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The molecular weight dependence of properties of [poly(n-butylamino)$_{2-x}$ (di-allylamino)$_x$]$_n$ phosphazenes

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Poly(n-butylamino) (di-allylamino) phosphazenes were prepared by the reaction of samples of $(NPCl_2)_n$ having a molecular weight of either 5×10^4 or 10×10^6 with n-butylamine, and di-allylamine. Films were prepared by the casting method, and the molecular weight dependence of properties of the film were determined with an Erma refractometer, an oxygen gas permeater, and a tensilon and reho-vibron-orientec. It was found that the refractive index of the film did not depend on the molecular weight and n-butylamine or di-allylamine contents. Also, the glass transition temperature of the films decreased with increasing di-allylamine content. The oxygen gas permeability D_k value increased with increasing di-allylamine content. However, a plot of the Young's modulus values versus amine contents or D_k values did not produce a straight line. In order to make a film having the highest D_k value, the polymer has to have an antisymmetric structure.

1. Introduction

The Otsuka chemical company has developed a series of fluoroalkoxyphosphazene fluids, "Phospharol NF", that exhibit an excellent lubricating ability, oxidative stability, chemical compatibility with plastics, and fire resistance [1, 2]. The Idemitsu petroleum company has commercialized "PPZ" which is, N_3P_3–$(OR)_6$ ($R = CH_2CH_2OOCCH_3CH_2$) as a hard coating material [3, 4]. They are cyclomatrix phosphazene polymers. Polyphosphazenes have attracted considerable attention as an unusual class of inorganic macro- molecules [5–9] since the soluble poly(dichlorophosphazene) was discovered by Allcock and Kugel [10–13] in the early 1960's. For linear poly(organophosphazenes), PNF elastomers, Eypel A and F or Olgarflex A and F have also been commercialized by the Firestone Tire and Rubber, Ethyl Co and Elf Atochem Co, respectively. Also, the Hygenic Co [13–15] have manufactured "NOVUS" a soft denture liner from "Eypel F". They were used as high performance elastomers. Kajiwara [16] reported the study of cultivation bed with some poly(organophosphazenes) and gas permeability and separation or oxygen gas permeability in water [17, 18]. For example, in order to make lens materials with poly(organophosphazenes), they must have a high Young's modulus and tensile strength such as PVA or PE. This paper describes the optical, mechanical and electrical properties and also the oxygen gas permeability of poly(n-butylamino)$_{2-x}$ (di-allylamino)$_x$ phosphazene films.

2. Experimental procedure

2.1. Preparation of poly(n-butylamino)$_{2-x}$ (di-allylamino)$_x$phosphazene (PBA)

The samples of polydichlorophosphazene $(NPCl_2)_n$ used in this study were donated by Elf Atochem Co of France. One had a molecular weight of 10×10^6 $\bar{M}$w whilst the other was 5×10^4 $\bar{M}$w. The following procedure was followed for both of the $(NPCl_2)_n$ samples. Initally the $(NPCl_2)_n$ was dissolved in THF and was then added to a THF solution containing di-allylamine and triethylamine and the mixture was stirred for 24 h at room temperature under a dry N_2 gas flow. At this point n-butylamine which had been predissolved in THF was added to the reaction mixture which was stirred for a further 24 h at room temperature under the dry N_2 flow. At this point, the reaction was considered to be completed and the mixture was filtered. When ethanol was dripped into the filtered solution a white coloured precipitate appeared. This precipitate was separated from the solution by filtration and was then re-dissolved in THF. This solution was then treated with ethanol and the resulting white precipitate was filtered off from the solution. This purification process was repeated several times. The purified polymer was washed with distilled water to remove any remaining Et_3N:HCl and was then dried at 25 °C for 24 h.

2.2. Film preparation

The films of PBA were prepared by the casting method. Initially 5 g of PBA were dissolved in

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30–50 mL of THF and the solution was filtered with 0.5 μm filter and then the solution was placed in a glass vessel and kept at room temperature until the film formed. The prepared film thus was dried at 70–80 °C for 24 h under a vacuum.

2.3. Analysis of the poly(n-butylamino)$_{2-x}$ (di-allylamino)$_x$phosphazene(PBA)

The value of x in the PBA was determined with ^{1}H-nuclear magnetic resonance (NMR) techniques. In addition the degree of replacement with amine groups was determined with ^{31}P-NMR using THF. The refractive index of the films prepared using the casting method was determined with an Erma refractometer. The Young's modulus, the tensile strength, elongation per cent, breaking strength and elongation breaking point were determined with a Toyo Badmin Co Ltd UM II-20 Tensilon.

The dynamic storage (E′) and loss (tan δ) of the film were determined with a DDV-OPA III Rehovibron-Orientec, whilst the oxygen gas permeability value (D_k) in water of the film was determined with a Seikaken type oxygen permeater. The dielectric constant and resistance of the films were determined with an impedance meter (Mitamura D-51S or 12 K). The dc resistance was measured with a digital multimeter (Advantest TR-6848). Measurements were always performed in an air bath (Yamato Coolnics CRT-520), the inside of which was kept dry with silica gel. The sample was formed into a disc shape (3 mm × 0.3 mm).

3. Results

3.1. The analysis of [NP(n-butylamino)$_{2-x}$ (di-allylamino)$_x$]$_n$ (PBA)

In order to determine the value of x in PBA, ^{1}H-NMR of the lower molecular weight polymer was determined, and a typical ^{1}H-NMR spectrum is presented in Fig. 1. The value of x in PBA is determined from the proton ratio, and the results are summarized in Table I. In addition, the proton ratio of PBA having a high molecular weight was determined using the ^{1}H-NMR technique, and these results are also presented in Table I. The ^{31}P-NMR spectra of PBA having x = 0.6 (high Mw) and x = 0.7 (low Mw) were recorded, and the results are presented in Fig. 2.

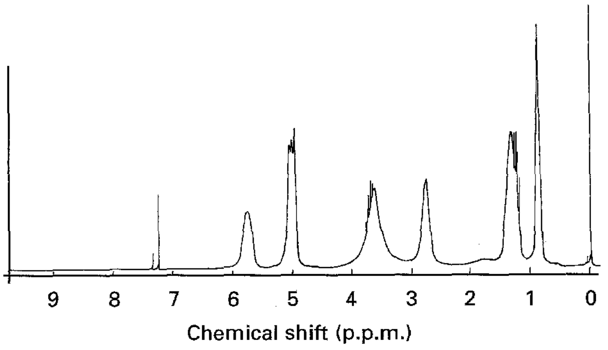


Figure 1 ^{1}H-NMR spectrum of poly(n-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene (Mw = 5×10^4).

TABLE I The value of x determined with ^{1}H-NMR

High Mw [NP(n-butylamino)$_{2-x}$ (di-allylamino)$_x$]$_n$ x	Low Mw x
1.4	1.3
0.9	0.7
0.5	0.3

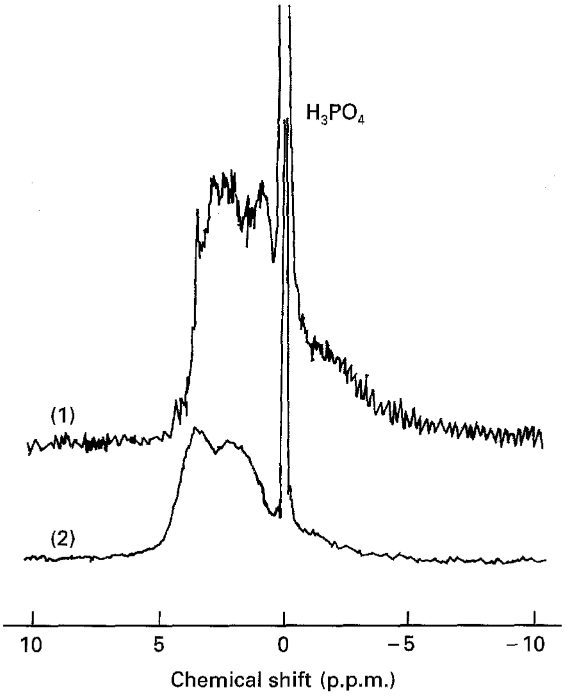


Figure 2 ^{31}P-NMR spectrum of poly(n-butylamino)$_{2-x}$(d-allylamino)$_x$phosphazene. (1): Mw = 10×10^6, x = 0.6, (2) Mw = 5×10^4, x = 0.7.

TABLE II Refractive index and glass transition temperature of [NP(n-butylamino)$_{2-x}$(di-allylamino)$_x$]$_n$

	[NP(n-butylamino)$_{2-x}$ (di-allylamino)$_x$]$_n$ x	Refractive index	T_g (°C)
High Mw	1.4	1.3451	−32.3
	0.9	1.3450	−37.5
	0.5	1.3431	−48.0
Low Mw	1.3	1.3439	−41.3
	0.7	1.3437	−49.1
	0.3	1.3435	−51.4

3.2. Optical properties of PBA

The refractive index of the film was determined, and the results are given in Table II.

3.3. Dynamic storage and loss modulus of PBA

The dynamic storage (E′) and loss modulus (E″) or tan δ of the polymer film having x = 1.4 (high Mw) and x = 1.3 (low Mw) were determined, and the results are shown in Figs 3 and 4, respectively.

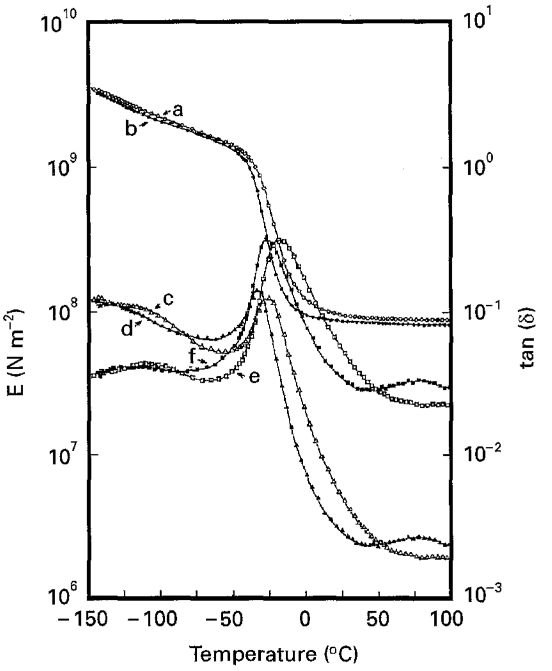


Figure 3 Dynamic storage (E) and loss modulus (tan δ) of poly (n-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene (Mw = 10×10^6, x = 1.4). a (○): E′ at 3.5 Hz, b (●): E′ at 110 Hz, c (△): E″ at 3.5 Hz, d (▲): E″ at 110 Hz, e (□): tan(δ) at 3.5 Hz, f (■): tan(δ) at 110 Hz.

In addition, the dynamic storage and loss modulus of other films having different x values were measured, and the glass transition temperature (T_g) was obtained from their curves and are summarized in Table II.

3.4. Mechanical properties and oxygen gas permeability (D_k) of PBA

The mechanical properties of the polymer were determined, and the results are summarized in Table III. Also the D_k value of the films prepared using both low and high molecular weight polymer were determined, and these results are summarized in Table IV.

In addition the modulus values as a function of n-butylamine content for the polymer is presented in Fig. 5.

3.5. Electrical properties of PBA

The electric resistance as a function of temperature was determined for the polymers x = 0.9 high $\bar{M}$w and x = 1.3 low $\bar{M}$w. The relation between 1/T and

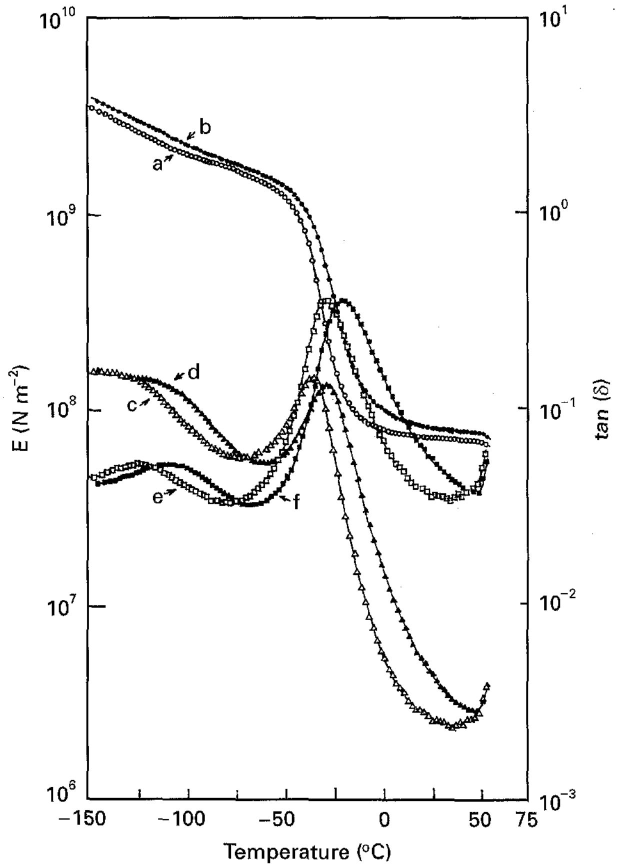


Figure 4 Dynamic storage (E) and loss modulus (tan δ) of poly (n-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene. Mw = 5×10^4, x = 1.3; a (○): E′ at 3.5 Hz, b (●): E′ at 110 Hz, c (△): E″ at 3.5 Hz, d (▲): E″ at 110 Hz, e (□): tan(δ) at 3.5 Hz, f (■): tan(δ) at 110 Hz.

TABLE IV Oxygen gas permeability of [NP(n-butylamino)$_{2-x}$ (di-allylamino)$_x$]$_n$ phosphazene

Mw	[NP(n-butylamino)$_{2-x}$ (di-allylamino)$_x$]$_n$ x	Thickness (mm)	D_k (ml cm s^{-1} mmHg) $\times 10^{-11}$
10×10^6	1.4	0.160	60.5
	0.9	0.163	48.5
	0.5	0.052	30.5
	0	0.258	44.2
5×10^4	1.3	0.123	34.0
	0.7	0.266	53.9
	0.3	0.251	55.6

TABLE III The mechanical properties of [NP(n-butylamino)$_{2-x}$(di-allylamino)$_x$]$_n$

	[NP(n-butylamino)$_{2-x}$ (di-allylamino)$_x$]$_n$ x	Thickness (mm)	YM (kg/cm^2)	TS (kg/cm^2)	E (%)	BF (kg/cm^2)	EB (%)
High Mw	1.4	0.21	344	26	13	22	46
	0.9	0.12	500	21	7	34	38
	0.5	0.23	319	15	14	10	74
Low Mw	1.3	0.18	404	24	16	17	7
	0.7	0.09	385	25	10	17	44
	0.3	0.19	380	23	10	22	40

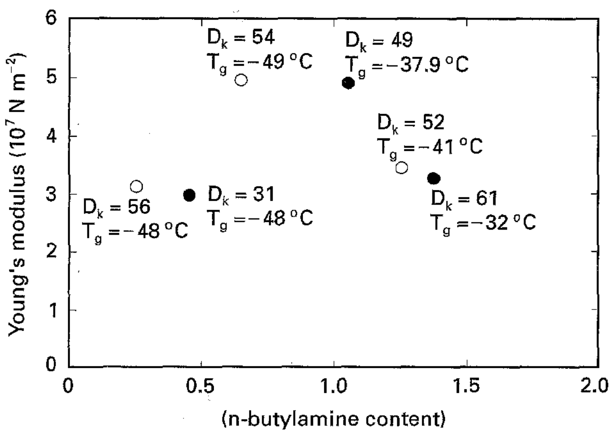


Figure 5 Young's modulus versus n-butylamine content for poly (n-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene films. ○: Low Mw. ●: High Mw.

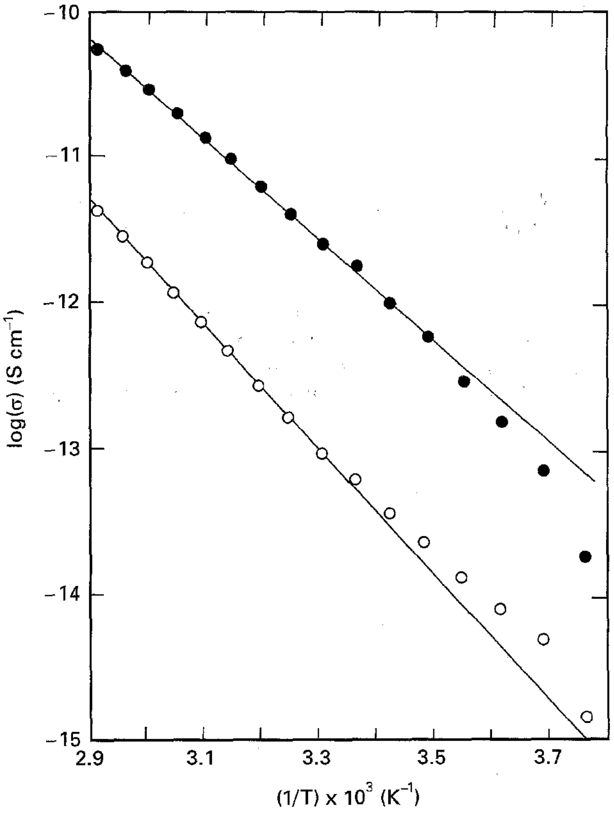


Figure 6 The relation between log(σ) and 1/T. ○: poly(n-butylamino)$_{1.1}$(di-allylamino)$_{0.9}$phosphazene. High Mw; ●: poly (n-butylamino)$_{0.7}$(di-allylamino)$_{1.3}$phosphazene. Low Mw.

log T for both samples are shown in Fig. 6. In addition the relation between the dielectric constant (ε′) and temperature was determined at 120 Hz, 1 kHz and 10 kHz, and the results are presented in Fig. 7 and Fig. 8.

4. Discussion

It is found from Fig. 1 that the protons of the $-CH_3$, $-CH_2$ and –NH groups appear near 0.8, 3.5, 1.2, 5.0 and 2.7 ppm. It is also found from Table I that the values of x are fair agreement with the original compositions. Fig. 2 shows that a broad peak exists between 0–5 ppm, however, this signal is unlikely to be the signal due to P–Cl which would occur near − 18.0 ppm. Furthermore, the amount of $Et_3N{:}HCl$ found in the reaction by-products agrees closely with the values in the reaction. Consequently, we con-

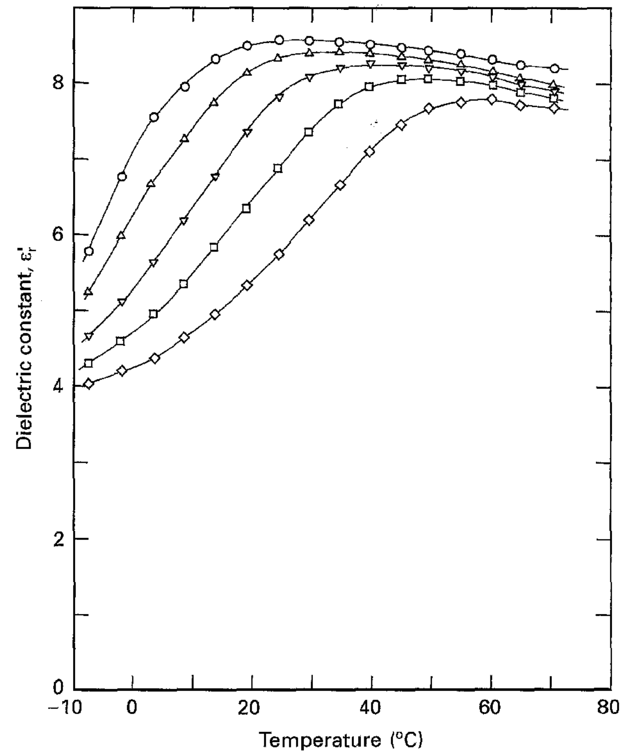


Figure 7 Dielectric constant of poly(n-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene versus temperature (Mw = 4 × 10^4, x = 1.3). Frequencies are 120 (○), 300 (△), 1 k (▽), 3 k (□) and 10 kHZ (◇), respectively.

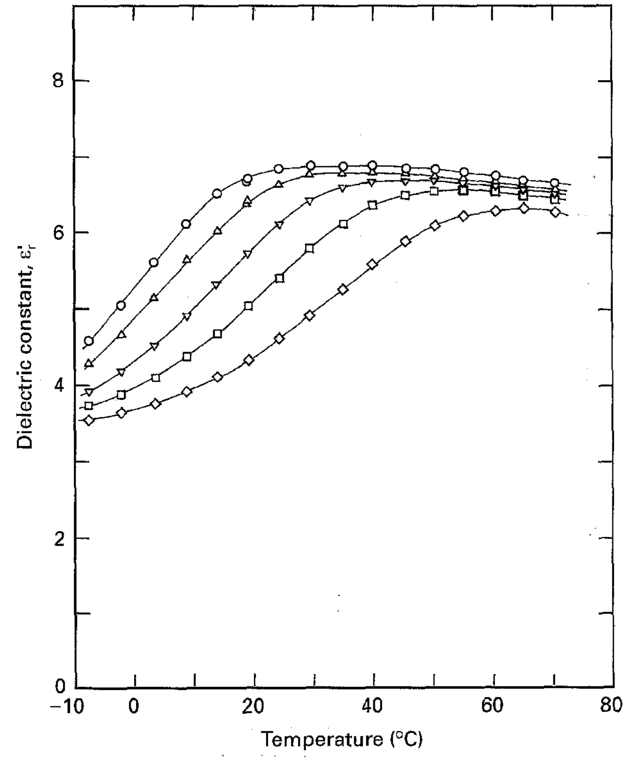
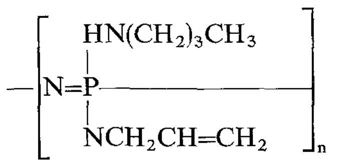


Figure 8 Dielectric constant of poly(n-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene versus temperature (Mw = 10 × 10^6, x = 0.9). Frequencies are 120 (○), 300 (△), 1 k (▽), 3 k (□) and 10 kHZ (◇), respectively.

clude that almost all chlorine atoms in the $(NPCl_2)_n$ are substituted by di-allylamine and n-butylamine. Fourier transformed infrared (FTIR) studies on the PBA films having high and low molecular weights were determined with a Nicolet 5DX. It was found from the FTIR spectra that –NH or $-CH_3$, $-CH{=}CH_2-$ and $-P{=}N-$ groups appear at 3470–3370 cm^{-1}, 3100–3070 cm^{-1} and 1300 –1200 cm^{-1}, respectively. Thus it seems that each of the side groups of PBA is attached as an entity from the reactants as is shown in Scheme 1.

$(NPCl_2)_n + R_2NH + n\text{-}BuNH_2 \rightarrow$



$$-\left[N{=}\overset{\displaystyle HN(CH_2)_3CH_3}{\underset{\displaystyle NCH_2CH{=}CH_2}{P}} - \right]_n$$

The film prepared by the casting method is transparent, and has a light transmission of 95–100% in the visible region. Table II also shows that the refractive index of the film is constant even if the n-butylamine content is increased, that is, the refractive index of film is not dependent on the molecular weight and the side chain group content of the polymer.

It is found from Figs 3 and 4 and Table II that T_g decreases with decreasing di-allylamine content on the polymer regardless of the molecular weight. Also, that T_g of the polymer was more dependent on the molecular symmetry than the intermolecular forces. The T_g of the low molecular weight polymer is lower than that of the high molecular weight polymer as is shown in Table II. This shows that the lower molecular weight polymer is more flexible than the high molecular weight polymer. This means that the molecular symmetry is decreased with the side chain group content. Also, generally the storage modulus (E′) of an amorphous polymer is about 10^7 N m^{-2}. On the other hand, (E′) of cross-linked polymers is about 10^2 N m^{-2}. It is found from dynamic mechanical spectrum data, as shown in Figs 3 and 4 that the polymer prepared in this study has no cross-linking because (E′) is about 10^{10} N m^{-2}, that is, cross-linking density is very low.

As for the films prepared from the high molecular weight polymer, the Young's modulus, tensile strength and breaking strength have their highest values for a film having $x = 0.9$, however, elongation per cent of this film is lower than the other films. For the case of the film prepared from the low molecular weight polymers, the Young's modulus and elongation per cent have their maximum values for the film with $x = 1.3$, but the tensile strength, breaking strength and elongation at break point are lower for this film than for the other films. The mechanical properties of the polymer films prepared in this study are inferior to those of PVA or PE films.

It is found from Table IV that the D_k value of the high molecular weight film increases with increasing T_g. Whilst in the film having low molecular weight, the D_k value is increased with decreasing di-allylamine content and T_g. This means that the D_k value is related to the polymer molecular symmetry, that is, the symmetric or anti-symmetric structure of the polymer will be related to gas permeability and glass transition temperature. In order to prepare a film having a high D_k value, the polymer has to possess an antisymmetric structure because they have a higher free volume. Bowman *et al.* [19] have investigated the variation of modulus values versus silicone content for silicone-methacrylate copolymers. They report that a plot of the modulus versus silicone content gives a straight line, that is, the modulus is decreased with increasing silicone content, and D_k values decrease with silicone content. In our case a plot of the modulus values versus n-butylamine content shown in Fig. 5, is not a straight line.

As for the relation between electrical resistance and temperature, the resistance of the two polymers decreases with increasing temperature. The activation energy ΔE was calculated from the slope of the line as shown in Fig. 6. It is found that the activation energy is about 0.37 eV for the high Mw polymer and 0.29 eV for the low Mw polymer. As for the activation energy ΔE of $[NP(HNBu\text{-}n)_2]_n$, Hayashi and Saito [20] described that ΔE was about 1.5 eV (20–70 °C) and 0.84 eV (70–125 °C). The value obtained in this study is lower than that of Hayashi and Saito, who did not determine the molecular weight of their polymer.

It is found from Fig. 7 and Fig. 8 that (ε′) increases with increasing temperature and decreasing the frequency, that is (ε′) of the two polymers has a temperature and frequency dependence, however, (ε′) reaches a steady state near 50–60 °C. The steady state temperature of the high molecular weight polymer is lower than that of the low molecular weight polymer.

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