Synthesis and properties of poly (organophosphazenes) ionomers $[NP(HNC_6H_5)_{2-(x+y)}(HNC_6H_4SO_3H)_x(HNC_6H_4SO_3Li)_y]_n$

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Poly(anilino sulphamicphosphazenes) such as $[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n$ for polymer (I) $x = 0.3$ and for polymer (II) $x = 0.8$ were prepared by the reaction of poly-(anilinophosphazene) $[NP(HNC_6H_5)_2]_n$ and sulphonic chloride HSO_3Cl in tetrachloroethane solvent, several times. Also, H protons in the polymer (I) and (II) were prepared from lithum hydroxide in aqueous solution. It was found, by chemical analysis, that the product prepared with (I) and (II) had compositions such as $[NP(HNC_6H_5)_{1.7}(HNC_6H_4SO_3H)_{0.1}(HNC_6H_4SO_3Li)_{0.2}]_n$(III) and $[NP(HNC_6H_5)_{1.2}(HN-C_6H_4SO_3Li)_{0.8}]_n$(IV). Also, the resistivity of products (III) and (IV) were determined and found to be 3.3×10^7 and $1.5 \times 10^7 \, \Omega\,cm^{-1}$, respectively.

1. Introduction

The various poly(organophosphazenes) have been prepared by researchers and one is commercially produced by Ethyl Co., Firestone Tire and Rubber Co. and Atochem Co. Recently, Shriver [1] reported that poly(bismethoxyethoxy) ethoxyphosphazene complexed with metal trifuroroethane sulphonate has good conductivity at room temperature and make promising candidates for use in high-energy-density batteries. Also, Abraham [2] described a novel approach to utilize the excellent conducting properties of rechargeable solid-state Li batteries using poly(bismethoxyethoxy) ethoxyphosphazene-poly(ethylene oxide) mixed polymer. However, there are no papers on 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-linked reaction occurred. This paper describes synthesis and properties of polyphosphazenes electrolytes such as $[NP(HNC_6H_5)_{2-(x+y)}(HNC_6H_4SO_3H)_x(HNC_6H_4SO_3Li)_y]_n$.

2. Experimental procedure

2.1. Preparation of hexachlorocyclotriphosphazene $(NPCl_2)_3$ and poly(dichloro)-phosphazene $(NPCl_2)_n$

$(NPCl_2)_3$ was prepared by the method described by

Saito [3]. Purified $(NPCl_2)_3$ had a melting point of 112 °C. Also, $(NPCl_2)_n$ was prepared by the method described by Kajiwara [4] using a catalyst such as sulphur recrystallized from benzene.

2.2. Preparation of poly(bisanilino)phosphazene $[NP(HNC_6H_5)_2]_n$ and poly(anilino sulphonic)phosphazene $[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n$ (NPSO)

$[NP(HNC_6H_5)_2]_n$ was prepared by the modified technique described by Allcock [6]. That is, a solution of poly(dichloro)phosphazene prepared from the solution polymerization method reported by Kajiwara [4] using a sulphur compound catalyst, was added to a solution of aniline in THF and the mixture was then boiled at reflux for 48 h and then allowed to stand at 25 °C for one week. The precipitated aniline hydrochloride was filtered off and the polymer was isolated by dropwise precipitation of the filtrate into absolute ethanol. The white fibrous polymer was then reprecipitated from a benzene solution into ethanol, from THF into a large excess of water, and several times from dioxane into water. Also, synthesis of poly(bisulphonic)phosphazene $[NP(HNC_6H_4SO_3H-p)_2]_n$ was very difficult to prepare with the reaction between $(NPCl_2)_n$ and bifunctional nucleophilic

reagents such as sulphonic acid $HO_3SC_6H_4NH_2$ because cross-linking reaction occurred. If the substitution reaction of chlorine atoms in $(NPCl_2)_n$ with sulphonic acid was to proceed, the product prepared would be insoluble in most organic solvents. Then, $[NP(HNC_6H_5)_2]_n$ was reacted with HO_3SCl in tetrachloroethane solvent to prepare a polymer such as $[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n$. That is, after 5 g of $[NP(HNC_6H_5)_2]_n$, having a molecular weight of about $4.5–15.7 \times 10^4$, dissolved in 100 ml of tetrachloroethane, an adequate amount of HO_3SCl diluted with tetrachloroethane was added dropwise to tetrachloroethane solution of dissolved $[NP(HNC_6H_5)_2]_n$. They were reacted with vigorous stirring at room temperature for 4 h. After the reaction was over, 10 g of anhydrous acetic acid was added to the solution to decompose unreacted HO_3SCl, they were added dropwise to n-heptane. The product precipitated was purified by the reprecipitation technique several times. The x value of (NPSO) was determined by chemical analysis of sulphur concentration in the purified polymer. It was found from the analysis that the x value was 0.3 and 0.8, respectively. Also, (NPSO) was used to prepare a polymer such as $NP(HNC_6H_5)_{2-(x+y)}$ $(HNC_6H_4SO_3H)_x(HNC_6H_4SO_3Li)_y]_n$.

2.3. Preparation of $[NP(HNC_6H_5)_{2-(x+y)}$ $(HNC_6H_4SO_3H)_x(HNC_6H_4SO_3Li)_y]_n$

The H proton in (NPSO) can be exchanged with cations such as Li, Na or K. The typical exchange reaction of (NPSO) with lithium hydroxide aqueous solution was described as follows: that is, about 1 g of (NPSO) having an x value of 0.3 or 0.8 was reacted with 100 ml of 0.1M or 0.55M LiOH aqueous solution with vigorous stirring at room temperature. The ion exchange rate was determined by titration with 0.1M HCl. The product was separated with filtration after the ion exchange rate was steady state. Furthermore, they were washed with water, acetone and finally dried at 65 °C under vacuum condition for 48 h. Two kinds of sample were prepared by this method. It was found from X-ray diffraction analysis that they were amorphous solids.

2.4. Analysis of the products

Infrared absorption spectra of the products were determined using the pressed KBr disc technique with a Shimazu Co. IRG-2 type spectrometer. Electrical conductivity of the products containing Li ions were measured by the four probe method using a Takeda TR-8651 type ammeter, Pt and D.C. Samples were moulded under a pressure of about $2.5\ t\ cm^{-2}$ with CIP to form a pellet 1.3 cm in diameter and 0.09–0.13 cm in thickness. To determine the glass transition and decomposition temperatures of the products, differential thermal analysis were carried out using Shimazu TMH-20, DT-20B and R-202 instruments at heating rate of $5\ deg\ min^{-1}$ in air or nitrogen atmosphere.
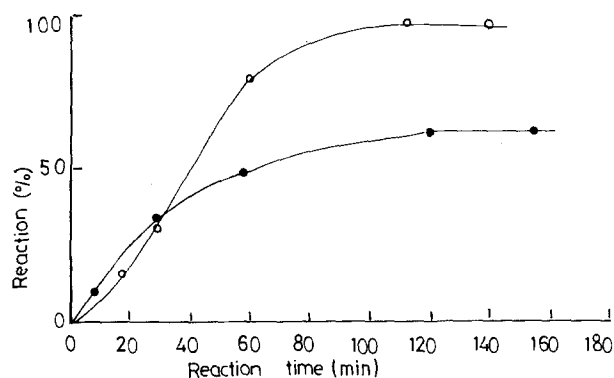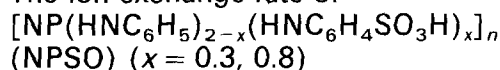

Figure 1 The relation between reaction time and reaction per cent of $[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n$ (($\bigcirc$) $x = 0.3$; ($\bullet$) $x = 0.8$) with Li^+.

3. Results and discussion

3.1. The ion exchange rate of $[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n$ (NPSO) $(x = 0.3, 0.8)$

The ion exchange rate of (NPSO) with lithium hydroxide aqueous solution is determined by the titration method. The relation between the concentration of lithium hydroxide and the reaction time is investigated to find the steady state, and the results obtained are shown in Fig. 1.

It is found that the steady state is reached after 2 h and the product using $x = 0.3$ or $x = 0.8$ has 1.7 or 2.5 wt % of Li. Also, theoretically, 1 g of the polymer having $x = 0.3$ or $x = 0.8$ can exchange with about 27 mg or 24 mg of Li ion as shown by Equation I

$[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3H)_x]_n + LiOH =$

$[NP(HNC_6H_5)_{2-x}(HNC_6H_4SO_3Li)_x]_n + H_2O$ (I)
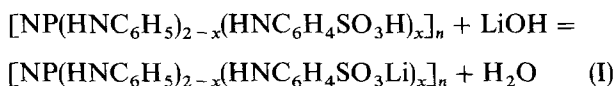
Also, it is found from Fig. 1 that all H protons in $-SO_3H$ of the polymer $(x = 0.8)$ are exchanged by Li ions, however, in the case of the polymer $(x = 0.3)$, about 63% of all the H protons of $-SO_3H$ are exchanged by Li ions. Consequently, it seems that the products prepared with the polymers $(x = 0.3, 0.8)$ has compositions such as $[NP(HNC_6H_5)_{1.7}\ (HNC_6H_4SO_3H)_{0.1}\ (HNC_6H_4SO_3Li)_{0.2}]_n$ (III) and $[NP(HNC_6H_5)_{1.2}(HNC_6H_4SO_3Li)_{0.8}]_n$ (IV), respectively.

3.2. Analysis of $[NP(HNC_6H_5)_{2-(x+y)}$ $(HNC_6H_4SO_3H)_x(HNC_6H_4SO_3Li)_y]_n$ (III) $x = 0.1$, $y = 0.2$; (IV) $x = 0$, $y = 0.8$

Lithium concentration and specific gravity of products (III) and (IV) prepared with (I) and (II) are summarized in Table I. The specific gravity and lithium concentration of the product (V) is larger than that of the product (III).

Infrared absorption spectra of (III) and (IV) are given in Fig. 2. It is found that the $-SO_3H$ group in the original polymers (I) and (II) without Li ions and sulphonic acid $H_2NC_6H_4SO_3H$-p (A) appears near 1160, 1120, 830 and $630\ cm^{-1}$, respectively. However, in the case of (III) and (IV), the absorption intensity appeared at 1160 and $860\ cm^{-1}$, increases due to

| Compound | Li (wt%) | Density (g cc^{-1}) | Property | | Conductivity (Ω cm^{-1}) |
			T_g (°C)	T_d (°C)	
(I) $x = 0.3$, $y = 0$			−2, +40	150	2.5×10^7
(II) $x = 0.8$, $y = 0$			−16, +53	200	2.7×10^4
(III) $x = 0.1$, $y = 0.2$	1.7	1.21	60	180	3.4×10^7
(IV) $x = 0$, $y = 0.8$	1.2	1.23	73	220	1.6×10^7
(V) $x = y = 0$			81	150	1.0×10^{15}

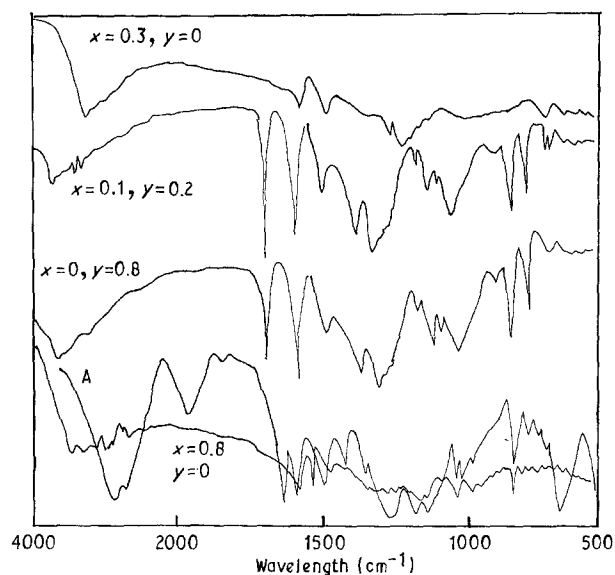T_g = Glass transition temperature T_d = Decomposition temperature

Figure 2 Infrared absorption spectra of $H_2NC_6H_4SO_3H$-p(A) and $[NP(HNC_6H_5)_{2-(x+y)}(HNC_6H_4SO_3H)_x(HNC_6H_4SO_3Li)_y]_n$.

Figure 3 Ohm's law under different temperatures; (———) 5, (— — — —) 15 (···) 25, (— —) 36; (— ·—) 41; (— — — —)4 °C.

Figure 4 The relation between voltage and time with various currents at (a) 5 °C and (b) 15 °C, (———) 0.0002, (···) 0.0004, (····) 0.0006, (— —) 0.0008, (— ·—) 0.0010, (— — —) 0.0012 mA.

exchanging $-SO_3H$ groups with Li^+ ions. This result is in agreement with the ion exchange rate curves as shown in Fig. 1.

Glass transition and decomposition temperatures of products (III) and (IV) or (I) and (II) are determined by differential scanning calorimetry, and the results are summarized in Table 1. It is shown in the fourth column of Table 1 that polymers (I) and (II) have two kinds of glass transition temperatures. This supports the theory that the polymers have different side chains such as $-P-HNC_6H_4SO_3H$ or $-P-HNC_6H_5$. On the other hand, glass transition temperatures of products (III) and (IV) are increased with $-SO_3Li$ groups as compared with that of polymers (I) and (II). Also, glass transition temperatures located in the lower temperature side can be regarded as $-P-HNC_6H_4SO_3H$ groups. However, products (III) and (IV) have higher decomposition temperatures than that of the original polymers (I) and (II).

3.3. Electrical properties of $[NP(HNC_6H_5)_{1.2}$ $(HNC_6H_4SO_3Li)_{0.8}]_n$

Voltage–current $(V–I)$ characteristics of product (IV) determined at different temperatures are shown in Fig. 3. It is found from Fig. 3 that $V–I$ characteristics of product (IV) show a slight change with increasing temperature, but follow Ohm's law between 4×10^{-4}
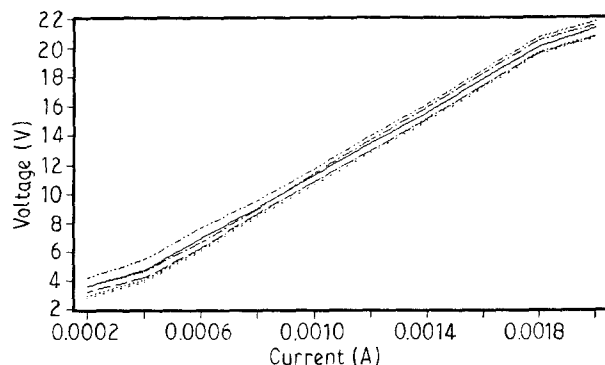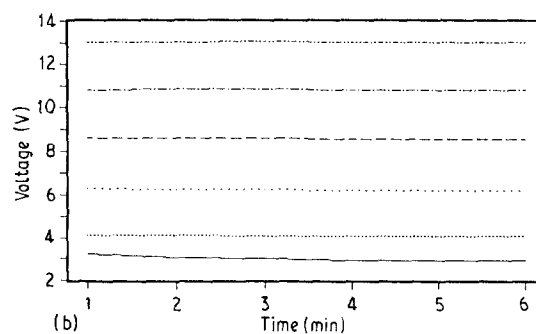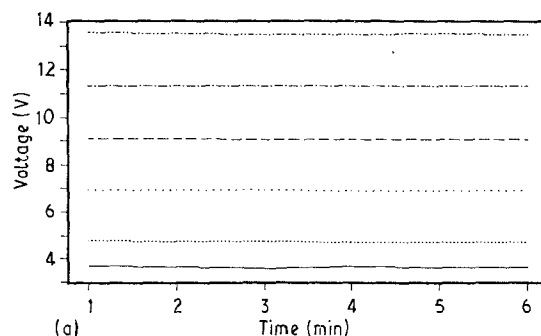
and 18×10^{-4} mA. Also, the relation between voltage and time is determined using the various currents at 5 and 15 °C, respectively. The results obtained at 5 and 15 °C are shown in Fig. 4a and b. As shown in Fig. 4a and b, the most remarkable feature of voltage is its independence of time. Furthermore, electric conduct-
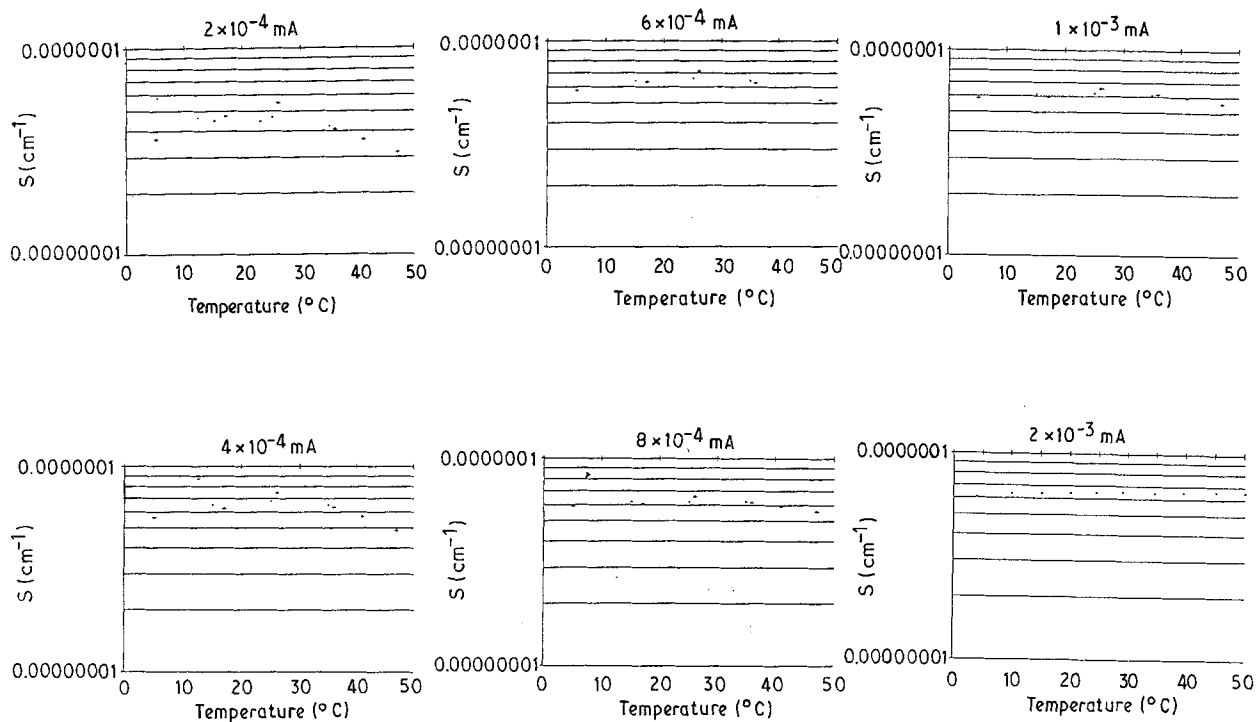
Figure 5 Conductivity with a rise (+) and drop (−) in temperature using the various currents.

ivity of product (IV) is determined under various currents with a rise and drop in temperature. The results obtained are summarized in Fig. 5.

It is found from Fig. 5 that product (IV) shows a small change in conductivity with a rise and drop in temperature because of ionic conductivity. Furthermore, the value of the energy gap, ΔE_G and $\log \rho$ is estimated using Equation 2

$$\rho = \rho_0 \exp(- E/RT) = \rho_0 \exp(E_G/2RT) \qquad (2)$$

The activation energy estimated for conduction of product (IV) is about 1.1 eV, and it is lower than that of $[NP(HNC_6H_5)_2]_n$ described by Hayashi [5] owing to Li ions in $-SO_3Li$ groups of product (IV).

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