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Oxygen gas permeability and the mechanical properties of poly (*n*-butylamino)-(di-*n*-hexyamino) phosphazene membranes

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Poly(*n*-butylamino)-(di-*n*-hexylamino)-phosphazene was prepared by the reaction of poly(dichlorophosphazene), di-*n*-hexylamine and *n*-butylamine using tetrahydrofuran (THF) solvent and triethylamine at room temperature. To increase the mechanical properties of polymer films, cross-linking agents, such as neopentyl glycidyl diether and trimethylol propane triglycidyl diether, were added to the original polymer. The original and agent-added polymer films were prepared by a casting method. The films with cross-linking agents were heated at 60 and 120 °C, and then transparent films were prepared. The oxygen gas permeability and the mechanical properties of the original and the cross-linked films were determined. It was found that the oxygen gas permeability and the mechanical properties, such as Young's modulus, of the cross-linked films were greater than for the original film.

1. Introduction

Linear poly(organophosphazenes) are typical inorganic–organic polymers. A variety of organic side-groups bound to each phosphorus can be easily introduced and modified. For example, poly(organophosphazenes) bearing suitable side-groups can be used as membrane materials in the field of gas permeation [1], organic liquid separation and evaporation [2–5], ion separation [6], ultrafiltration [7] and microfiltration [8]. After Bittrava *et al.* [9] described gas permeation and separation of oxygen, nitrogen and argon using a poly(diamyloxyphosphazene) membrane, patents and reports were described by many companies [10–13] and investigators [14]. However, only one report [15] describes oxygen gas permeability of poly(organophosphazene) membranes under wet conditions. This paper describes oxygen gas permeability in water, and the mechanical properties of the poly(*n*-butylamino)-(di-*n*-hexylamino) phosphazene membrane and the membranes cured with cross-linking agents.

2. Experimental procedure

2.1. Preparation of hexachlorocyclotriphosphazene and polydichlorophosphazene

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was synthesized by the method of Saito and Kajiwara [16]; i.e. $(NPCl_2)_3$ was prepared by reaction of 500 g of phosphorus pentachloride, PCl_5, and 200 g of ammonium chloride, NH_4Cl, using 1500 ml of tetrachloroethane or chlorobenzene. Pure trimer was obtained by repeated fractional crystallization from light petroleum ether.

Linear polydichlorophosphazene $(NPCl_2)_n$ was prepared by the method of Kajiwara and Shiomoto [17]; i.e. 5 g of trimer and 0.1 g of sodium dibutyldithiocarbamate were placed in a three-necked flask equipped with a stirrer and condenser, which was then evacuated to 13.33×10^2 Pa for 1 h. Then, 5 g of dichlorobenzene was added to the flask and the mixture heated to 190 °C for 24 h in a flow of dry nitrogen gas. After the reaction was finished, the polymer–oligomer mixture was dissolved in 200 ml of dry tetrahydrofuran (THF). To remove the oligomer, the THF solution was added to 500 ml of *n*-heptane. After the polymer precipitated, the precipitate was separated by decantation, followed by dissolution in THF and reprecipitation. This purification procedure was repeated several times, and the purified polymer was then dissolved in 100 ml of THF.

2.2. Preparation of poly(*n*-butylamino)-(di-*n*-hexylamino) phosphazene

Linear $(NPCl_2)_n$ soluble in THF or benzene was prepared with bulk polymerization of $(NPCl_2)_3$. Also, poly(*n*-butylamino)-(di-*n*-hexylamino) phosphazene was prepared with reaction of $(NPCl_2)_n$, di-*n*-hexylamine and *n*-butylamine using triethylamine in THF at room temperature bubbling dry nitrogen gas. After the reaction was over, triethylamine hydrochloride obtained was filtered off. When the filtrated solution was added to ethanol, a white coloured polymer was

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precipitated. The polymer prepared was dissolved in THF, and then the solution was added to ethanol. This purification procedure of the polymer was repeated several times.

2.3. Preparation of the membranes

The purified polymer was dissolved in THF and the solution was filtered off with 0.5 μm of the filter to remove the cross-linked polymers. The filtrated solution was added to a Petri dish and was maintained at room temperature until a membrane formed. Also, to increase the mechanical properties of the membrane, cross-linking agents, such as neopentyl glycidyl diether (NPG) and trimethylol propane triglycidyl diether (TMP), were added to the solution involving the polymer. The membranes prepared were heated in an oven at 60 and 120 °C. Cross-linking agents such as NPG and TMP are selected because they are transparent liquids and are handled easily.

2.4. Determination of oxygen gas permeability of the membranes

Measurement of oxygen gas permeability, D_k, in water was determined with an Seikaken type oxygen permeameter at 25–35 °C using Equation 1

$$D_k = K \times i \times l \times 760/P' \qquad (1)$$

where P' is the measured pressure of the sample; i the sample current; and l, the sample thickness. Also, K is determined from Equation 2

$$K = 14.2 \times P/i \times l \times 760 \qquad (2)$$

where P is the pressure of standard plate (Teflon, mmHg); i, the standard plate current (mA); and l, the standard plate thickness (mm).

2.5. Characterization of poly (*n*-butylamino)-(di-*n*-hexyamino) phosphazene and the cross-linked polymers prepared with NPG and TMP

Poly (*n*-butylamino)-(di-*n*-hexylamino) phosphazene and the cross-linked polymers were determined by nuclear magnetic resonance (H-NMR), (P-NMR), Fourier transform infrared analysis (FTIR) and gas permeation chromatography (GPC).

2.6. Mechanical properties of poly (*n*-butylamino)-(di-*n*-hexylamino) phosphazene and the cross-linked polymers

Mechanical properties, Young's modulus, tensile strength or elongation, of the original and cured polymer films were determined by Toyo Baldmin Co. Ltd, UTM II-20 (Tensilon). The test film size was $30 \times 5 \times 0.05$–$0.15\ \text{mm}^3$, and the tension rate was $10\ \text{mm min}^{-1}$, using 20 mm distance between bench markers. After three test films were determined, the average value was estimated from the measurement. Also, after the conditions (20 °C, 65% RH) were maintained for 4 h, determination was attempted. Young's modulus (YM), tensile strength (TS), breaking strength (BS), elongation yield (YP) and elongation breaking (BP) were estimated from Equations 3–7, respectively

$$\text{YM}(\text{kg cm}^{-2}) = a/0.02 \times S \qquad (3)$$

$$\text{TS}(\text{kg cm}^{-2}) = b/S \qquad (4)$$

$$\text{BS}(\text{kg cm}^{-2}) = c/S \qquad (5)$$

$$\text{YP}(\%) = \left(e \times \frac{1/10}{2.0}\right) \times 100 \qquad (6)$$

$$\text{BP}(\%) = \left(d \times \frac{1/10}{2.0}\right) \times 100 \qquad (7)$$

where S is the cross-section of the polymer film; a, is the load produced by 2% strain; b, the maximum load; c, the breaking load; d, the elongation at breaking point; and e, the elongation owing to the maximum load, respectively.

3. Results and discussion

3.1. Characterization of poly(*n*-butylamino)-(di-*n*-hexylamino)phosphazene and the cross-linked polymer films

At first, the molecular weight of poly(*n*-butylamino)-(di-*n*-hexylamino)phosphazene was determined with GPC using THF solvent and calibration curves prepared with polyethylene. It was found that the molecular weight of the polymer is about 5×10^4. Also, H-NMR for the polymer is shown in Fig. 1.

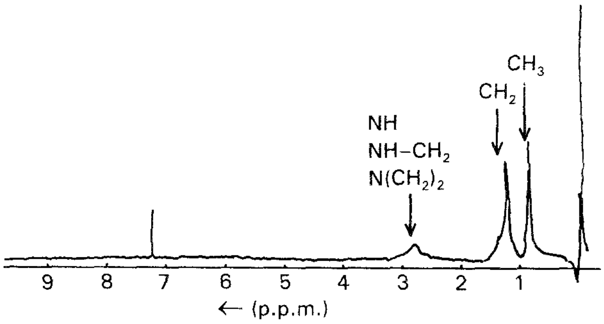


Figure 1 H-NMR of Poly (*n*-butylamino)-(di-*n*-hexylamino) phosphazene.

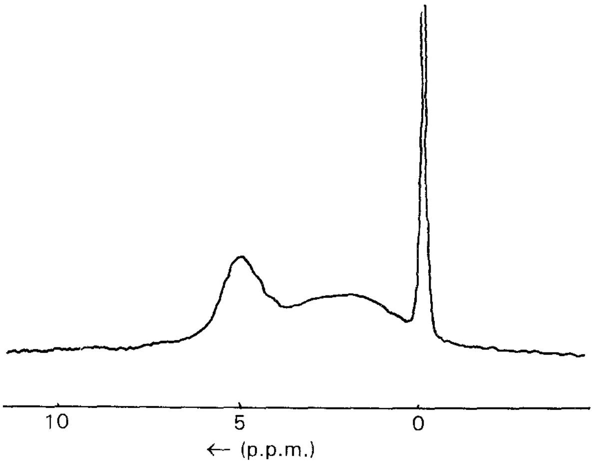
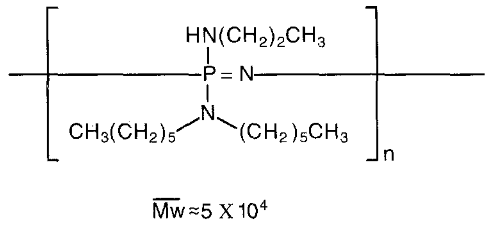


Figure 2 P-NMR of poly (*n*-butylamino)-(di-*n*-hexylamino) phosphazene.



Scheme I

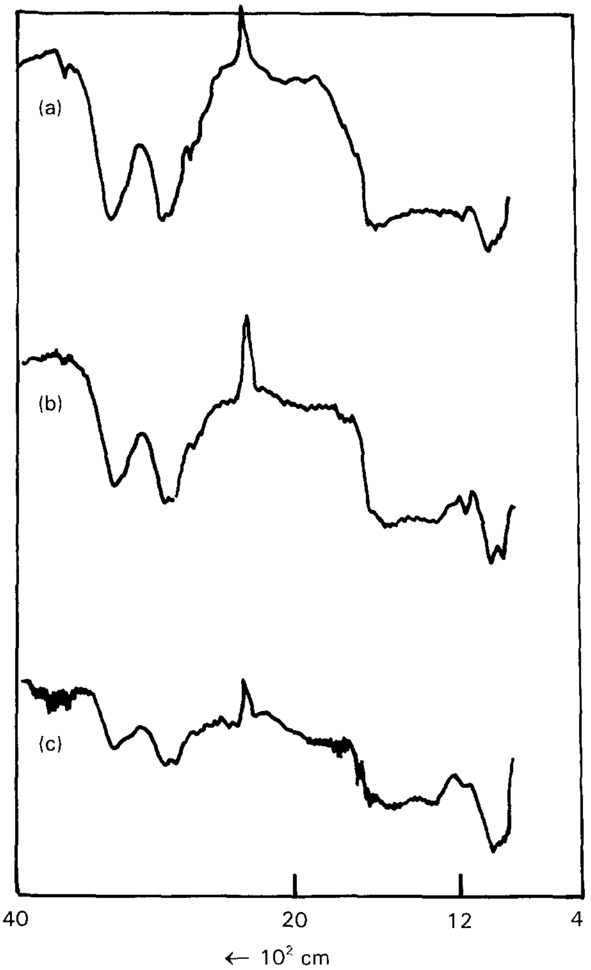
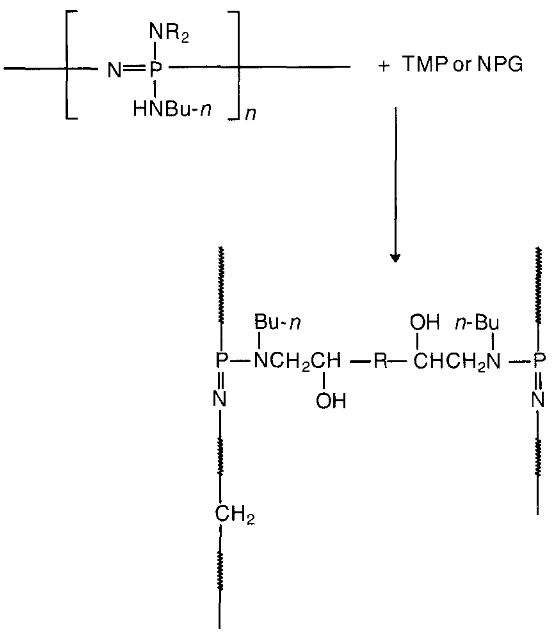


Figure 3 FTIR of (a) original and cured films (b) TMP 0.05 wt %, 120 °C, 24 h and (c) TMP 0.1 wt %, 120 °C, 24 h.



Scheme II

The peak appearing near 2.5 p.p.m. belongs to the primary and secondary amine protons. Also, peaks appearing near 1.2 and 0.8 p.p.m. are assigned to $-CH_2$ and $-CH_3$ respectively. Furthermore, the proton ratio ($NH:CH_2:CH_3$) estimated from Fig. 1. is similar to 2:4:3. P-NMR for the polymer is given in Fig. 2. A broad peak appears near 5 p.p.m. However, an unsubstituted P–Cl bond ocurring in the lower field (− 19.0 p.p.m.) cannot be identified in Fig. 2. Consequently, it is assumed that nearly all the chlorine atoms in the $(NPCl_2)_n$ polymer were substituted by two kinds of amines, and that the polymer has the structure shown in Scheme I.

Also, the polymers cured with NPG and TMP are not dissolved in THF or other organic solvents. FTIR of the original and the cured polymer films are determined, and the results are given in Fig. 3. It is found from FTIR that –NH groups appeared near 3470 cm^{-1}, and that the 3370 cm^{-1} peak decreases with the increase of –CH(OH) groups appearing near 1350–1260 and 1100 cm^{-1} [18]. It is assumed that the cross-linked reaction will occur as given in Scheme II, i.e. the PNG or TMP epoxy ring is cleaved with a HNBu-*n* proton, including the polymer; the intermolecular cross-linked reaction is proceeded by heating. Also, the polymer films cured with NPG or TMP are transparent.

3.2. Mechanical properties of the original and cross-linked polymer films

Young's modulus and tensile strength of the original and the cross-linked polymer films, with 0.05 and 0.1 wt % NPG and TMP, are given in Figs 4–7, respectively.

For Figs 4 and 5, it is found that Young's modulus and tensile strength of the films cured with 0.05 wt % NPG decrease with increasing curing time, compared with that of the original film. Also, Young's modulus and tensile strength of the film cured with TMP, as

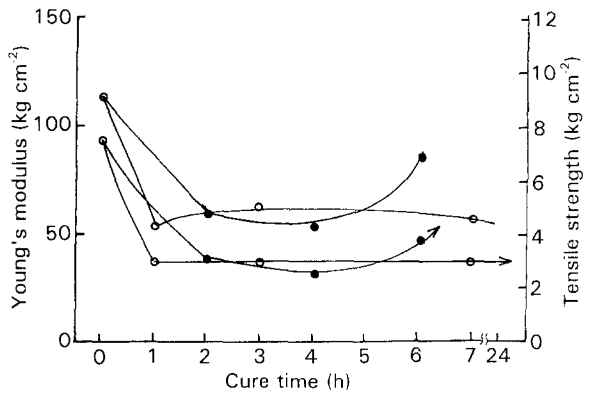


Figure 4 Mechanical properties of poly(*n*-butylamino)-(di-*n*-hexylamino)phosphazene films cured with 0.5 wt % NPG at (–○–) 50 °C and (–●–) 100 °C respectively.

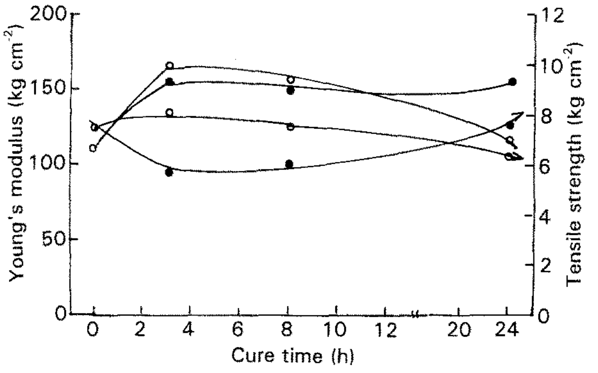


Figure 5 Mechanical properties of poly(*n*-butylamino)-(di-*n*-hexylamino)phosphazene films cured with 0.1 wt % NPG at (–○–) 60 °C and (–●–) 120 °C.

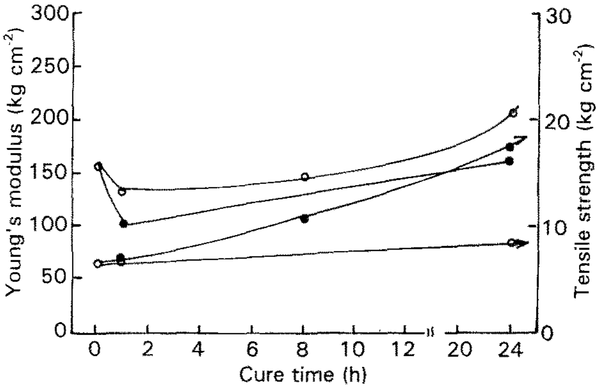


Figure 6 Mechanical properties of poly(*n*-butylamino)-(di-*n*-hexylamino)phosphazene films cured with 0.05 wt % TMP at (–○–) 70 °C and (–●–) 120 °C.

shown in Figs 6 and 7, increase with increasing curing time. Furthermore, the results of elongation and estimated breaking strength of the films are summarized in Tables I and II for samples cured with NGP and TMP, respectively.

It is found that the values of elongation yield and breaking point of the cured films are lower than those of the original film. On the other hand, the breaking strength of the film cured with 0.1 wt % NPG at 60 and 120 °C are higher than that of the original film. As for the films cured with TMP, the elongation yield and breaking point are lower than those of the original film; but the breaking strength is higher than that of the original film.

TABLE I. Elongation (yield and breaking point) and breaking strength of poly(*n*-butylamine)-(di-*n*-hexylamine)phosphazene films cured with NGP

NPG (wt %)	Cure		Film thickness (mm)	E(%)		BS (kg/cm^{-2})
	Temperature (°C)	Time (h)		YP	BP	
0.00			0.47	16	58	3.1
0.05	50	1	0.26	14	20	2.4
		3	0.23	13	18	2.7
		7	0.31	16	23	2.8
	100	2	0.29	14	16	3.0
		4	0.22	13	15	2.6
		6	0.27	12	34	3.4
0.10	60	3	0.18	12	34	5.0
		8	0.18	13	28	3.7
		24	0.24	13	23	5.9
	120	3	0.31	12	29	5.0
		8	0.24	14	20	5.9
		24	0.18	14	30	5.7

TABLE II Elongation (Yield and breaking point) and breaking strength of poly (*n*-butylamino) (di-*n*-hexylamino) phosphazene films cured with TMP

TMP wt %	Cure		Film thickness (mm)		E (%)		Breaking strength (kg/cm^{-2})
	Temperature (°C)	Time (h)		(cm^{-2})	YP	BP	
0.00			0.47		16.0	58.0	3.1
0.05	70	1		0.020	16.0	36.5	4.8
		24		0.019	15.8	40.2	5.0
	120	1		0.026	7.8	32.2	4.3
		8		0.022	10.8	44.2	7.0
		24		0.025	17.6	44.3	15.1
0.10	70	1		0.069	17.8	30.5	4.0
		7		0.069	12.2	20.8	4.4
		24		0.060	17.3	30.3	3.8
	120	3		0.013	16.5	23.0	4.5
		6		0.013	11.0	25.5	5.2
		24		0.013	14.8	31.5	5.4

[a] TMP, trimethyrol propane trigecidel diether.

TABLE III Oxygen gas permeability (in water) of poly(n-butylamino)-(di-n-hexylamino)phosphazene films cured with NPG and TMP

Cure	Agent (wt. %)	Cure Temperature (°C)	Cure Time (h)	Film thickness (mm)	$D_k \times 10^{11}$ ml cm^{-1}/cm^2 s^{-1} mm Hg^{-1}	YM (kg/cm^{-2})
NPG[a]	0.10	60	24	0.290	102.3	135
TMP[b]	0.10	120	24	0.784	140.4	207
	0.05	120	24	0.979	153.9	209
	0.00			0.132	52.0	126

[a] NPG, neopentyl glycolgrecidyl diether; epoxy equivalent, 135–165

[b] TMP, trimethrol propane triglycidyl diether; epoxy equivalent, 130–150

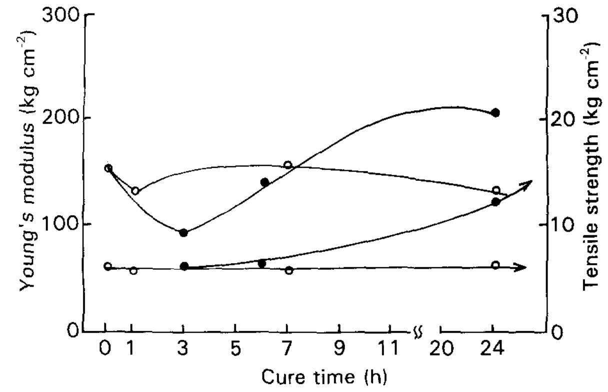


Figure 7 Mechanical properties of poly(n-butylamino)-(di-n-hexylamino)phosphazene films prepared with 0.1 wt % TMP at (–○–) 70 °C and (–●–) 120 °C.

3.3. Oxygen gas permeability of the films cured with NPG and TMP

Even if the film having the highest Young's modulus is prepared with a curing agent such as PNG or TMP, the modulus value is lower than that of polyvinyl alcohol (PVA) or polyethylene films. Oxygen gas permeability, D_k, of the film cured with NPG and TMP, higher Young's modulus or higher tensile strength, are determined, and the results obtained are summarized in Table III.

It is found from Table III that D_k values of the cured film are higher than those of the original film. Also, the film cured with 0.05 wt % TMP has the highest D_k value. Generally, it is said that the film having higher cross-linking density gives lower D_k values compared to the original film. This value is about three times higher compared with that of the original film. However, the highest D_k value is lower than that of silicon polymer films, such as dimethylpolysiloxane.

4. Conclusions

NPG and TMP are good cross-linking agents for poly(n-butylamino)-(di-n-hexylamino)phosphazene.

Also, oxygen permeability and Young's modulus of the films cured with NPG and TMP are higher than those of the original polymer film.

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