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Synthesis and Characterization of Poly(alkoxy- and aryloxyphosphazene) Copolymers

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Copolymers with two different side groups, 2,2,2-trifluoroethoxy and *p*-chlorophenoxy groups, have been synthesized by reaction of poly(dichlorophosphazene) with their sodium salts, and characterized by elemental analysis, gel permeation chromatography, IR and NMR spectroscopies. The molecular weight measurement has shown that the weight average molecular weight, \bar{M}_w of the copolymers are all above 10^6 and their molecular weight distributions are monomodal and narrow ($\bar{M}_w/\bar{M}_n < 4$). Thermal properties of these copolymers measured by DSC and TGA exhibited to be intermediate between those of the two corresponding homopolymers.

Introduction

Since hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$, was first thermally polymerized to a soluble high molecular weight poly(dichlorophosphazene), $(\text{NPCl}_2)_n$, by Allcock,¹ many different types of poly(organophosphazenes) were prepared by nucleophilic substitution of the chlorine atoms with various organic groups.²⁻⁶ A wide variety of chemical and physical properties of poly(organophosphazenes) is given depending on the kinds of the organic substituents. It is known that, in particular, poly(organophosphazenes) with alkoxy and/or aryloxy groups, $[\text{NP}(\text{OR})(\text{OR}')]_n$, exhibit excellent elastomeric properties.^{6,7} In general, when R and R' are the same aromatic groups, the homopolymers are microcrystalline and thermally stable but show low tensile strength. On the other hand, when R and R' are not the same and one or both of them are aliphatic, the copolymers exhibit noncrystalline and flexible properties but are thermally unstable.⁸⁻¹⁰ In an attempt to prepare an elastomer with improved mechanical and thermal properties we have prepared copolymers by substitution of poly(dichlorophosphazene) with trifluoroethoxy and *p*-chlorophenoxy groups, and characterized by means of

elemental analysis, gel permeation chromatography and various spectroscopic techniques.

Experimental

Chemicals. Hexachlorocyclotriphosphazene (Aldrich) used for polymerization was purified by sublimation at 50°C under vacuum (~0.1 mmHg). Sodium (Nakarai), reagent grade *p*-chlorophenol and 2,2,2-trifluoroethanol (Aldrich) were used as received. 1,4-Dioxane (Kento) and all other solvents were thoroughly dried by distillation over sodium and benzophenone under nitrogen atmosphere before use.

Measurements. IR spectra of polymers were recorded on Analect FX-6160 FT-IR spectrometer in thin film between NaCl disks. ¹H-NMR and ³¹P-NMR were measured using Bruker AM-60 and Bruker AM-200 spectrometers, respectively. The chemical shifts for ³¹P-NMR are relative to reference of 85% aqueous phosphoric acid solution. Solution viscosity measurements were made with a Cannon-Ubbelohde Type No. 526 viscometer at 25°C (± 1) using DMF or THF as solvent for copolymers and acetone for homopolymers. Gel permeation chromatography data were obtained with the

use of a Waters 150C-ALC/GPC liquid chromatograph with a refractive index detector. μ Styragel (500, 10⁴, 10⁵, 10⁶, Å) columns were calibrated with narrow molecular weight polystyrene standards. The columns were previously calibrated with fractionated samples of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$. A 0.1 % solution of *n*-Bu₄NBr in THF was employed as the eluent. Glass transition temperature, T_g , were measured by a Stanton Redcroft DSC-700 under helium flow, and thermogravimetric analysis of the polymers was performed using Perkin-Elmer TGA-2.

Preparation of poly(dichlorophosphazene)(1). 1 was prepared according to the general procedure in the literatures.¹¹⁻¹³ Approximately 5 g of purified hexachlorotriphosphazene was placed in an ampoule made of 22 cm × 2.3 cm (O.D.) pyrex tube. The ampoule was subjected to vacuum (0.1 mmHg) for 30 min and then heated with the vacuum line closed until the content melted completely. The cooled ampoule was subjected to vacuum for another 30 min and then sealed after filled with argon gas. Polymerization reaction of the trimer was performed at 255(±1)°C in a specially designed reaction oven in which a metal axle holding the ampoules is rotating with 1 rpm for stirring the molten reactant. The reaction was stopped when the reactant became nonfluid. The reaction ampoule was broken in the glove box filled with argon gas and the reaction mixture was dissolved in 150 ml of dried dioxane. The solution mixture was then poured into a 500 ml *n*-heptane to obtain a precipitate of 1 with the unreacted trimer and formed oligomers remaining in the solution. The precipitate was dried at 55°C under vacuum (0.1 mmHg) (30% yield) and then redissolved in 100 ml of dioxane for further reaction.

Synthesis of copolymers, $[\text{NP}(\text{OC}_6\text{H}_4\text{Cl})_x(\text{OCH}_2\text{CF}_3)_{2-x}]_n$ (2). The solution of 1 (5.0 g, 0.043 mole) in 100 ml of dioxane was slowly added to a solution mixture of equimolar sodium *p*-chlorophenoxide (5.5 g, 0.043 mole) and equimolar sodium 2,2,2-trifluoroethoxide (5.9 g, 0.043 mole) which were prepared by reaction of the corresponding alcohol mixture with equimolar sodium metal in 100 ml of dioxane. A small amount of *n*-Bu₄NBr (0.5 g, 0.002 mole) was added as catalyst to this reaction mixture, which was then refluxed for 40 hours under nitrogen atmosphere. The solution was concentrated to one third of its initial volume by vacuum evaporation and then poured into 700 ml of distilled water. This aqueous mixture was neutralized with dilute HCl solution and stirred overnight. The resultant precipitate was filtered and dried. The rubbery product was dissolved in THF and the solution was poured again into distilled water to obtain a purified precipitate. Such purification process was repeated twice more using benzene or methanol instead of water to remove any of trimeric or oligomeric derivatives. The finally purified copolymer was dried at 55°C under vacuum. The same procedures were applied to obtain different copolymers of varied mole ratios of the side groups, which were obtained in 22 to 27% yield based on the trimer.

Results and Discussion

Copolymers with different mole ratios of trifluoroethoxy and *p*-chlorophenoxy side groups were prepared by simultaneous substitution¹⁴⁻¹⁹ of chlorine atoms in poly(dichlorophosphazene) with the two side groups in the desired mole

Table 1. ¹H-NMR Data of Polyphosphazene Polymers

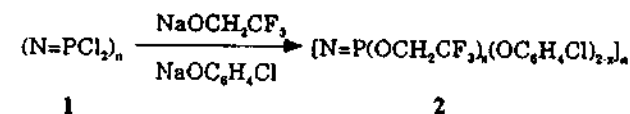
Compound	Chemical shift (δ, ppm)		Mole ratio of [OCH ₂ CF ₃]/[OC ₆ H ₄ Cl] by proton integration	Attempted mole ratio
	P(OCH ₂ CF ₃)	P(OC ₆ H ₄ Cl)		
2a	4.6		2 : 0	2 : 0
2b	5.2	6.8	14.3 : 0.57	2 : 1
2c	4.7	7.3	1.03 : 0.97	1 : 1
2d	4.5	7.3	0.75 : 1.25	1 : 2
2e		7.1	0 : 2	0 : 2

Table 2. Analytical Data for $[\text{NP}(\text{OCH}_2\text{CF}_3)_x(\text{OC}_6\text{H}_4\text{Cl})_{2-x}]_n$

Polymers	C, %		H, %		N, %	
	Clac.*	Found	Clac.*	Found	Clac.*	Found
2a	19.8	19.8	1.66	1.62	5.76	5.75
2b	29.1	28.2	2.00	1.97	5.40	5.41
2c	35.0	36.2	2.21	2.38	5.17	5.11
2d	38.8	40.4	2.35	2.92	5.03	4.65
2e	47.9	47.1	2.66	5.58	4.66	4.75

*Calculated based on the mole ratios obtained from the ¹H-NMR integration ratios in Table 1.

ratios as shown in the following reaction.



Variation of the mole ratios of the side groups resulted in copolymers with different composition which were estimated by comparing the integrated area ratios of the relevant protons of the two side groups, OCH₂CF₃ and OC₆H₄Cl in the ¹H-NMR spectrum of each copolymer. The ¹H-NMR data of those copolymers are listed along with those of the two corresponding homopolymers in Table 1. The measured mole ratios of the substituted side groups are seen to be proximate to the experimentally attempted, but trifluoroethoxide group seems to be more favorable than *p*-chlorophenoxide group for substitution.

The results of elemental analysis of those phosphazene polymers shown in Table 2 are not exactly matched but approximate to the values calculated from the mole ratios obtained from the ¹H-NMR data in Table 1.

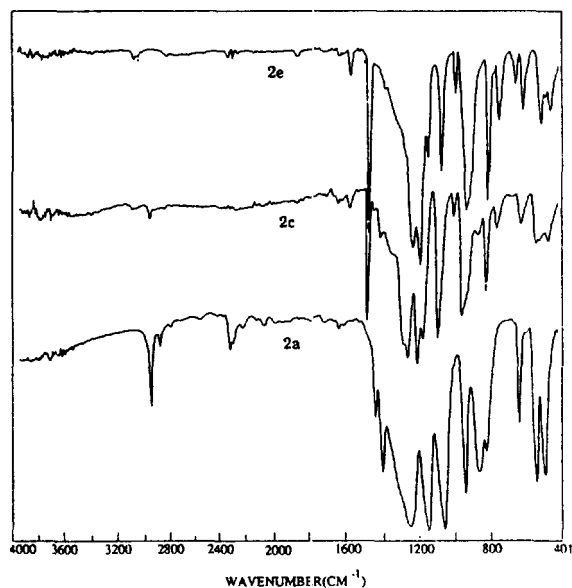
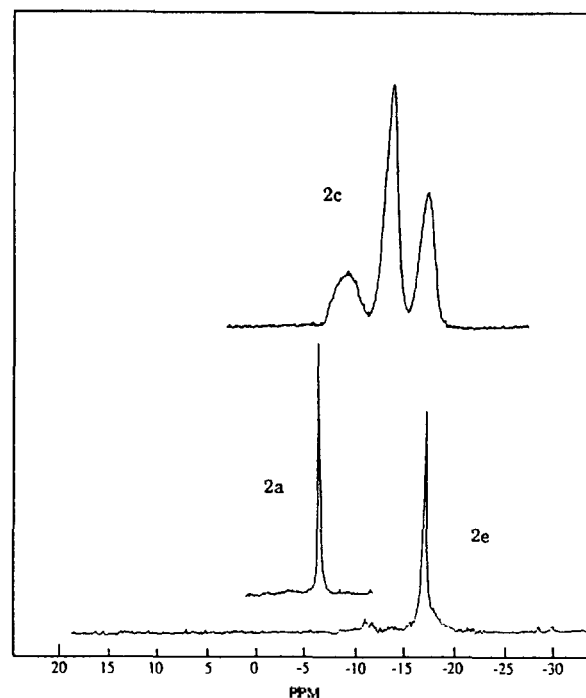
The molecular weights of all the phosphazene polymers have been measured by gel permeation chromatography in THF solution and the results are tabulated along with their properties in Table 3. Like most poly(organophosphazenes), the weight average molecular weights, M_w of our homo- and copolymers are all above 10⁶, but all their chromatograms exhibit a monomodal and narrow molecular weight distribution with low M_w/M_n values as is seen in the table, in contrast to more popular bimodal and broad ($M_w/M_n > 10$) molecular weight distributions in poly(organophosphazenes).^{6,9} There are a few reports^{20,21} for monomodal molecular weight distributions of poly(organophosphazenes) but its reasoning is not clearly explained. The above copolymers were further

Table 3. Molecular Weights and Properties for Phosphazene Polymers

Polymers	\bar{M}_n ($\times 10^5$)	\bar{M}_w ($\times 10^5$)	\bar{M}_w/\bar{M}_n	Intrinsic viscosity [dl/g]	Yield (%)	Solvents	Film properties
2a	2.60	1.34	5.2	1.54	25	THF, Acetone	fiber
2b	3.83	1.44	3.77	2.58	22	THF, Acetone	flexible thermoplastic
2c	7.61	2.06	2.7	2.30	25	THF, Acetone	elastomer
2d	4.00	1.35	3.39	2.12	26	THF, DMSO CHCl_3	flexible thermoplastic
2e	3.01	2.27	7.49	2.05	27	THF, DMSO CHCl_3	flexible thermoplastic

Table 4. Selected Band Assignments of Polyphosphazene Polymers

Polymers	ν (N=P)	ν (P-O-C)	ν (C-H)	ν (C-F)
$[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ (2a)	1272	1419, 1082, 964, 888	2973	1170
$[\text{NP}(\text{OC}_6\text{H}_4\text{Cl})_2]_n$ (2e)	1244	1204, 946	3099	
$[\text{NP}(\text{OCH}_2\text{CF}_3)(\text{OC}_6\text{H}_4\text{Cl})]_n$ (2c)	1256, 1280(Sh)	1203, 1089, 960	2965, 3097	1172

**Figure 1.** IR spectra of homo- and copolymers.**Figure 2.** ^{31}P -NMR spectra of homo- and copolymers.

characterized by means of IR and ^{31}P -NMR spectroscopies.

The IR spectrum of the copolymer with equimolar side groups (2c) is shown along with those of each homopolymers in Figure 1 and some relevant band assignments are given in Table 4. The major band assignments for the homopolymers are already known in the literature.^{13,14,16,18} It is seen in the figure that the spectrum of the copolymer comprises most of the strong bands appearing in the two corresponding homopolymers, but it should also be noted that some relevant bands undergo a considerable shift or disappear. For instance, although both aliphatic and aromatic C-H stretching bands observed with minor red shifts in the copolymer, one of the P-O-C stretching bands appearing at 888 cm^{-1} in the homopolymer with trifluoroethoxy group completely disappears in the copolymer, and the further important aspect is that the P=N stretching band of the copolymer seems not to be simply a combination of the two homopolymer bands in the respect both of band shape and position as is seen in the figure and table. In other words, the spectral

data imply that the copolymers are not a simple combination of the two homopolymer units, but the aliphatic and aromatic side groups are randomly distributed. However, the ^{31}P -NMR spectrum of the copolymer with equimolar side groups shown in Figure 2 suggests that the two substituent groups are not evenly distributed in the N=P back-bone of the copolymer. In the figure the two homopolymers 2a and 2e exhibit sharp singlets at -6.3 ppm and -17.0 ppm ,¹⁹ respectively, but in the copolymer 2c three broad peaks are observed at -9.2 , -13.5 , and -17.2 ppm , which indicates that there are at least three chemically different microenvironments around the phosphorus atom in the polymer back-bone, which, however, can not be easily figured out at the present time.

Thermal Properties. Thermogravimetric analyses were performed for the copolymers and both homopolymers, and

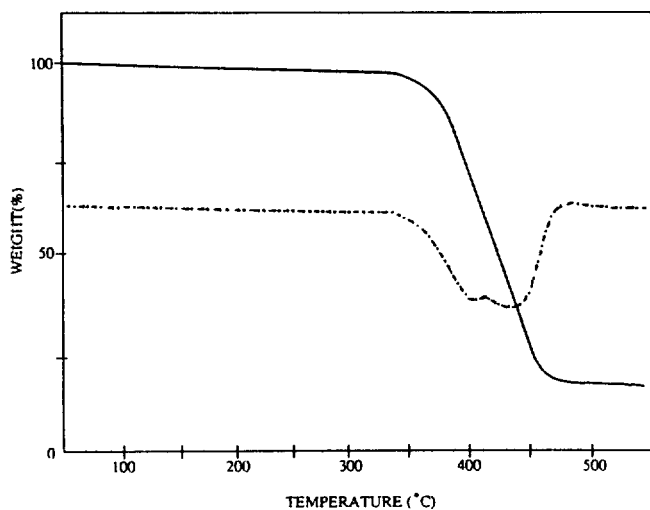


Figure 3. TGA (—) and DTG (---) curves of a copolymer (2c).

Table 5. Thermal Properties of Polyphosphazene Polymers

Polymers	Degradation temp.(°C)		T_g (°C)	T_{max} (°C)
	initial	final		
2a	333	431	-57	408
2b	334	438	-47	404 420
2c	335	456	-25	404 430
2d	337	460	-16	412 430
2e	338	479	10	429

typical TGA and DTG curves of a copolymer 2c were shown in Figure 3. It is seen from the thermogram in the figure that degradation of the copolymer starts at 335°C and ends up at around 456°C with two step decomposition. The first step decomposition with T_{max} value at 404°C seems to be due to dissociation of the more volatile trifluoroethoxy group from the inorganic P=N backbone and the 2nd step decomposition with T_{max} at 430°C due to the *p*-chlorophenoxy group. T_{max} is a temperature at which the rate of weight loss is maximum. Similarly, the values of the thermal parameters of other copolymers (2b, 2d) and homopolymers were obtained from their thermograms and were tabulated in Table 5 along with their glass transition temperatures, T_g , measured by differential scanning calorimetry.

As is seen in the table, the degradation temperature of

the polymers increases as the content of the *p*-chlorophenoxy group increases. Thus the thermal stability of the copolymers is intermediate between those of the two homopolymers as expected. The glass transition temperature of the copolymers exhibits the similar tendency: the T_g value (-25°C) of the copolymer with equimolar side groups (2c) is in the median range of that of the flexible trifluoroethoxy polymer (-57°C) and that of the more rigid *p*-chlorophenoxy polymer (10°C).

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