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Synthesis and properties of poly(organophosphazenes) electrolyte $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H\text{-}p)_x]_n$

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Poly(anilino sulphanic)phosphazene $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H)_x]_n$ was prepared by the reaction between poly(anilino)phosphazene $[NP(NHC_6H_5)_2]_n$ and sulphonic chloride (HSO_3Cl) in tetrachloroethane solvent. It was found that the glass transition temperature and conductivity of poly(anilino sulphanic)phosphazene increased with increasing value of x. In addition, the storage power of the polymer with $x = 0.74$ was determined and they were possible to charge by repitation of the use.

1. Introduction

Various poly(organophosphazenes) have been prepared by many researchers and one or two have been commercially produced by the Ethyl Co. Recently, Blonsky and Shriver [1] reported that poly(*bis*-methoxy ethoxy)ethoxy phosphazene complexed with metal trifuroroethane sulphonate has good conductivity at room temperature and is a promising candidate for use in high-energy–density batteries. There have been no papers published on the synthesis of polyphosphazenes electrolytes without complexes. Usually, poly(dichloro)phosphazene $(NPCl_2)_n$ was not reacted with nucleophilic reagents such as bi- or trifunctional reagents, because a cross-linking reaction occurred. This paper describes the synthesis and properties of polyphosphazenes electrolytes.

2. Experimental procedures

2.1. Preparation of hexachlorocyclotriphosphazene $(NPCl_2)_3$ and poly(dichlorophosphazene $(NPCl_2)_n$

$(NPCl_2)_n$ was prepared by the method given by Saito and Kajiwara [2]. Purified $(NPCl_2)_3$ had a melting point of 112° C. $(NPCl_2)_n$ was also prepared by the method given by Kajiwara and Shiomoto [3] using a catalyst such as sulphur recrystallized from benzene.

2.2. Preparation of poly(*bis*anilinophosphazene) $[NP(NHC_6H_5)_2]_n$ and poly(anilino sulphanic)phosphazene $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H)_x]_n$

$[NP(NHC_6H_5)_2]_n$ was prepared by the modified technique described by Allcock and Kugel [4]; i.e. a solution of poly(dichlorophosphazene) prepared by the solution polymerization method reported by Kajiwara and Shiomoto [3] using as catalyst a sulphur compound, was added to a solution of aniline in tetrahydrofuran (THF) and the mixture was then boiled at reflux for 48 h and then allowed to stand at 25° C for 1 week. The precipitated aniline hydrochloride was filtered off and polymer was isolated by dropwise precipitation of the filtrate into absolute ethanol. The white fibrous polymer was then reprecipitated from benzene solution into ethanol, from THF into a large excess of water, and several times from dioxane into water. Synthesis of poly(*bis*sulphonicphosphazene) $[NP(NHC_6H_4SO_3H)_2]_n$ was also very difficult from the reaction between $(NPCl_2)_n$ and bifunctional nucleophilic reagents such as sulphonic acid $HSO_3C_6H_4NH_2$ because of cross-linking reactions which occurred. If the substitution reaction of chlorine atoms in $(NPCl_2)_n$ with sulphonic acid proceeded, the product prepared was insoluble in most organic solvents.

$[NP(NHC_6H_5)_2]_n$ was then reacted with HSO_3Cl in tetrachloroethane solvent, after dissolving 5 g $[NP(NHC_6H_5)_2]_n$ having a molecular weight about 4.5 to 15.7×10^4, in 100 ml tetrachloroethane, adding an adequate amount of HSO_3Cl diluted with tetrachloroethane dropwise into the tetrachloroethane solution containing the dissolved $[NP(NHC_6H_5)_2]_n$. They were reacted with vigorous stirring at room temperature for 4 h. After the reaction was completed, 10 g anhydrous acetic acid was added dropwise to the n-heptane solution to decompose any unreacted HSO_3Cl. The precipitated product was purified by repeating the reprecipitation technique several times.

2.3. Analysis

The molecular weight of the polymer was determined by gas-phase chromatography (GPC) using THF solvent, and a Toyosoda HLC-801A type instrument and

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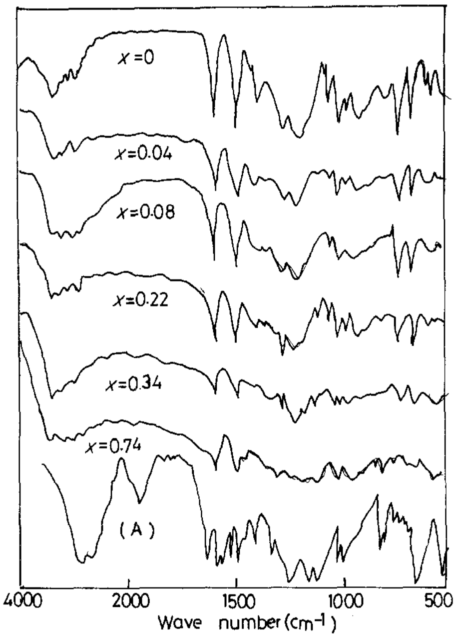

Figure 1 Infrared absorption spectra of $H_2NC_6H_4SO_3H$-*p*(A) and $[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n$.

with G2000 + G3000 or G5000 + G4000 columns. An infrared absorption instrument (Shimazu IR-450) was also used. The thermal analysis of the product was determined using a Shimazu thermal analyser DT-20B. The resistivity of the product was determined with a Takeda TR-8651 type ammeter using platinum and guarded electrodes to eliminate the surface current by the method described by Kajiwara *et al.* [5].

3. Results and discussion

3.1. Preparation of poly(anilonophosphazene) $[NP(NHC_6H_5)_2]_n$ and poly(anilino sulphonic phosphazenes) $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H)_x]_n$

The molecular weight of poly(*bis*anilinophosphazene) prepared by the modified method, was determined by GPC and the results obtained are summarized in Table I. Infrared absorption spectra of $[NP(NHC_6H_5)_2]_n$, the product formed using various concentrations of chlorosulphonic acid and sulphonic acid, are given in Fig. 1.

It was found that the $-SO_3H$ group in the product and sulphonic acid appears near 1160 and 680 cm^{-1}, and the absorption intensity of the product increases with increasing $-SO_3H$ groups. It appears that the $-SO_3H$ group binds to the para position of benzene because absorption bands of $NH_2C_6H_4SO_3H$-*p* appears near 1160, 1120, 830 and 630 cm^{-1}.

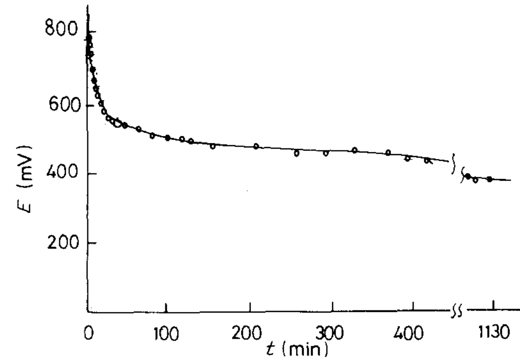

Figure 2 The relation between current and time after 10 h of charging using $[NP(HNC_6H_5)_{1.26}(HNC_6H_4SO_3H)_{0.74}]_n$.

The amount of sulphur in the product prepared under various concentrations of chlorosulphonic acid was determined by chemical analysis, and the results are shown in Table I. It was found that the reaction rate of chlorosulphonic acid was about 34% to 55% under these experimental conditions. The product with many introduced $-SO_3H$ groups can dissolve in the highest polar solvents such as methanol or water. Although poly(*bis*anilinophosphazen) had a composition such as $[NP(NHC_6H_5)_2]_n$, the compositions of the product prepared from the reaction with $[NP(NHC_6H_5)_2]_n$ and HSO_3Cl were type (II), i.e. they had $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H\text{-}p)_x]_n$ with $x \simeq 0.04$ to 0.74 from chemical analysis.

3.2. Electrical properties of poly(anilinosulphonicphosphazenes) $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H\text{-}p)_x]_n$

It is assumed that the polymer prepared in this study has proton conductivity in a similar manner to heteropolycompounds such as molybdenum silicate ($H_4SiMo_{12}O_{40}$), tungsten silicate ($H_4SiW_{12}O_{40}$) or phosphoryltriamide compounds such as $H_2N\{P(O)(NH)_2\}_nH$ described by Kajiwara and Kurachi [6]. The relationship between conductivity and *x* in $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H\text{-}p)_x]_n$ was investigated, and the results are summarized in Table II.

TABLE I Chemical analysis, properties and appearance of the products prepared from the reaction between $[NP(NHC_6H_5)_2]_n$ and $ClSO_3H$ in tetrachloroethane solvent at room temperature for 4 h

Polymer $[NP(NHC_6H_5)_2]_n$		Product							
		Chemical analysis*				Properties†			Appearance
$\bar{M}_w$ ($\times 10^{-4}$)	*n*	1	2	3	4	5	6	7	
8.5	373	0	0	0	0	81	36	51	Light brown powder
4.6	160	0.40	0.22	55.0	10.4	63, −18	35	48	White powder
8.5	373	0.10	0.04	40.0	2.1	63, −18	39	51	Light brown powder
10.4	456	0.20	0.08	40.0	4.0				Brown powder
11.0	382	1.00	0.34	34.0	17.0	40, −2	28	51	Light brown powder
15.7	545	2.00	0.74	37.0	37.0	53, −16	18	57	Brown powder

*1, The number of moles of $ClSO_3H$ using the reaction; 2, the number of moles of $-SO_3H$ determined by chemical analysis; 3, reaction per cent; 4, $-SO_3H/NHC_6H_5$ (mol %).

†5, Glass transition temperature (°C); 6, weight loss (%) at 300°C; 7, weight loss (%) at 500°C.

TABLE II Resistivity of poly(anilino sulphonicphosphazenes) $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H)_x]_n$

x in $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H)_x]_n$	Resistivity (Ω cm)
0	1.0×10^{15}
0.2	2.0×10^{10}
0.4	2.5×10^{7}
0.8	2.7×10^{4}

The proton content in the modified polymers and the conductivity of the polymers increased with increasing value of x as shown in Table II. However, the mother polymer, such as poly(*bis*anilinophosphazene) $[NP(NHC_6H_5)_2]_n$, was the insulator. It was found that the polymers modified with $-SO_3H$ groups became conductive materials. In addition, in order to use the modified polymers having $x = 0.74$ as a battery, their charges and discharges were determined, and the results are given in Fig. 2.

It was found that the storage power of the polymer decreased with increasing time and that they could be repeatedly charged and discharged.

3.3. Thermal properties of poly(anilino sulphonicphosphazene) $[NP(NHC_6H_5)_{2-x}(NHC_6H_4SO_3H)_x]_n$

The glass transition temperature of the modified polymer with $-SO_3H$ groups was determined by DSC, and the results given are summarized in Table I. It is seen in the fifth column of Table I that the polymer has two kinds of glass transition temperature. This is support for the polymer having a different side chain such as $NP(NHC_6H_5)$ or $NP(NHC_6H_4SO_3H)$. Furthermore, the glass transition temperature of the polymer decreased with increasing $-SO_3H$ groups compared with that of the mother polymer. Also, the glass transition temperature located at the higher temperature side belongs to the $NP(NHC_6H_5)$ group, and that located at the lower temperature side belongs to $NP(NHC_6H_4SO_3H)$ groups.

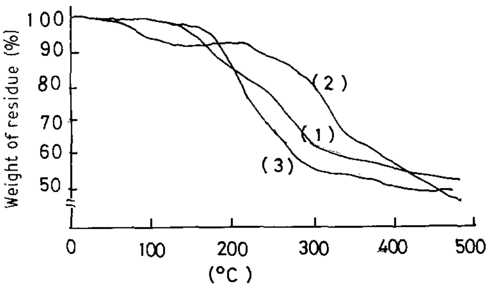

Figure 3 TG curves of $[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n$ on heating at a rate of 5° C min^{-1}. 1, $x = 0$; 2, $x = 0.74$; 3, $x = 0.34$.

The weight losses of the modified and mother polymers determined by thermogravimetry are shown in Table I and Fig. 3. It was found that the modified polymers having $x = 0.34$ or 0.74 were stable on heating at 300° C compared to the mother polymer and the other modified polymers, because their weight loss was less. On the other hand, the weight loss occurring at 500° C was almost the same, independent of x.

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