Synthesis and properties of poly (organophosphazenes) ionomers

\[ \text{[NP(HNC}_6\text{H}_5)_2-(x+y)(\text{HNC}_6\text{H}_4\text{SO}_3\text{H})_x(\text{HNC}_6\text{H}_4\text{SO}_3\text{Li})_y]_n } \]

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Poly(anilino sulphamicphosphazenes) such as \[ \text{[NP(HNC}_6\text{H}_5)_2-x(\text{HNC}_6\text{H}_4\text{SO}_3\text{H})_x]_n \] for polymer (I) \( x = 0.3 \) and for polymer (II) \( x = 0.8 \) were prepared by the reaction of poly(anilinophosphazene) \[ \text{[NP(HNC}_6\text{H}_5)_2]_n \] and sulphonic chloride \( \text{HSO}_3\text{Cl} \) in tetrachloroethane solvent, several times. Also, \( \text{H} \) protons in the polymer (I) and (II) were prepared from lithium hydroxide in aqueous solution. It was found, by chemical analysis, that the product prepared with (I) and (II) had compositions such as \[ \text{[NP(HNC}_6\text{H}_5)_1.7(\text{HNC}_6\text{H}_4\text{SO}_3\text{H})_{0.1}(\text{HNC}_6\text{H}_4\text{SO}_3\text{Li})_{0.2}]_n \] (III) and \[ \text{[NP(HNC}_6\text{H}_5)_1.2(\text{HN}-\text{C}_6\text{H}_4\text{SO}_3\text{Li})_{0.8}]_n \] (IV). Also, the resistivity of products (III) and (IV) were determined and found to be \( 3.3 \times 10^7 \) and \( 1.5 \times 10^7 \ \Omega \text{cm}^{-1} \), 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 trifluoroethane 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 \( (\text{NPCl}_2)_n \) 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 \[ \text{[NP(HNC}_6\text{H}_5)_2-x(\text{HNC}_6\text{H}_4\text{SO}_3\text{H})_x(\text{HNC}_6\text{H}_4\text{SO}_3\text{Li})_y]_n } \.

2. Experimental procedure

2.1. Preparation of hexachlorocyclophosphazene \( (\text{NPCl}_2)_3 \) and poly(dichloro)phosphazene \( (\text{NPCl}_2)_n \)

\( (\text{NPCl}_2)_3 \) was prepared by the method described by Saito [3]. Purified \( (\text{NPCl}_2)_3 \) had a melting point of 112°C. Also, \( (\text{NPCl}_2)_n \) was prepared by the method described by Kajiwara [4] using a catalyst such as sulphur recrystallized from benzene.

2.2. Preparation of poly(bisulphonic)phosphazene \[ \text{[NP(HNC}_6\text{H}_5)_2-x(\text{HNC}_6\text{H}_4\text{SO}_3\text{H})_x(\text{NPSO})_n } \]

\( (\text{NPSO})_n \) was prepared by the modified technique described by Allcock [6]. That is, a solution of poly(dichlorophosphazene 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 \[ \text{[NP(HNC}_6\text{H}_5\text{H}_4\text{SO}_3\text{H}_2]_n } \] was very difficult to prepare with the reaction between \( (\text{NPCl}_2)_n \) and bifunctional nucleophilic
reagents such as sulphonic acid HO₃SC₆H₄NH₂ because cross-linking reaction occurred. If the substitution reaction of chlorine atoms in (NPC₁₂)₂ was to proceed, the product prepared would be insoluble in most organic solvents. Then, [NP(HNC₆H₄₂)₂]ₙ was reacted with HO₃SCl in tetrachloroethane solvent to prepare a polymer such as [NP(HNC₆H₄₂)₂₋ₓ(HNC₆H₄SO₃H)ₓ]ₙ. That is, after 5 g of [NP(HNC₆H₄₂)₂]ₙ having a molecular weight of about 4.5×10⁴ dissolved in 100 ml of tetrachloroethane, an adequate amount of HO₃SCl diluted with tetrachloroethane was added dropwise to tetrachloroethane solution of dissolved [NP(HNC₆H₄₂)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 HO₃SCl, 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(HNC₆H₄ₓ)₂₋ₓ(HNC₆H₄SO₃H)ₓ]ₙ (IV) x = 0.1, y = 0.2.

2.3. Preparation of [NP(HNC₆H₄ₓ)₂₋ₓ( HNC₆H₄SO₃Li)ₓ]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 reaction was determined by titration with 0.1M HCl. The product was separated with filtration after the ion exchange reaction 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](image-url) The relation between reaction time and reaction per cent of [NP(HNC₆H₄ₓ)₂₋ₓ(HNC₆H₄SO₃H)ₓ]ₙ (NPSO) (x = 0.3, 0.8)

3. Results and discussion

3.1. The ion exchange rate of [NP(HNC₆H₄ₓ)₂₋ₓ(HNC₆H₄SO₃H)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:

\[ \text{[NP(HNC₆H₄ₓ)₂₋ₓ(HNC₆H₄SO₃Li)ₓ] + LiOH} \rightarrow \text{[NP(HNC₆H₄ₓ)₂₋ₓ(HNC₆H₄SO₃Li)ₓ] + H₂O} \] (I)

Also, it is found from Fig. 1 that all H protons in -SO₃H 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 -SO₃H 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(HNC₆H₄ₓ)₁₋ₓ(HNC₆H₄SO₃Li)ₓ]ₙ (III) and [NP(HNC₆H₄ₓ)₂₋ₓ(HNC₆H₄SO₃Li)ₓ]ₙ (IV), respectively.

3.2. Analysis of [NP(HNC₆H₄ₓ)₂₋ₓ( HNC₆H₄SO₃H)ₓ]ₙ

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 -SO₃H group in the original polymers (I) and (II) without Li ions and sulphonic acid H₃NC₆H₄SO₃H-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