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Synthesis of New Polyphosphazenes. The Reactions of Poly(dichlorophosphazene) with Aminotetraalkoxycyclotriphosphazene and Sodium Phenoxide

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ABSTRACT

A new poly(organophosphazenes) copolymer was formed from the reaction of aminopentafluoroethoxycyclotriphosphazene, sodium phenoxide, and poly(dichlorophosphazene). The polymer was thermoplastic and the T_g increased with an increasing amount of the phenol group. The T_g of the polymer with aminopentafluoroethoxycyclotriphosphazene attached as a pendant group was similar to the T_g of polyfluoroethoxyphosphazene.

INTRODUCTION

The study of linear organophosphazenes has attracted increasing attention in the past 10 years, both from the viewpoint of fundamental research and technological development. Interest has centered around the investigation of synthetic pathways and fundamental properties, and the development of these polymers for rubbers and plastices applications.

All of the side groups of poly(organophosphazenes) consist of such organic compounds as alkoxy, amine, and phenoxy. In this report the synthesis of a new type of polyphosphazenes using monofunctional cyclic inorganic compound is described.

EXPERIMENTAL

Preparation of the Starting Materials

Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was prepared by the reaction method of Kajiwara [1]. The pure trimer was obtained by repeated distillation. The trimer had a melting point of 112°C.

Aminopentachlorocyclotriphosphazene, $N_3P_3Cl_5NH_2$, was prepared by the method of Feistel [2].

Aminopentafluoroethoxycyclotriphosphazene, $N_3P_3NH_2(OCH_2CF_3)_5$, was prepared from the reaction of aminopentachlorocyclotriphosphazene and sodium fluoroethoxide, $NaOCH_2CF_3$, in THF as solvent. The purified product, using xylene, had a melting point of 61°C.

Linear poly(dichlorophosphazene), $(NPCl_2)_n$, was prepared as follows; after 5 g of purified $(NPCl_2)_3$ was placed in a Pyrex tube (200 cm × 2 cm) it was washed with distilled water and dried by heating, the tube was evacuated under 15×10^{-4} -10^{-3} mm for 1 h. After the polymerization was over, the tube was cooled to room temperature. Linear poly(dichlorophosphazene) was isolated from the tube by the method of Allcock [3].

Chlorine Substitution Reaction of Linear Poly(dichlorophosphazene)

A THF solution of aminopentafluoroethoxycyclotriphosphazene was added to a THF solution of linear poly(dichlorophosphazene). The mixed solution was refluxed under vigorous stirring for 24 h. Unreacted chlorine atoms in the polymer were reacted with sodium phenoxide, $NaOC_6H_5$. After the reaction was over, the solution was filtered to remove $(Et)_3NHCl$ and NaCl. The crude polyphosphazene was prepared when the filtered solution was evaporated. Polyphosphazene was purified by reprecipitation using n-heptane and THF as solvents. All of the reactions were carried out under dried N_2.

Analysis of the Polymers

The molecular weight of the polymer was determined by gel permeation chromatography on a Toso HLC-802 model having a TSK GMH_6 column and a polystyrene calibration curve.

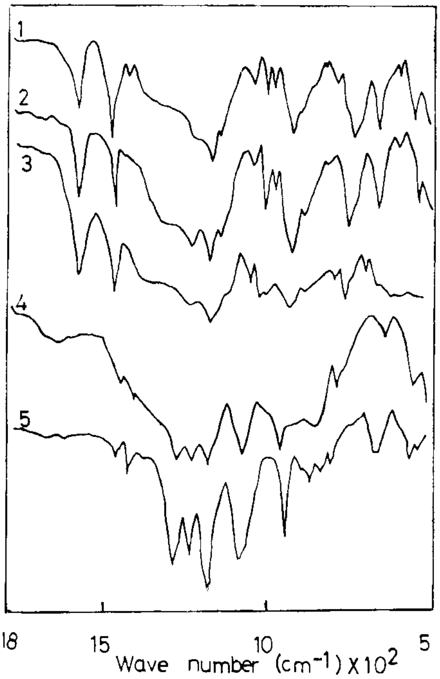


FIG. 1. Infrared spectra of the polymers $\{NP(OC_6H_5)_x[HNP_3N_3(OCH_2CF_3)_5]_{2-x}\}_n$: (1) x = 2, (2) x = 1.90, (3) x = 1.49, (4) x = 0.7, (5) x = 0.

The infrared spectra of the polymer were recorded with a Shimazu IR-450 model using the KBr disk method.

The glass transition, melting, and decomposition temperatures of the polymer were determined with a Shimazu DSC-50 MS model.

The viscosity of the polymer was determined with a Toki Sangyo E model viscometer at 23°C in benzene.

RESULTS AND DISCUSSION

The infrared spectra of the polymer is shown in Fig. 1. The frequency of the C_6H_5 groups in the polymers appeared at near 1500 and 1600 cm^{-1}, respectively. Their absorption maxima is reduced with an increasing amount of aminopentafluoroethoxycyclotriphosphazene. The considerable change of the –P=N– stretching vibration in the polymer due to phenol groups does not occur when compared

TABLE 1. The Amount of Phenol or Chlorine, and the $\overline{M}_w$, $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of the Polymers

$\{NP(OC_6H_5)_x[NHN_3\text{-}P_3(OCH_2CF_3)_5]_{x-2}\}_n$, x						
Calculated	Found[a]	Cl[b] (%)	η (dL/g)	$\overline{M}_w \times 10^4$	$\overline{M}_n \times 10^4$	$\overline{M}_w/\overline{M}_n$
2.00	2.00	0.09	1.26	172	19.33	8.9
1.95	1.95	-	0.56	57	12.95	4.4
1.90	1.90	0.07	0.54	60	10.91	5.5
1.80	1.75	0.06	0.54	35	12.07	2.9
1.50	1.49	0.04	0.30	39	16.25	2.4
0.70	-	-	-	-	-	-
0.00	0.00	0.04	0.90	60	-	-

[a] Ultraviolet method using methanol as the solvent.
[b] Absorption spectroanalysis method.

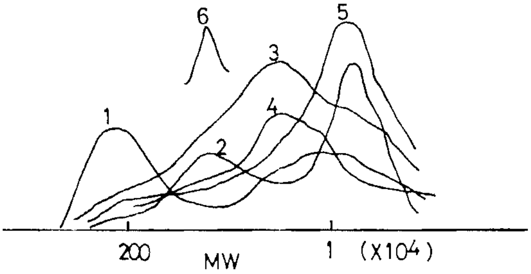


FIG. 2. Molecular weight distribution curves of the polymers $\{NP(OC_6H_5)_x[HNP_3N_3(OCH_2CF_3)_5]_{2-x}\}_n$: (1) x = 2, (2) x = 1.95, (3) x = 1.90, (4) x = 1.75, (5) x = 1.49, (6) x = 0.

with the polymer having only aminopentafluoroethoxycyclotriphosphazene as the side chain.

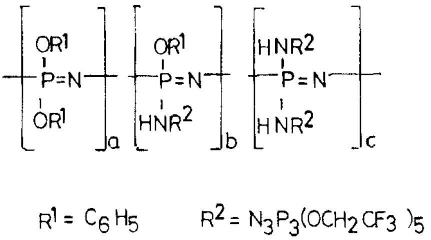
The amount of phenol or chlorine is determined by ultraviolet absorption or chemical analysis, and the results are summarized in Table 1. The experimental data are in good agreement with theoretical results. A small amount of unsubstituted chlorine remained in the polymer.

TABLE 2. Glass Transition and Decomposition Temperatures of the Polymers

$\{NP(OCH_2CF_3)_x\text{-}[NHN_3P_3(OCH_2CF_3)_5]_{x-2}\}_n$, x	T_g (°C)	T_d (°C)	Appearance
2.00	-10	300	White, thermoplastic
1.95	-11	270	Pale green, thermoplastic
1.90	-13	258	Milk white, thermoplastic
1.75	-9	238	White, thermoplastic
1.49	-11		
	-27	176	White, thermoplastic
0.70	-22		
	-33		
	-52	160	White, thermoplastic
0.00	-64	119	White, thermoplastic

The molecular weight distribution curves of the polymer are shown in Fig. 2. The $\overline{M}_w$, $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and the degree of dispersion or intrinsic viscosity of the polymers are summarized in Table 1. The different distribution curves appear due to the poly(dichlorophosphazene) which was not prepared in the same batch. On the other hand, when the degree of dispersion ranges from 2.4 to 8.9, the size of the molecular is a homogeneous system as shown in Table 1.

The glass transition T_g or the decomposition temperature T_d of the polymers was determined by DSC, and the results are summarized in Table 2. The T_g of the polymer decreases with a decreasing concentration of the phenol groups. According to the determination of T_g, the thermal stability of the polymers bonded to two kinds of side groups decreases with an increasing amount of aminopentafluoroethoxycyclotriphosphazene. This may mean that the symmetry of the polymer molecule is significantly altered by aminopentafluoroethoxycyclotriphosphazene. It is also found that the stable polymer has a higher T_g upon heating. A thermal stable polymer will be formed if a diaminocyclotriphosphazene such as the $(NH_2)_2N_3P_3R_4$ moiety can be attached in the polymer chain as in carborane polymers [4].



SCHEME 1.

Furthermore, a doublet or triplet T_g is observed when the value of x is 1.5 to 0.7, respectively. Thus it seems that each side of the polymer is attracted as a block as shown in Scheme 1. However, it is difficult to determine the values of a, b, and c. In the case of the polymer $[NP(NHP_3N_3R_2]_n$, where R is a OCH_2CF_3 group, the T_g is similar to that of the polymer $[NP(OCH_2CF_3)_2]_n$. Consequently, $HNP_3N_3(OCH_2CF_3)_5$ in the polymer may be working in the same manner as the OCH_2CF_3 group.

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