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Oxygen gas permeability in water and mechanical properties of poly(*n*-butylamino)-(di-allylamino) phosphazene membranes cured with the irradiation

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Poly(*n*-butylamino) (di-allylamino)phosphazenes were prepared by the reaction of $(NPCl_2)_n$ with *n*-butylamine and di-allylamine. After the membranes were prepared by the casting method, they were irradiated by ultraviolet electron beam, ^{60}Co γ-rays. It was found from Fourier transform–infrared data that the $CH{=}CH_2/N{-}H$ ratios of the irradiated membranes decreased with increasing dose. Also, the membrane did not dissolve in tetrahydrofuran or other organic solvents. This supported the idea that the $CH{=}CH_2$ bond was cleaved by the irradiation and the cross-linking occurred intermolecularly. Oxygen gas permeability values, D_k, of the irradiated membrane were determined from oxygen permeability and mechanical properties were determined with a Tensilon instrument. D_k values decreased with increasing Young's modulus in the case of low concentrations of di-allylamine.

1. Introduction

Generally, poly(organophosphazenes) have been prepared by the reaction between polydichlorophosphazene $(NPCl_2)_n$ and nucleophilic reagents, such as alkoxide phenoxides and amine compounds. For use, PNF elastomer, Eypel A and F were commercialized by Firestone Tire and Rubber and Ethyl Co. Also, the Hygenic Co. [1–4] manufactured with "Novus" as a soft denture liner with "Eypel F".

In France, the Elf Atochem Co. discovered a new process to prepare $(NPCl_2)_n$ [5, 6], that is, $(NPCl_2)_n$ was prepared with the polymerization of $Cl_3P{=}N{-}P(O)Cl_2$, and Orgaflex A and F were commercialized by the Elf Atochem Co. They had the same composition as that of Eypel A and F.

Patents pertaining to gas separation with poly(organophosphazene) membranes have been proposed by many companies [7–10] and Kajiwara [11–13] after Bittrava *et al.* [14] was the first to describe the gas permeability of oxygen, nitrogen and argon using a poly(diamyloxyphosphazene) membrane. However, these patents and Bittrava et al.'s report concerned gas permeability under dry conditions. Oxygen gas permeability in wet conditions or water using poly(organophosphazene) membranes was described by Kajiwara [15]. The present paper describes mechanical properties and oxygen gas permeability in water of irradiated poly(*n*-butylamino) (di-allylamino)phosphazene membranes.

2. Experimental procedure

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

Polydichlorophosphazene $(NPCl_2)_n$ used in this study was donated by the Elf Atochem Co., France. The molecular weights of $(NPCl_2)_n$ were about 5×10^4 and 1×10^7. $(NPCl_2)_n$ was reacted with *n*-butylamine and di-allylamine using tetrahydrofuran (THF) solvent at room temperature for 24 h with stirring and flowing dry nitrogen gas. That is, after 30 g $(NPCl_2)_n$ was dissolved in THF, the solution was added to a THF solution containing the chemical equivalent of di-allylamine and triethylamine, and the reaction was carried out for 24 h with stirring. After the reaction was completed, THF solution-dissolved *n*-butylamine was added. Then the substitution reaction was carried out at room temperature for 24 h in flowing dry nitrogen gas. After the reaction was finished, the reaction mixture solution was filtrated. When the filtrate was dropped into ethanol, a white coloured precipitate appeared. The precipitate separated by the filtration was dissolved in THF, and then added to ethanol. This purification process was repeated several times. The polymer, purified by the precipitation method, was washed with distilled water to remove any remaining $Et_3N{:}HCl$, and then were kept under drying at 25 °C for 24 h.

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2.2. Preparation of poly(*n*-butylamino) (di-allylamino)phosphazene membranes (PBA)

An example illustrating the preparation of typical PBA membranes is described below. The PBA membranes were prepared by a casting method. After 5 g PBA was dissolved in 30–50 ml THF, the solution was filtered with 0.5 μm filter. The filtrate was added to a glass vessel, and kept at room temperature until the film was formed. The prepared film was dried at 70–80 °C for 24 h under vacuum conditions.

2.3. Spectroscopic analysis of PBA and the irradiated PBA

The value of x in the original PBA was determined with ^{1}H-NMR using DMSO. The degree of the replacement with amine groups was also determined, with ^{31}P-NMR using THF, the amount of $Et_3N{:}HCl$ and Fourier transform–infrared spectroscopy (FT–IR). The irradiated PBA membranes were also determined using FT–IR.

2.4. Mechanical properties and oxygen gas permeability of PBA and the irradiated PBA membranes

Mechanical properties, such as Young's modulus, tensile strength, elongation per cent, breaking strength and elongation breaking point, were determined using a Toyo Badmin Co. Ltd UM II-20 Tensilon. The values were calculated using Equations 1–5, respectively

$$\text{Young's modulus (YM)} = a/0.02\,S \tag{1}$$

$$\text{tensile strength (TS)} = b/S \tag{2}$$

$$\text{breaking strength (BS)} = c/S \tag{3}$$

$$\text{elongation yield (EY)} = (e \times 1/10/2.0) \times 100 \tag{4}$$

$$\text{elongation breaking (BP)} = (d \times 1/10/2.0) \times 100 \tag{5}$$

where S is the cross-section of the polymer film, a is the load produced by 2% strain, b is the maximum load, c the load breaking, d elongation at breaking point, and e elongation due to maximum load. Also, the oxygen gas permeability value, D_k, was estimated from Equations 6 and 7. That is

$$K = 14.2\,p/i\,l\,760 \tag{6}$$

$$D_k = K\,i'\,l'\,760/p' \tag{7}$$

where p(mm Hg) is the determined atmospheric pressure of the standard sample (Teflon), i(mA) the determined electric current and l(mm) sample of thickness; p' is the determined atmospheric pressure of the sample, i' the determined electric current, and l' the sample thickness, respectively.

3. Results and discussion

3.1. The analysis of poly(*n*-butylamino)$_{2-x}$ (di-allylamino)$_x$phosphazene (PBA)

To determine the value of x on PBA, ^{1}H-NMR of lower molecular weight polymer was determined, and the typical ^{1}H-NMR given in Fig. 1. It was found from Fig. 1 that the H proton of $-CH_3$, $-CH_2$ and $-NH$ groups appears near 0.8, 3.5, 1.2, 5.0 and 2.7 p.p.m. The value of x on PBA was determined from the proton ratio. The proton ratio of PBA, having higher molecular weight, was determined with ^{1}H-NMR. ^{31}P-NMR of PBA having higher and lower molecular weight were determined, and the results are shown in Figs 2 and 3. It was found from Figs 2 and 3 that a broad peak appears near 0–5 p.p.m.; however, the signal of the P–Cl bond occurred at a lower field, near − 18.0 p.p.m. Furthermore, the amount of $Et_3N{:}HCl$ which produced the by-products agrees closely with the theoretical value. Consequently, most of the chlorine atoms in $(NPCl_2)_n$ are substituted by di-allylamine and *n*-butylamine. FT–IR of PBA films having higher

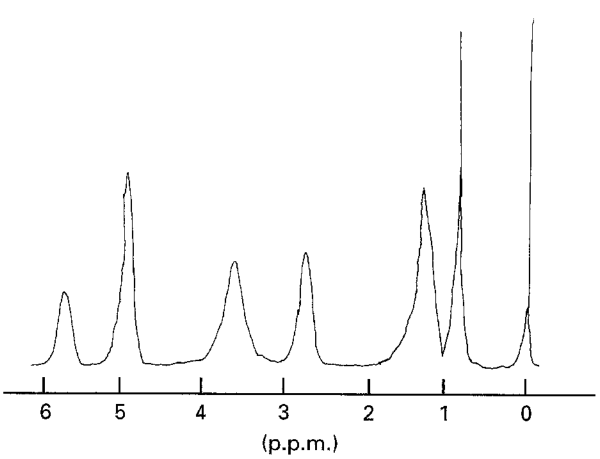


Figure 1 ^{1}H-NMR of poly(*n*-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene.

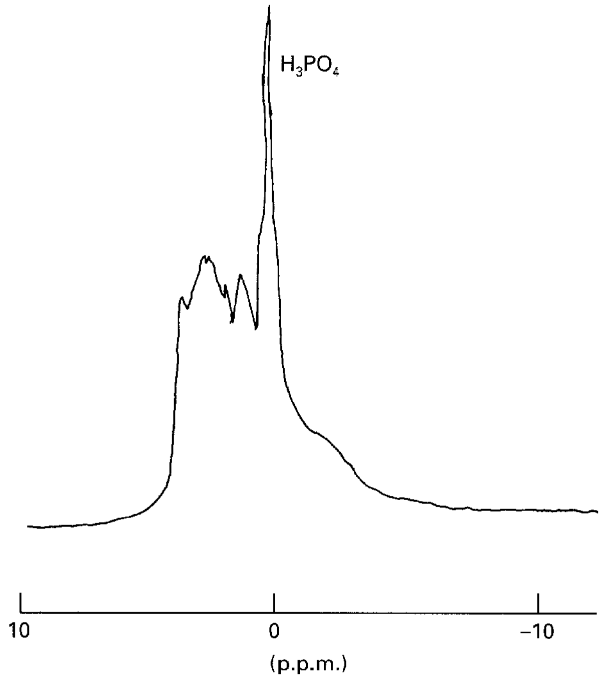


Figure 2 ^{31}P-NMR of poly(*n*-butylamino)(di-allylamino)phosphazene ($M_w = 1 \times 10^7$).

and lower molecular weights were determined using a Nicolet 5DX, and the results are given in Fig. 4. It was found from Fig. 4a and b that –NH or –CH_3, –CH =CH_2 and –P=N– groups appear near 3.470 or 3.100–3.70 and 1.300–1.200 cm^{-1}, respectively. Therefore, PBA can be prepared from Equation, that is

$$(NPCl_2)_n + R_2NH + n\text{-}BuNH_2 = [NP(NHBu\text{-}n)_{2-x}(NR_2)_x]_n \quad (8)$$

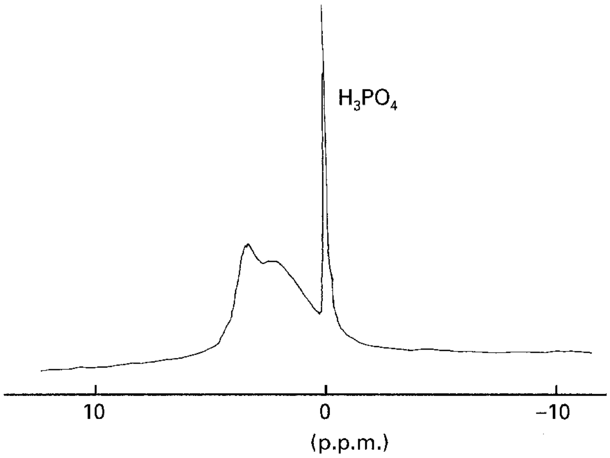


Figure 3 ^{31}P-NMR of poly(*n*-butylamino)(di-allylamino)phosphazene ($M_w = 5 \times 10^4$).

3.2. FT–IR spectrum of the irradiated PBA membranes

Ultraviolet light having 634 mJ cm^{-2}, was irradiated on the PBA membrane ten times, and the electron beam was irradiated on the PBA membrane with an intensity of 150 keV. However, the CH=CH_2/NH ratio for irradiated membranes estimated from FT–IR data was not so dramatically changed compared with that of the original unirradiated PBA membrane. Then, the electron beam at 250 keV was irradiated on the PBA membrane, and the results are shown in Fig. 4c and d. Also, CH=CH_2/NH ratios were calculated from FT–IR data, and the results are given in Fig. 5.

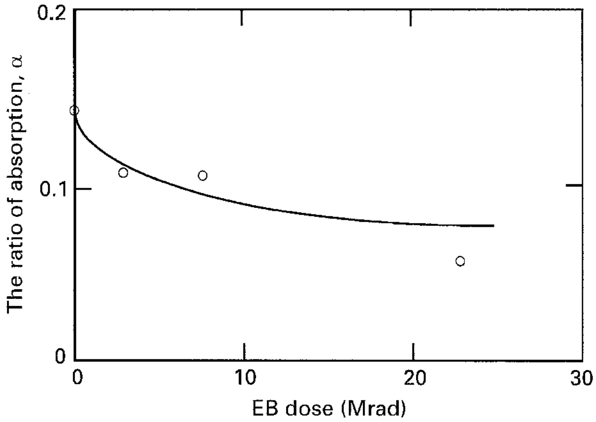


Figure 5 The ratio of absorption, α, versus electron beam (EB) irradiation dose, = (absorption of C=C at 1640 cm^{-1})/(absorption of N–H at 3300 cm^{-1}).

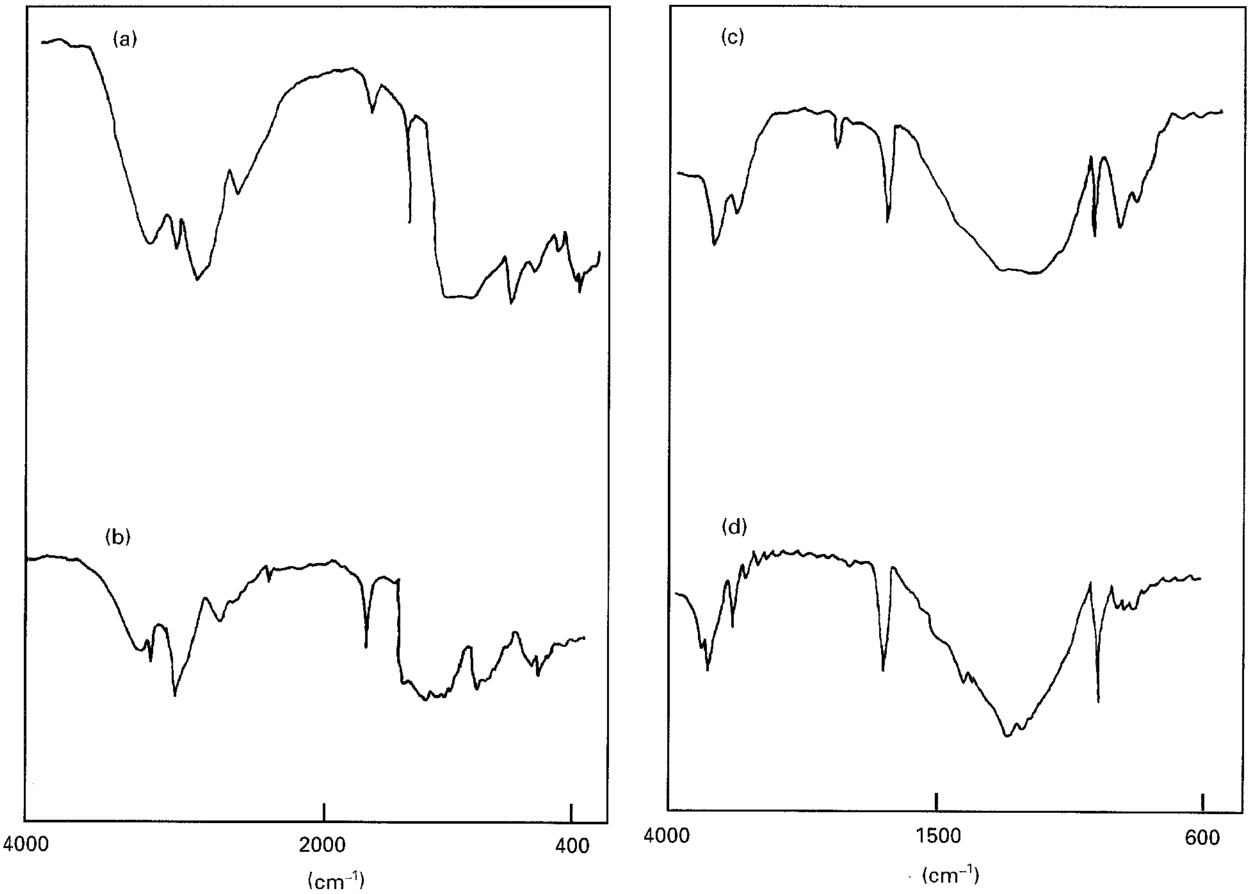


Figure 4 FT–IR of poly(*n*-butylamino)(di-allylamino)phosphazene membranes. (a) Original ($M_w = 1 \times 10^7$). (b) Original ($M_w = 5 \times 10^4$). (c) Irradiated membrane of (a) with an electron beam of 22.8 Mrad. (d) Irradiated membrane of (b) with an electron beam of 7.6 Mrad.

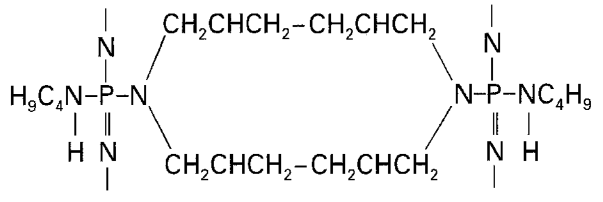
TABLE I Mechanical properties of poly(n-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene membrane prepared by electron beam (EB) irradiation (250 keV), $M_W = 5 \times 10^4$

x	EB (Mrad)	Film (mm)	Young's modulus (kg cm^{-2})	Tensile strength (kg cm^{-2})	Breaking strength (kg cm^{-2})	Elongation %	
						Yield	Breaking
1	0	0.18	404	24	17	16	7
	2.3	0.15	626	28	35	10	97
	4.3	0.18	921	43	57	13	85
0.25	0	0.09	385	25	17	10	44
	2.3	0.21	529	30	35	15	177
	4.3	0.10	633	34	44	11	94
0.125	0	0.19	380	23	22	10	
	2.3	0.17	435	28	27	9	140
	4.3	0.17	510	32	38	10	123

TABLE II Mechanical properties of poly(n-butylamino)$_{2-x}$(di-allylamino)$_x$ phosphazene membrane prepared by electron beam irradiation (250 keV), $M_W = 1 \times 10^7$

x	EB (Mrad)	Film (mm)	Young's modulus (kg cm^{-2})	Tensile strength (kg cm^{-2})	Bending strength (kg cm^{-2})	Elongation %	
						Yield	Breaking
1	0	0.208	344	26	22	13	46
0.25	0	0.12	500	21	34	7	38
	2.3	0.09	688	33	35	8	79
	4.3	0.15	674	37	43	10	86
0.125	0	0.23	319	15	16	14	74
	2.3	0.12	494	24	24	13	122
	4.3	0.17	453	23	38	14	166

It is seen in Fig. 5 that the $CH=CH_2/NH$ ratio decreases with increasing electron beam dose, indicating that the $C=C$ bond is cleaved by the electron beam. Also, ^{60}Co γ-rays were irradiated on PBA membranes and FT–IR measurements were taken on the irradiated membranes. The results were the same as those for electron beam irradiation. The irradiated membranes were insoluble in THF or other organic solvents. Consequently, it is proposed that the structure of the irradiated PBA is as shown in Scheme I.



(I)

3.3. Mechanical properties of irradiated PBA membranes

The mechanical properties of EB-irradiated PBA membrane are summarized in Table I ($M_w = 5 \times 10^4$) and Table II ($M_w = 1 \times 10^7$). It is seen from Table I that Young's modulus decreased with decreasing diallylamine content and the modulus increased with increasing dose of the electron beam irradiation. The highest values of Young's modulus were given by the PBA membrane with $x = 1 (M_w = 5 \times 10^4)$ with an irradiation dose of 4.3 Mrad. Mechanical properties of PBA membranes irradiated with ^{60}Co γ-rays were determined, and the results are summarized in Table III. As for Young's modulus, the mechanical properties increased with increasing ^{60}Co γ-ray dose or with increasing cross-linking density.

3.4 Oxygen gas permeability value, D_k, of irradiated PBA membranes

The oxygen gas permeability value of irradiated (electron beam) PBA membrane in water was determined and the results are given in Tables IV and V. It was found that the D_k value of the original PBA membrane increased with decreasing x value. Thus D_k is related to the polymer's molecular symmetry, i.e. the symmetric or antisymmetric structure of the polymer will be related to gas permeability. In other words, to produce a membrane with the highest D_k value, the polymer must develop antisymmetric structure, in order to have a higher free volume. In the case of low molecular weight PBA membrane, except for $x = 1$, the D_k value of the irradiated PBA membrane decreased with increasing electron beam dose. On the other hand, the lowest D_k value appeared at 2.3 Mrad irradiation for the high molecular weight PBA membrane. The D_k value of ^{60}Co γ-ray irradiated PBA membrane was also determined and the results are given in Table VI.

It is seen from Table VI that the highest D_k value occurs for 2.55 Mrad and 3 h.

TABLE III Mechanical properties of poly(*n*-butylamino)(di-allylamino)phosphazene membranes prepared by ^{60}Co γ-irradiation, $M_w = 5 \times 10^4$

Time (h)	Dose (Mrad)	Film (mm)	Young's modulus (kg cm^{-2})	Tensile strength (kg cm^{-2})	Bending strength (kg cm^{-2})	Elongation %	
						Yield	Breaking
0	0	0.208	344	26	22	13	46
1	0.85	0.153	488	26	21	17	47
2	1.70	0.236	508	23	20	11	50
3	2.55	0.240	477	31	26	20	77
5	4.26	0.285	515	35	32	22	124
8	6.81	0.221	595	39	38	25	284

TABLE IV Oxygen gas permeability of poly(*n*-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene membranes prepared by electron beam irradiation, $M_w = 5 \times 10^4$

x	EB (Mrad)	Film thickness (mm)	D_k (10^{-11} cm^2 s^{-1} mm Hg^{-1})
1	0	0.123	34.0
	2.3	0.195	45.5
	4.3	0.095	28.3
0.25	0	0.266	53.9
	2.3	0.196	39.9
	4.3	0.064	23.4
0.125	0	0.251	55.6
	2.3	0.213	48.4
	4.3	0.215	48.7

TABLE V Oxygen gas permeability of poly(*n*-butylamino)$_{2-x}$(di-allylamino)$_x$phosphazene membranes prepared by electron beam irradiation, $M_w = 1 \times 10^7$

x	EB (Mrad)	Film thickness (mm)	D_k (10^{-11} cm^2 s^{-1} mm Hg^{-1})
1	0	0.216	52.0
	2.3	0.096	26.3
	8.6	0.149	37.3
0.25	0	0.266	53.9
	2.3	0.073	25.2
	4.3	0.156	37.3
0.125	0	0.251	55.6
	2.3	0.115	35.2
	4.3	0.211	51.3

TABLE VI Oxygen gas permeability of poly(*n*-butylamino)(di-allylamino)phosphazene membranes prepared by ^{60}Co γ-irradiation, $M_w = 5 \times 10^4$

Irradiation time (h)	Dose (Mrad)	Film thickness (mm)	D_k (10^{-11} cm^2 s^{-1} mm Hg^{-1})
0	0	0.132	52
2	1.72	0.246	55.6
3	2.55	0.262	66.1
5	4.26	0.200	46.0
8	6.81	0.14	40.6

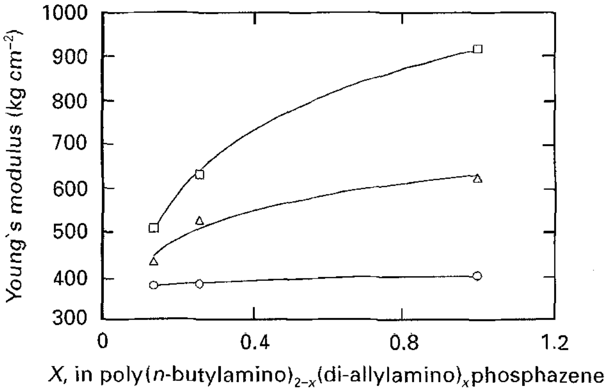


Figure 6 The relation between Young's modulus and x for electron beam irradiated PBA membranes ($M_w = 5 \times 10^4$). Electron beam doses: (○) 0 Mrad, (△) 2.3 Mrad and (□) 4.3 Mrad. D_k values are also shown in parentheses.

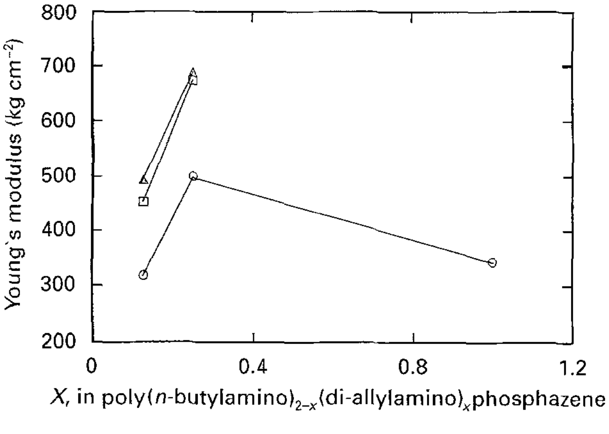


Figure 7 The relation between Young's modulus and x for electron beam irradiated PBA membranes ($M_w = 1 \times 10^7$). EB doses (○) 0 Mrad, (△) 2.3 Mrad and (□) 4.3 Mrad. D_k values are also shown in parentheses.

3.5. The relation between Young's modulus and oxygen gas permeability, D_k of irradiated PBA membranes

The relation between Young's modulus and D_k values of electron beam irradiated PBA membrane is given in Fig. 6 ($M_w = 5 \times 10^4$) and Fig. 7 ($M_w = 1 \times 10^7$), respectively. It is found from Figs 6 and 7 that Young's modulus increases with decreasing D_k value in the case of low di-allylamine content. This phenomenon occurs for silicon-methacrylate copolymer membranes, that is, the modulus decreases with increasing silicon content, and a plot of the modulus versus silicon gives a straight line. However, there are no straight lines between D_k and the modulus in the case of high di-allylamine content such as $x = 1$.

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