Electrical properties of poly(*n*-butylamino) (di-allylamino) phosphazene

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A new organic–inorganic hybrid polymer, poly(*n*-butylamino)(di-allylamino) phosphazene, is synthesized and electrical properties of the polymer are reported. From the results of Fourier transform infrared (FTIR), [1]H-nuclear magnetic resonance (NMR) and ^{31}P-NMR measurements, it was confirmed that the synthesized polymer was poly(*n*-butylamino)(di-allylamino)phosphazene. From an Arrhenius plot of d.c. conduction it was found that experimental points fit to two straight lines, that the discontinuous point could be the glass transition ($T_g = 268.9$ K) and that the activation energies are 0.74 and 1.5 eV at temperatures higher and lower than T_g, respectively. Dielectric constant and dielectric loss factors were measured over the temperature range from $-20\,°C$ to $70\,°C$ with frequency $100\,Hz \sim 100\,kHz$, and a dielectric loss contour was obtained. A relaxation process with the activation energy of 1.44 eV was found from the dielectric loss contour, which can be attributed to α relaxation. A comparison was made between the present results and those of other phosphazene polymers. Because the polymer was non-flammable and shows high resistance and low dielectric constant, it could be used as an insulator in the field of electronics. © *1998 Kluwer Academic Publishers*

1. Introduction

As for the structure of phosphazene polymers a few types are known. One typical type is a phosphazene polymer with $(P=N)_n$ structure as a main chain. It is known that organic polymers become non-flammable when phosphor additives are included. Therefore, phosphazene polymers are essentially non-flammable. These $(P=N)_n$ polymers are generally synthesized from cyclotri(dichlorophosphazene) which is polymerized to give polydichlorophosphazene. Because two chlorine atoms on P can be replaced with many organic groups [1], it is still possible to obtain new non-flammable and organic–inorganic hybrid polymers. Phosphazene polymers are valued for their application in many fields such as a solid electrolyte for lithium batteries [2], biomedical encapsulations [3] and oxygen permeable membranes [4, 5].

A few works have reported on the electrical properties of neat polyphosphazene polymers [6–9] and phosphazene polymers with a functional group or with some dopants [10–12]. We have studied previously electrical properties of polyphosphazenes with acrylic side groups. It is found that these phosphazene polymers with acrylic groups have higher conductivity and higher dielectric constant when the polymers are not rigid [9]. However, this is not desirable for insulating materials. Thus, we have synthesized polyphosphazenes with allylamine side groups on P atoms. This is because flexible films can be obtained from

polyphosphazene with allylamine groups whereas hard films are also obtained by crosslinking the polymer with ^{60}Co γ-ray or u.v.-irradiation. Double bonds of allylic groups are cleaved by the irradiation, which results in crosslinking.

In the present work the synthesis of poly(*n*-butylamino)(di-allylamino) phosphazene and its electrical properties are reported; namely d.c. conduction was measured over the temperature range between -12 and $70\,°C$. The dielectric constant was also measured at frequencies of $100\,Hz \sim 100\,kHz$ and a dielectric relaxation process is discussed.

2. Experimental procedure
2.1. Synthesis of poly(*n*-butylamino) (di-allylamino)phosphazene (PBAP)

Polydichlorophosphazene $(NPCl_2)_n$ was from Atochem Co. (France) and the molecular weight was 5×10^4. *n*-Butylamine, di-allylamine, triethylamine and tetrahydrofuran (THF) were Tokyo Kasei guaranteed reagent grade. First, 50% of Cl atoms on P of $(NPCl_2)_n$ are replaced with di-allylamino groups: $(NPCl_2)_n$ (20 g) added in a flask and then dissolved in THF (100 ml). Into this solution mixture of di-allylamine (40.0 ml), triethylamine (27.9 ml) and THF (50 ml) in a separating flask was slowly added under N_2 atmosphere with stirring. The solution was kept for 24 h at room temperature under N_2 in the dark in

order to complete the reaction. After this procedure a mixture of *n*-butylamine (20.5 ml), triethylamine (27.9 ml) and THF (50 ml) were added to the solution by the same procedure and kept for 24 h at room temperature in the dark under N_2. The purpose for the addition of triethylamine was the separation of the reaction by-product, HCl, as a form of $Et_3N:HCl$ complex. The solution was filtered to take off $Et_3N:$ HCl complex, ethanol was added to the filtrate and then white flake-shaped precipitation was observed. At this stage 33.1 g of precipitation was obtained (yield: 90%). The precipitation was separated, dissolved into THF, precipitation was again obtained by adding ethanol to the solution and the precipitation was filtered out. This procedure was repeated several times. The precipitation was washed several times with distilled water in order to take off residual $Et_3N:$ HCl complex and dried at room temperature. Finally, 31 g of polymer was obtained. The molecular weight of the polymer was determined with gel permeation chromatograph (GPC) to be 50 000.

2.2. Sample preparation

The obtained polymer was dissolved into THF and films were obtained by cast method. The sample for measuring d.c. conductance and dielectric constant was disc shaped (diameter: 30 mm, thickness: 80 μm) and electrodes were made by physical vapor deposition (PVD) of Au.

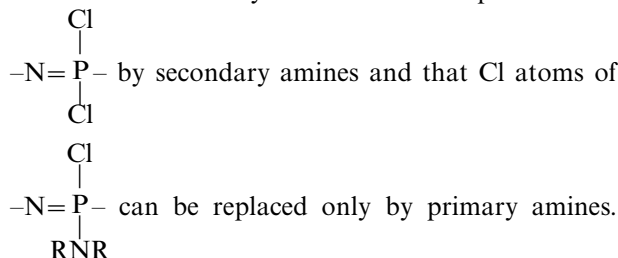## 2.3. Measurement of d.c. conductance and dielectric constant

The measurement of d.c. conductance was made with a d.c. power source (Kikusui PAB 250) and a picoammeter (Takeda Riken TR8641). The dielectric constant was measured with an impedance meter (Mitamusen 12 K) and a wave generator (Trio AG 203). Measurements were performed in a temperature-controlled air bath (Komatus-Yamato CTR-520).

3. Results and discussion
3.1. Poly(*n*-butylamino)(di-allylamino) phosphazene (PBAP)

It is known that the reactivity of amines with poly-dichlorophosphazene is higher for primary amines, lower for secondary amines, and the reaction is not observed for tertiary amines [13]. Thus triethylamine acts as the scavenger for the by-product, HCl. It is also known that only one Cl can be replaced from
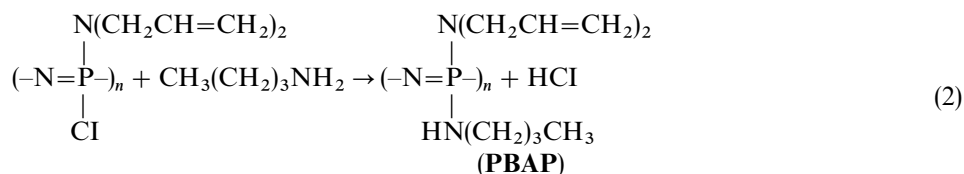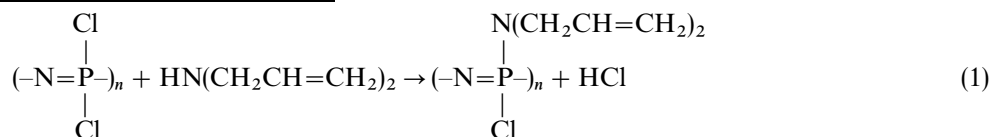
$$\begin{array}{c} Cl \\ | \\ -N=P- \\ | \\ Cl \end{array}$$ by secondary amines and that Cl atoms of

$$\begin{array}{c} Cl \\ | \\ -N=P- \\ | \\ RNR \end{array}$$ can be replaced only by primary amines.

Since we used excess amount of di-allylamine at the first stage and the amount of $Et_3N:HCl$ complex was just as expected, it can be said that the obtained polymer is poly(*n*-butylamino)(di-allylamino)phosphazene. In order to confirm this further the following spectroscopic measurements were carried out.

Fig. 1 shows the Fourier transform infrared (FTIR) spectrum of the obtained polymer. As is seen in Fig. 1, the absorption at ~ 3300 cm^{-1} is ascribed to –N–H. The absorptions at ~ 3000 cm^{-1} and 1640 cm^{-1} are ascribed to =C–H and C=C, respectively. The absorptions at ~ 2800 cm^{-1} and ~ 1800 cm^{-1} can be ascribed to CH–H. Absorptions of P=N, N–P=N and P=N–P should appear at 1240 cm^{-1}, 585 cm^{-1} and 490 cm^{-1}, respectively, but we were unable to identify those because of the overlap with other absorptions. The absorption of P–Cl (~ 500 cm^{-1}) is not observed in Fig. 1. Thus, actually whole Cl atoms of $[N=PCl_2]_n$ are replaced with *n*-butylamine and di-allylamine.

Fig. 2 shows ^{1}H-nuclear magnetic resonance (NMR) of the obtained polymer. In Fig. 2 peaks at ~ 0.8 p.p.m. ~ 1.3 p.p.m. and ~ 2.7 p.p.m. can be ascribed to –CH$_3$, –CH$_2$CH$_2$–, and –N–CH$_2$ of the *n*-butylamino group, respectively. Peaks at 3.6 p.p.m. can be ascribed to –N–CH$_2$– of the di-allylamino group. Peaks at ~ 5 p.p.m. and ~ 5.8 p.p.m. can be ascribed to –C=CH$_2$ and –HC=C– in allylic part.

Fig. 3 shows the ^{31}P-NMR spectrum of the obtained polymer. Peaks are observable at $0 \sim 5$ p.p.m. Any signal corresponding to –P–Cl which should appear at ~ 18 p.p.m. [14] is not observable. The obtained polymer was white and flake-shaped.

From the data on FTIR and NMR described above it can be concluded that the obtained polymer is poly(*n*-butylamino)(di-allylamino)phosphazene. The reaction scheme is given below
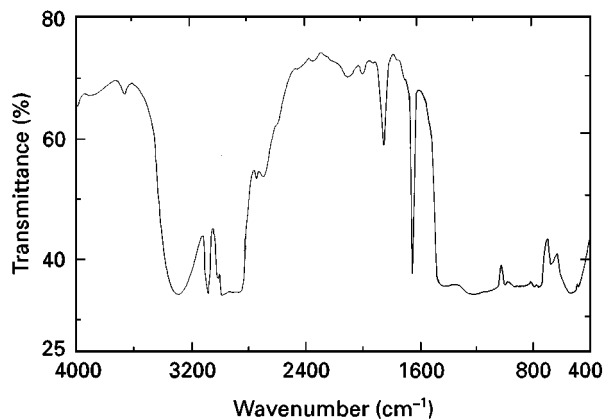
$$\begin{array}{c} Cl \\ | \\ (-N=P-)_n \\ | \\ Cl \end{array} + HN(CH_2CH=CH_2)_2 \rightarrow \begin{array}{c} N(CH_2CH=CH_2)_2 \\ | \\ (-N=P-)_n \\ | \\ Cl \end{array} + HCl \qquad (1)$$

$$\begin{array}{c} N(CH_2CH=CH_2)_2 \\ | \\ (-N=P-)_n \\ | \\ Cl \end{array} + CH_3(CH_2)_3NH_2 \rightarrow \begin{array}{c} N(CH_2CH=CH_2)_2 \\ | \\ (-N=P-)_n \\ | \\ HN(CH_2)_3CH_3 \end{array} + HCl \qquad (2)$$

$$\textbf{(PBAP)}$$

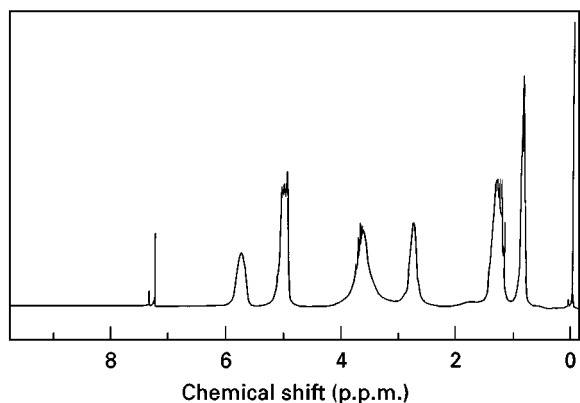*Figure 1* FTIR spectrum of poly(*n*-butylamino)(di-allylamino)phosphazene.

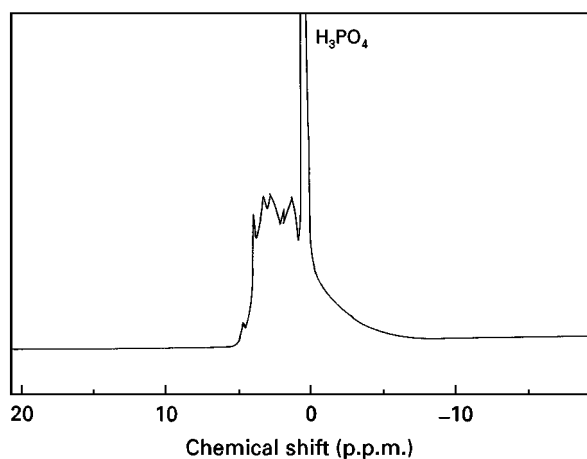*Figure 2* ^{1}HNMR spectrum of poly(*n*-butylamino)(di-allylamino)phosphazene.

Figure 3 ^{31}PNMR of poly(*n*-butylamino)(di-allylamino)phosphazene.

We have confirmed that u.v. or ^{60}Co-γ irradiation causes decreases in the i.r. absorption at $1640\,cm^{-1}$ and the polymer is insoluble as a result of the irradiation. This could be due to crosslinking which is caused by the cleavage of C=C double bonds in allylic part.

3.2. D.C. conductance of PBAP

D.C. conductance of PBAP is shown as a function of the inverse absolute temperature in Fig. 4. As is seen in Fig. 4, experimental points fit to two straight lines. A discontinuous point is seen at $3.719 \times 10^{-3}\,K^{-1}$, namely, 268.9 K. Activation energies for
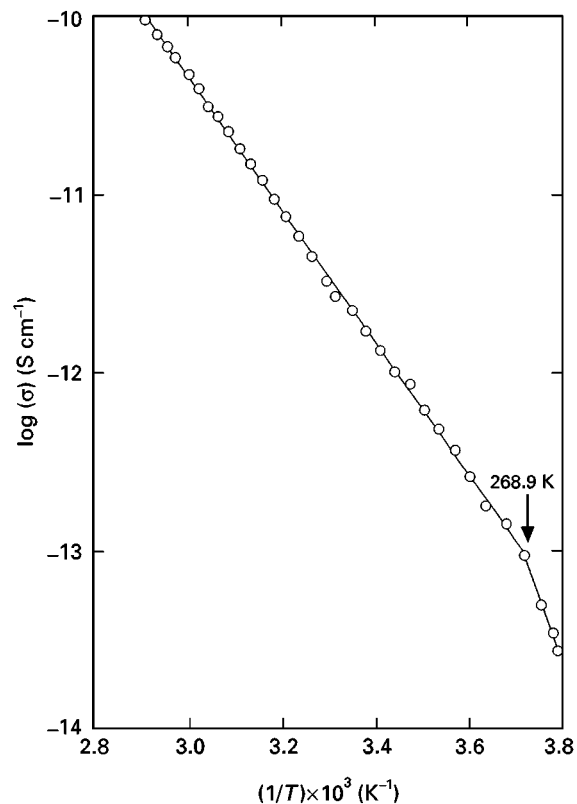

Figure 4 D.C. conductance of poly(*n*-butylamino)(di-allylamino) phosphazene versus inverse of the absolute temperature.

d.c. conduction obtained from the slopes in Fig. 4 are 0.74 eV at temperatures higher than 268.9 K and 1.5 eV at the lower temperature side. Charge carriers of d.c. conduction in PBAP could be impurity ions, as is generally seen in insulators. The discontinuous point in d.c. conduction could be the glass transition temperature (T_g). Namely, this could be the transition temperature of the micro-Brownian motion of main chains of PBAP.

3.3. Dielectric constant of PBAP

Dielectric constant can be expressed as a complex form

$$\varepsilon_r^* = \varepsilon_r' - i\varepsilon_r'' \tag{3}$$

The real part of the dielectric constant (ε_r') is usually called the dielectric constant and the complex part (ε_r'') the dielectric loss or dielectric loss factor. ε_r' of PBAP are shown in Fig. 5 as a function of frequency at the temperatures specified. As is seen in Fig. 5, the dielectric constant decreases with increasing frequency. At frequencies higher than 20 kHz an abrupt decrease is seen. In Fig. 6 the relation between dielectric constant and temperature is shown. The dielectric constant increases with increasing temperature. The rate of increase is higher for lower frequencies, reflecting local motion of the polymer chain.

3.4. Comparison of dielectric constant of PBAP with those of other phosphazene polymers

As described above, dielectric constants are reported for a few types of phosphazene polymers. In
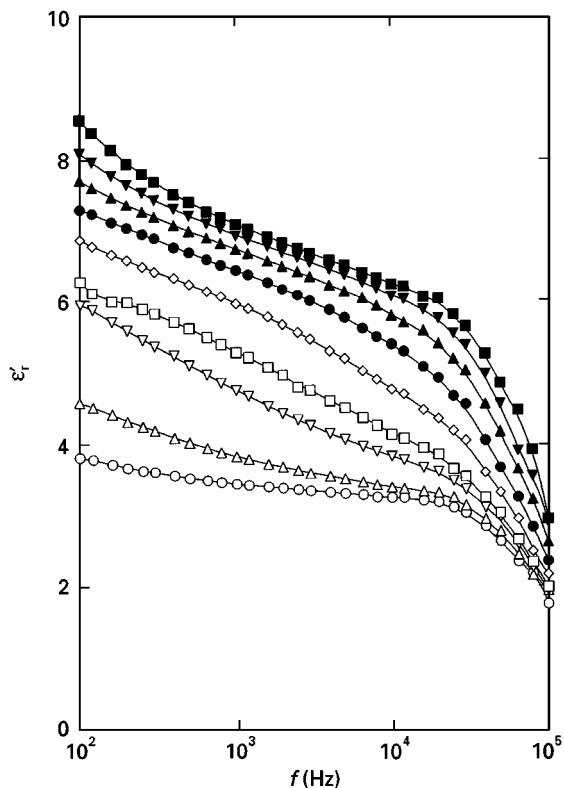
Figure 5 ε'_r of poly(*n*-butylamino)(di-allylamino)phosphazene versus frequency. Temperatures (°C) are, -12.1 (○), -1.9 (△), 9.0 (▽), 19.5 (□), 30.2 (◇), 40.6 (●), 50.4 (▲), 59.9 (▼) and 70.5 (■), respectively.
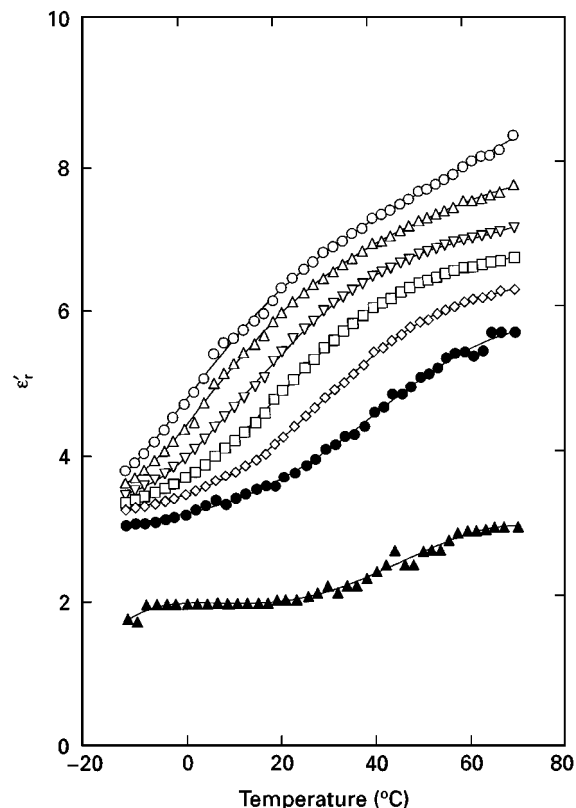

Figure 6 ε'_r of poly(*n*-butylamino)(di-allylamino)phosphazene versus temperature. Frequencies (Hz) are, 120 (○), 300 (△), 1000 (▽), 3000 (□), 10 000 (◇), 30 000 (●) and 100 000 (▲), respectively.

Table I dielectric constants at 20 °C measured at 120 Hz are shown for PBAP as well as for two different types of polymer. In the case of PPZ, PNF and PPI-OEA in Table I, acrylic groups are included in the polymer. PPZ is a rigid polymer (it is said to correspond to 9H pencil hardness), whereas PNF and PPI-OEA are flexible. Therefore, it could be concluded that the dielectric constant of phosphazene polymers which include acrylic groups are higher when the polymers are flexible and lower when the polymer is rigid. On the other hand, PBAP is a flexible polymer; however, the dielectric constant is not too high. Thus, phosphazene polymers such as PBAP may be used as an insulator for electronics because of their high resistance, low dielectric constant and non-flammability.

3.5. Dielectric relaxation process in PBAP

The dielectric loss factor of PBAP was measured over the temperature and frequency range, $-12 \sim -70$ °C and 100 Hz $\sim$ 100 kHz, respectively. The dielectric loss factors are a function of frequency (f) and temperature (T). It may be desirable to express those in a three-dimensional plot. However, we have to display them on two-dimensional paper. Thus, in this work ε''_r is expressed as dielectric loss contours, as is shown in Fig. 7. A straight line can be drawn along the ridge

TABLE I Dielectric constant of phosphazene polymers at 20 °C ($f = 120$ Hz)

	Ref.	ε'_r	Structure
PBAP	this work	6.2	Eq. (2)
PPZ	15	4.7	[I], R=R′=–OCH$_2$CH$_2$C(O)CH$_3$C=CH$_2$
PNF	8	43	[I], R=–OCH$_2$CH$_2$C(O)CH=CH$_2$
			R′=–OCH$_2$CF$_3$
PPI-OEA	9	130 (quick cool)	[II], R=–OCH$_2$CH$_2$C(O)CH=CH$_2$
		23 (slow cool)	
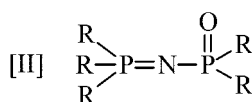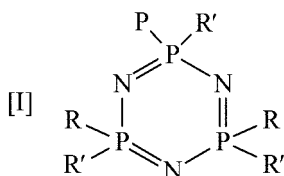
PPZ, PNF and PPI-OEA are obtained from UV-induced polymerization of the corresponding monomer shown above.
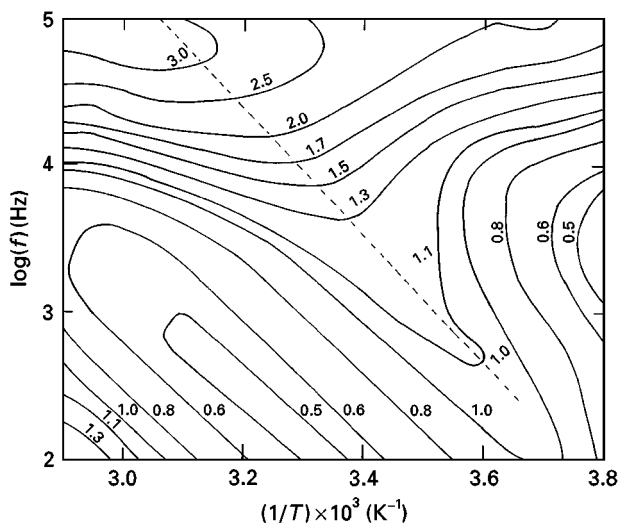
Figure 7 Dielectric loss contour of poly(*n*-butylamino)(di-allylamino) phosphazene.

	Ref.	R_1, R_2	E (eV)
PBAP	this work	$-NH(CH_2)_3CH_3$ $-N(CH_2CH=CH_2)_2$	1.44
PBFP	[7]	$R_1=R_2=-OCH_2CF_3$	1.73
PBPP	[7]	$R_1=R_2=-OCH_2CH_2CH_3$	0.963
PBPAP	[7]	$R_1=R_2=-HNCH_2CH_2CH_3$	1.04

as shown by the dotted line in Fig. 7. The ε_r'' value on the dotted line shows the maximum value at a fixed frequency. Taking the values of the frequency (f_m) and the inverse of the absolute temperature ($1/T$) on the straight line in Fig. 7, the following relation holds between them

$$f_m = A \exp(-E/kT) \qquad (4)$$

where A is a constant, k is the Boltzmann constant and E is the activation energy of a relaxation process. From the slope of the dotted line in Fig. 7 E can be obtained as 1.44 eV. As described above, T_g of the PBAP polymer could be determined from the d.c. conductance as 268.9 K ($1/T = 3.719 \times 10^{-3}$ K^{-1}). It should be noted that the lower temperature edge of the relaxation in Fig. 7 is close to T_g. Therefore, this relaxation can be attributed to an α relaxation process, namely a relaxation by micro-Brownian motion of the segments of the PBAP main chain. The activation energy of the α relaxation process (1.44 eV) is higher than that of d.c. conduction (0.77 eV) in the corresponding temperature region. The reason for this is as follows. In the case of ion conduction small-sized ions hop between ion-trap sites. Thermal motions of small segments are effective for ion conduction whereas the much bigger segments in the polymer main chains must oscillate for any α relaxation process.

Comparison is made for the activation energies of the dielectric relaxation process in phosphazene polymers. The activation energies of the α relaxation process in phosphazene polymers are given in Table II. The present results for the activation energy is similar to those in Ref. 7, as is shown in Table II. Activation energies for the β relaxation process are smaller and appear at lower temperatures. We are now continuing dielectric measurements over a much wider temperature range. Thus, we will report on the β relaxation process in the near future.

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