷

The copolymers were flame-retardant under normal atmospheric conditions. Qualitative tests were

conducted simply on holding a flame source to the powdered copolymer. The flame retardation of the phosphazene system was superior to that of an organopolymer, i.e., PSTY, PMMA, and PVBC. The order was V > IV > III.

Tensile Tests

Polymer films for the mechanical measurements were prepared by casting THF (DMAC or CH₂Cl₂) solutions of polymers. The films of III and V were too brittle to form the specimen. Table IV shows stress-strain data for IV. It exhibits a high Young's modulus. As the incorporated amount of I increases, Young's modulus tends to decrease and the polymer becomes softer and ductile.

Table IV Tensile Properties for Copolymers

Copolymer	Mol % of Ia		% Strain at Peak	% Strain at Break	Stress at Peak (MPa)	Stress at Break (MPa)	Young's Modulus (MPa)
	In Feed	In Copolymer					
IVa	16.7	3.87	7.18	7.18	28.25	28.25	648
	10.0	2.48	7.67	7.67	36.21	36.21	730
	6.3	1.40	5.81	5.81	29.64	29.64	865
	3.2	1.07	8.07	8.07	43.79	43.79	986
	1.6	1.12	12.79	12.79	43.29	43.29	978
IVb	16.7	4.95	7.09	7.09	31.11	31.11	590
	10.0	2.19	12.45	12.45	46.87	46.87	772
	6.3	1.53	6.57	6.57	41.22	41.22	903
	3.2	0.82	7.12	7.12	43.87	43.87	859
PMMA	1.6	0.49	17.91	17.91	55.72	55.72	1093
	0	0	8.28	8.28	52.87	52.87	1194

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