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Phosphonitrilic Chloride. XXXVIII. Study of Electrical Conductivity of Diisothiocyanophosphazene Polymer and Hexaisothiocyanocyclotriphosphazene

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ABSTRACT

The electrical conductivity of hexaisothiocyanocyclotriphosphazene $N_3P_3(NCS)_6$ and linear diisothiocyanophosphazene polymer $(NP(NCS)_2)_n$ was determined. It was found that hexaisothiocyanocyclotriphosphazene is ionic and linear diisothiocyanocyclotriphosphazene polymer has predominantly electron conductivity.

INTRODUCTION

Hexaisothiocyanocyclotriphosphazene $N_3P_3(NCS)_6$ was prepared from hexachlorocyclotriphosphazene $N_3P_3Cl_6$ and potassium isothiocyanate KSCN by Audrith [1]. Hexaisothiocyanocyclotriphosphazene was polymerized in the same way by heating hexachlorocyclotriphosphazene. Also, linear diisothiocyanophosphazene polymer was prepared from linear dichlorophosphazene polymer and potassium isothiocyanate by Audrith [2].

This paper describes determinations of electrical conductivity of linear diisothiocyanophosphazene polymer and hexaisothiocyanocyclotriphosphazene.

EXPERIMENTAL

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was prepared from the reaction with phosphorus pentachloride (PCl_5) and ammonium chloride (NH_4Cl) by the method of Kajiwara [3]. The melting point of the pure trimer was about 112°C.

Hexaisothiocyanocyclotriphosphazene was prepared by a modification of the method of Audrith [1]. Potassium isothiocyanate, 29.15 g, was dissolved in 100 ml of dry acetone, and the solution was added to 100 ml of dry acetone containing 17.8 g hexachlorocyclotriphosphazene.

After warming and vigorously stirring the mixture for some time, the reaction solution was filtered on a No. 4G glass filter. The filtrate was placed in Dry Ice for 2 hr. After the white colored crystals obtained were filtered off, they were washed with cooled dry acetone and then recrystallized from n-heptane. The melting point of the crystalline material was about 40°C.

Linear diisothiocyanophosphazene polymer was prepared by the method of Allcock [4].

Infrared spectra of the products were obtained using the pressed KBr disk technique with a Shimazu Co. IRG-2 type spectrometer.

The variation of resistivity with temperature for the products was measured by the method described by Kajiwara [5].

RESULTS AND DISCUSSION

IR spectra of hexaisothiocyanocyclotriphosphazene and linear diisothiocyanophosphazene polymer are shown in Figs. 1 and 2, respectively.

The N_3P_3 frequency in hexaisothiocyanocyclotriphosphazene appears in the region of 890 cm^{-1}. The N_3P_3 frequency is not observed in diisothiocyanophosphazene polymer, while the P=N frequency is shifted towards high frequency owing to cleavage of the N_3P_3 ring.

Disks of hexaisothiocyanocyclotriphosphazene were prepared under pressures of 400 kg/cm^2 and 100 kg/cm^2 for 0.5 hr.

The electrical conductivity is shown in Figs. 3 and 4, respectively.

The energy gaps (ΔE) of the trimer calculated from the general semiconductor equation are 1.94 eV at 400 kg/cm^2 and 1.03 eV at 100 kg/cm^2. The value of the resistivity of the trimer is three orders of magnitude smaller than that for hexachlorocyclotriphosphazene.

This shows that hexaisothiocyanocyclotriphosphazene is easily

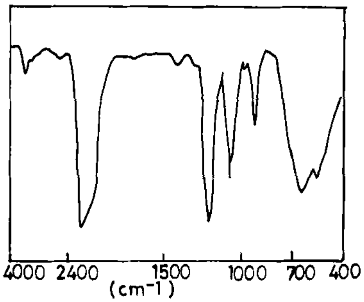

FIG. 1. IR spectra of $[NP(NCS)_2]_3$.

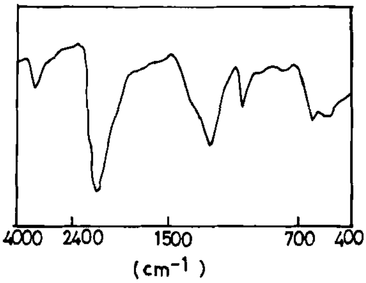

FIG. 2. IR spectra of $[NP(NCS)_2]_n$.

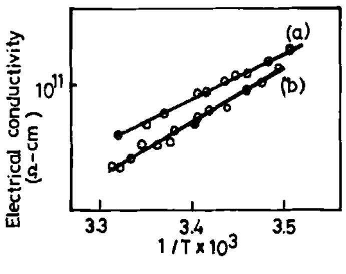

FIG. 3. Electrical conductivity of $[NP(NCS)_2]_3$: (a) from low temperature to high temperature; (b) from high temperature to low temperature.

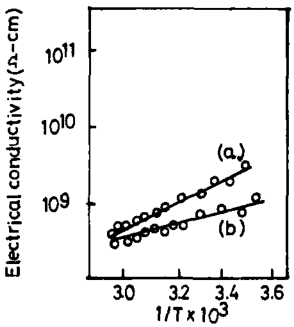

FIG. 4. Electrical conductivity of $[NP(NCS)_2]_n$: (a) from low temperature to high temperature; (b) from high temperature to low temperature.

ionized and polymerized. Variation of electrical conductivity of hexaisothiocyclotriphosphazene is not observed, though that of hexachlorocyclotriphosphazene shows the variation with time.

The electrical conductivity of linear diisothiocyanophosphazene polymer is lower than that of the trimer, as shown in Fig. 4. The energy gap (ΔE) of the trimer calculated is about 0.6 eV. The value of the energy or the resistivity is about two or three orders smaller than the trimer.

It seems that the mechanism of the electrical conductivity is different from that of the trimer, that is, the polymer shows predominantly electron conductivity.

The conductivity measured with increasing temperature does not coincide with the values measured with decreasing temperature due to deterioration of contact between the sample and the electrode on heating, due to degradation of the rubbery polymer.

REFERENCES

[1] G. Tesi, R. J. A. Otto, F. G. Sherif, and L. F. Audrith, *J. Amer. Chem. Soc.*, 82, 528 (1960).
[2] R. A. Otto and L. F. Audrith, *J. Amer. Chem. Soc.*, 80, 5894 (1958).
[3] H. Saito and M. Kajiwara, *Kogyo Kagaky Zasshi*, 66, 618 (1963).
[4] H. R. Allcock and R. L. Kugel, *J. Amer. Chem. Soc.*, 87, 4216 (1965).
[5] M. Kajiwara, M. Hashimoto, and H. Saito, *Polymer*, 14, 488 (1973); *Ibid.*, 16, 361 (1975).

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