Phosphonitrilic chloride: 36. Electrical conductivity of dichlorocyclophosphazene trimer and dichlorophosphazene polymer

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(Received 29 September 1976; revised 19 November 1976)

The resistivity of polycrystalline hexachlorocyclotriphosphazene was investigated over a range of moulding pressures. The best moulding pressure was about 400 kg/cm^2, and Ohm's law was obeyed to 300 V/cm. Although samples prepared under the same conditions gave different values of the resistivity, the equation $\rho = \rho_0 \exp^{(\Delta E/RT)}$ applied in all cases, and the activation energy was about 2.0 eV for all samples. The excitation energy derived from ultraviolet absorption was also about 2.0 eV and it has been assumed that ionic conductivity is predominant.

INTRODUCTION

Eley and Willis[1], and Reucroft[2] have described the electrical conductivity of single crystals and of powdery hexachlorocyclotriphosphazene $(NPCl_2)_3$ and octachlorocyclotetraphosphazene $(NPCl_2)_4$. Allcock and Best[3] reported the electrical conductivity and polymerization mechanism of liquid hexachlorocyclotriphosphazene. Recently, the conductivity of some phosphazene chelating polymers was described by Kajiwara[4,5]. This paper describes the conditions for accurate conductivity measurements of polycrystalline hexachlorocyclotriphosphazene and dichlorophosphazene polymer.

EXPERIMENTAL

Preparation of hexachlorocyclotriphosphazene $(NPCl_2)_3$

Hexachlorocyclotriphosphazene prepared by the modified method of Kajiwara[6] was recrystallized from light petroleum ether. Dichlorophosphazene polymer was prepared by the method of Gimblet[7].

Electron conductivity measurements

The electron conductivity of polycrystalline hexachlorocyclotriphosphazene and the polymer was investigated using the apparatus reported by Kajiwara[4,5]. The value of the electrical resistivity (ρ) was estimated from $\rho = RA\,V/L$, where R is the electrical resistance, A is the plate area (1.3773 cm^2), L is the sample thickness (cm), and V is the volume fraction.

RESULTS AND DISCUSSION

Electrical conductivity of polycrystalline hexachlorocyclotriphosphazene prepared under differential pressure

In general, the resistivity of molecular crystals like phthalocyanine is reduced with increase in the moulding pressure. However, the resistivity reaches a constant value if the material is moulded under pressure above 80 kg/cm^2.

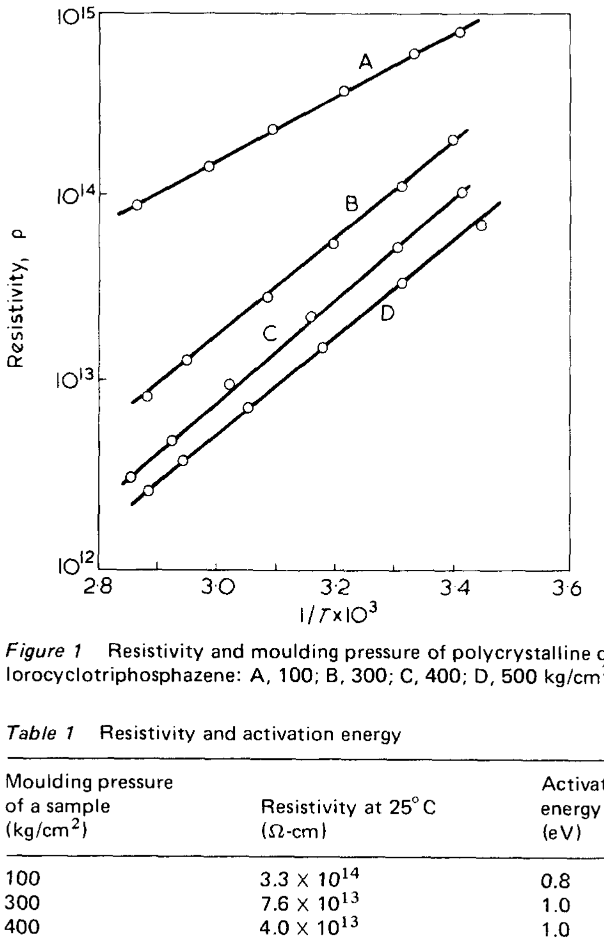

Figure 1 Resistivity and moulding pressure of polycrystalline dichlorocyclotriphosphazene: A, 100; B, 300; C, 400; D, 500 kg/cm^2

Table 1 Resistivity and activation energy

Moulding pressure of a sample (kg/cm^2)	Resistivity at 25°C (Ω-cm)	Activation energy, ΔE (eV)
100	3.3×10^{14}	0.8
300	7.6×10^{13}	1.0
400	4.0×10^{13}	1.0
500	3.1×10^{13}	1.0

The relationship between the resistivity of polycrystalline hexachlorocyclotriphosphazene subjected to various pressures for 10 min and at different temperatures is shown in *Figure 1*. It is found that the resistivity is inversely proportional to the moulding pressure, a phenomenon usually observed with molecular crystals. The activation energy ΔE given in *Table 1* was found to be the same although the re-

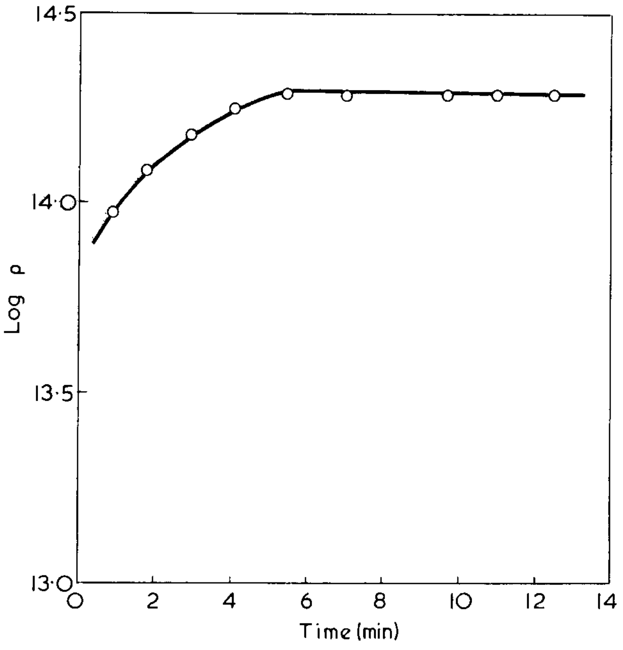

Figure 2 Time dependence of the resistivity of polycrystalline dichlorocyclotriphosphazene prepared under 400 kg/cm^2 for 10 min

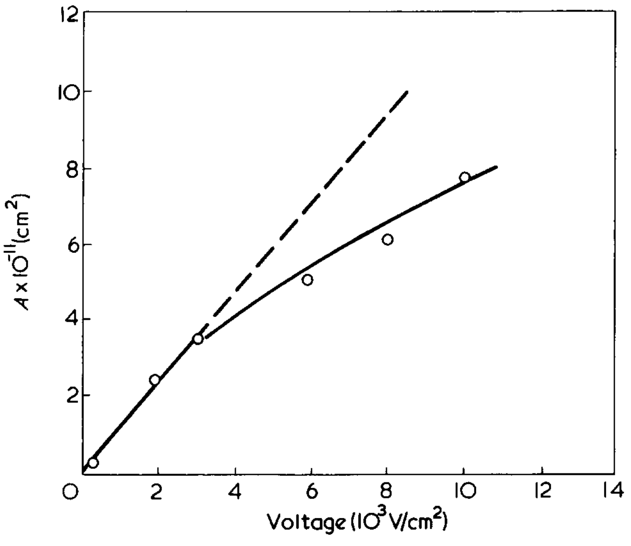

Figure 3 Variation of the resistivity with voltage

sistivity was different. In this case, it is assumed that the conductivity is produced by ions or by π-electrons in the N_3P_3 rings. The time dependence of the conductivity was investigated under constant pressure, and the results are shown in *Figure 2*. The resistivity increases with time and after 10 min, reaches a constant value. Consequently, it is found for the most suitable condition that the determination to be carried out is about 10 min after a sample is placed in the field. Also, the resistivity increases with time and after 10 min, reaches a constant value. This phenomenon is often observed in the case of ionic conductivity and the Hall effect or polarization occurs. If conductivity in the N_3P_3 ring is attributed to the π-electrons and the excitation energy obeys $\Delta E_{ph} \simeq hc/\lambda_{max}$, the theoretical value needed for the exciting state using the Mott–Gurney equation and 250 nm is about 5.04 eV. Ultraviolet absorption of hexachlorocyclotriphosphazene determined in n-heptane gave an excitation energy of 2.0 eV. The large difference in energy shows that the conductivity is governed by ions rather than π-electrons.

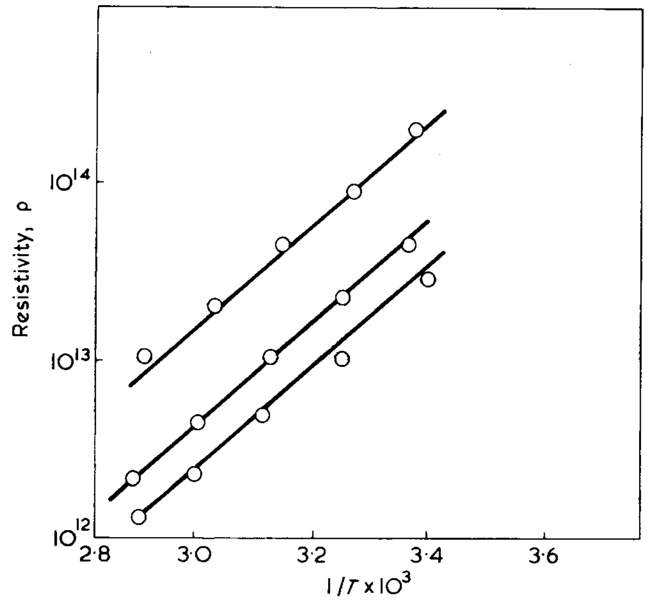

Figure 4 Reproducibility of the resistivity of polycrystalline dichlorocyclotriphosphazene:

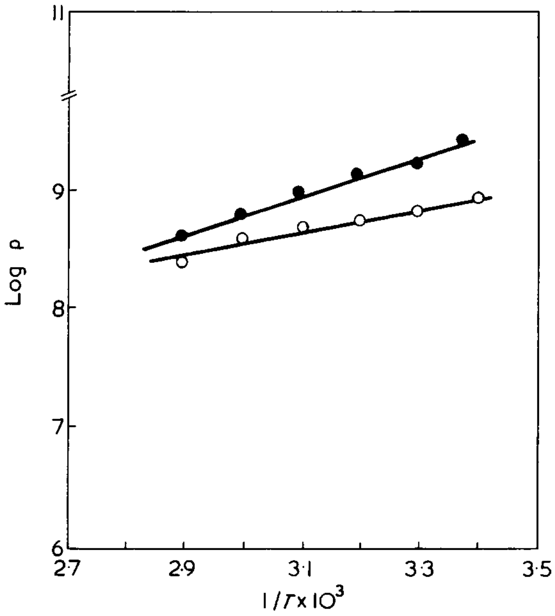

Figure 5 Relationship between the temperature and the resistivity of dichlorophosphazene polymer: ●, heating; ○, cooling

Relationship between the resistivity and voltage

The electric current was determined using a dielectric voltage from 3.0 to 100 V, and the results are shown in *Figure 3*.

Ohm's law was found to hold up to 300 V/cm but failed above this value. Many reports describe similar results, it is assumed that the cause is either an accumulation of a space charge or a barrier between the plate and specimen.

Reproducibility of the resistivity

It is very important to investigate the reproducibility of resistivity. Results for three discs prepared under the same conditions are shown in *Figure 4*. Although the plots were linear and obey the equation $\rho = \rho_0 \exp^{(\Delta E/RT)}$, different lines are obtained.

However, the activation energy ΔE to induce conductivity as calculated from these lines has the same value.

Electrical conductivity of dichlorophosphazene polymer

The change of resistivity of the polymer with temperature is shown in *Figure 5*. The value of the resistivity and the energy gap of the polymer ($\rho = 1.6 \times 10^9 \Omega$-cm, $\Delta E = 0.6$ eV) is decreased by delocalization of π-electrons compared with hexachlorocyclotriphosphazene. The resistivity of the polymer reaches a constant value, and there is no time dependence. Consequently, the resistivity of the polymer is governed by π-electrons rather than ions. Also, Giglio[8] reported that the P–Cl bond is strengthened by the π-electron in the case of the polymer and dissociation of P–Cl into Cl ions is unlikely.

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