Oxygen gas permeability of poly(organophosphazene) membranes in water

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Fifteen different poly(organophosphazenes) were synthesized by the reaction of poly(dichlorophosphazene) $(NPCl_2)_n$ with phenoxide, alkoxide and amine compounds. Membranes were prepared from the synthesized poly(organophosphazenes) by a casting method, and the oxygen gas permeability of the membranes was determined using a film oxygen gas permeater at 20°C in water. It was found that poly(diethylaminobutylaminophosphazene) had the highest oxygen gas permeability value, $Dk = 55.2 \times 10^{-11}$ cm^2 s^{-1} mmHg^{-1}. The glass transition temperatures and dielectric constants of the polymers were determined with an inductive-ratio-arm bridge to determine their effect on oxygen gas permeability. It was found that the oxygen gas permeability of poly(aminophosphazenes) was most directly related to the dielectric constant in the case of wet conditions (water).

(Keywords: gas permeability; membranes; synthesis; poly(organophosphazene))

INTRODUCTION

The oxygen gas permeability of many polymers has been determined under dry[1] or wet[2] conditions. For example, silicone polymer and silicone–methacrylate[3] copolymers (60–70% silicone and 40–30% methacrylate) have been tested for oxygen gas permeability under wet conditions, yielding 79×10^{-11} and 10×10^{-11} cm^2 s^{-1} mmHg^{-1} for the polymer and copolymer, respectively. At present, soft polymer membranes having higher oxygen gas permeabilities are needed for applications like contact lenses or O_2/N_2 gas separation membranes. Kajiwara[1] reported oxygen, nitrogen, hydrogen and other gas permeabilities using poly(organophosphazenes) under dry conditions. The oxygen gas permeability of poly(organophosphazenes) in water was determined after the membranes were prepared and the results obtained are described in this report.

EXPERIMENTAL

Preparation of hexachlorocyclotriphosphazene $(NPCl_2)_3$ and poly(organophosphazenes) $(NPR_2)_n$

$(NPCl_2)_3$ was synthesized by the method of Saito[4]. That is, $(NPCl_2)_3$ was prepared by the reaction of 500 g of phosphorus pentachloride (PCl_5) and 200 g of ammonium chloride (NH_4Cl) using 1500 ml of tetrachloroethane. Pure $(NPCl_2)_3$ (m.p. 112°C) was obtained by repeated fractional crystallization from light petroleum ether.

Linear poly(dichlorophosphazene) $(NPCl_2)_n$ was prepared by the method of Kajiwara[5]. That is, 5 g of $(NPCl_2)_3$ and 0.1 g of sodium dibutyldithiocarbamate were placed in a three-necked flask equipped with a stirrer and a condenser, which was then evacuated to 10 Torr for 1 h. Then 5 g of *o*-dichlorobenzene was added to the flask, and the mixture was heated to 190°C for 24 h in a flow of dry nitrogen. After the reaction was complete, 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 $(NPCl_2)_n$ precipitated, the precipitate was separated by decantation, followed by dissolution in THF and reprecipitation. This purification procedure was repeated several times and the purified $(NPCl_2)_n$ was then dissolved in 100 ml of THF.

Various poly(organophosphazenes) $(NRP_2)_n$ were formed using nucleophilic reagents such as alkoxide, phenoxide and amine compounds via a modified method due to Allcock[6]. The preparation of typical poly(organophosphazenes) is as follows.

Synthesis of $[NP(OCH_2CF_3)_2]_n$. A solution of sodium trifluoroethoxide was prepared by addition of sodium (6 g) to 2,2,2-trifluoroethanol (25 g) in dry THF (200 ml). The reaction mixture was added dropwise to a stirred solution of $(NPCl_2)_n$ dissolved in THF. The reaction was exothermic and the mixture was heated to keep the solvent boiling for 20 h. At the conclusion of the reaction, the mixture was cooled and acidified with dilute hydrochloric acid, and benzene was added to coagulate the polymer. After isolation of the polymer by filtration, it was washed with a large excess of water to remove salts and from THF into benzene to remove oligomer and low-molecular-weight polymers. The polymer was then exhaustively dried under vacuum.

Synthesis of $[NP(NEt_2)(NHBu^n)]_n$. A solution of $(NPCl_2)_n$ (20 g) dissolved in THF was added dropwise over 2 h to a stirred solution of diethylamine (21.2 g) in 100 ml of THF. The reaction was allowed to proceed at 25°C for 24 h. Then n-butylamine (15 g) and triethylamine

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(20 g) dissolved in 50 ml of THF were added dropwise over 2 h. The reaction mixture was allowed to remain at 25°C for 24 h. The mixture was then filtered to remove amine salts, and polymer was precipitated from the filtrate by addition to heptane. Purification was effected by precipitation of the polymer three times from solution in dilute aqueous sulphuric acid into dilute aqueous ammonium hydrochloride, and once from dilute acetic acid in ethanol into methanol which contained a trace of triethylamine. The polymer was then dried under vacuum over P_2O_5.

Preparation of poly(organophosphazene) membranes

Some 5 or 10 g of $(NPR_2)_n$ was dissolved in 100 g of THF, and the solution was filtered through a glass filter. The filtered solution was added to a Petri dish and a protective covering put over it. The Petri dish was kept at room temperature and the solvent was slowly evaporated over several hours until a film was formed in the presence of solvent at room temperature. The films thus prepared were dried further at reduced pressure at 50°C for 10 h.

Measurement of oxygen gas permeability of poly(organophosphazene) membranes in water

The oxygen gas permeabilities of $(NPR_2)_n$ and $(NPRR')_n$ membranes in water were measured using a film oxygen permeater of Seikaken type at 20°C. The dimensions of the membranes were 15 mm diameter × 0.2 mm thickness.

Measurement of glass transition temperature and dielectric constant

Each sample was moulded into a disc about 0.6 mm thick. An inductive-ratio-arm bridge (Ando Electr. Co. TR-10) was employed in the frequency range from 30 to 10^6 Hz. These results were reported by Murakami[7].

Measurement of water absorption and crystallinity of poly(organophosphazene) membranes

The water absorption of poly(organophosphazene) membranes was determined by the weight-loss method. A membrane having 15 mm diameter × 0.2 mm thickness was kept in water at 25°C for 24 h. The membrane was then taken out and dried under 10^{-5}–10^{-6} mmHg vacuum for 8 h. To investigate the water absorption of the membrane, the weight loss was determined with a balance. Also, the crystallinity of the membrane was investigated by X-ray diffraction analysis.

RESULTS AND DISCUSSION

Comparison of oxygen permeability values of poly(organophosphazene) membranes in water

The oxygen gas permeability of poly(aminophosphazene) and poly(aryloxyphosphazene) membranes determined in water are summarized in *Table 1*. It is found that the membrane having the highest oxygen gas permeability value is poly(diethylaminobutylaminophosphazene) $[NP(NEt_2)(NHBu^n)]_n$. In general, poly(aminophosphazene) membranes displayed higher permeability values than poly(aryloxyphosphazenes). The relation between the oxygen gas permeability values of poly(aryloxyphosphazene) membranes under dry conditions, as previously described by Kajiwara[1], and under wet (in water) conditions are given in *Figure 1*. Note that the pendant groups of poly(aryloxyphosphazene) membranes have lower oxygen permeability values than poly(aminophosphazenes) under both conditions.

Table 1 Oxygen gas permeabilities of poly(organophosphazene) membranes in water

$(NPRR')_n$		Dk
R	R'	(10^{-11} cm^2 s^{-1} mmHg^{-1})
$NHPr^n$	$NHPr^n$	15.5
$NHBu^n$	$NHBu^n$	44.2
NEt_2	$NHPr^n$	27.7
NEt_2	$NHBu^n$	55.2
NEt_2	NHC_5H_{11}	16.0
$N(CHMe_2)_2$	$NHPr^n$	24.3
$N(CHMe_2)_2$	$NHBu^n$	38.2
$N(CHMe_2)_2$	NEt_2	9.2
OCH_2CF_3	OCH_2CF_3	11.7
OC_6H_5	OC_6H_5	6.4
OC_6H_4Cl-*p*	OC_6H_4Cl-*p*	4.7
OC_6H_4Cl-*m*	OC_6H_4Cl-*m*	5.2
$OC_6H_4CH_3$-*p*	$OC_6H_4CH_3$-*p*	5.5
$OC_6H_4CH_3$-*m*	$OC_6H_4CH_3$-*m*	0.2
OC_6H_4Et-*p*	OC_6H_4Et-*p*	19.0

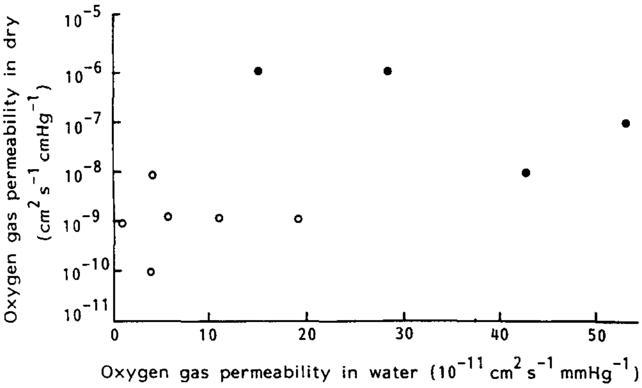

Figure 1 The relation between oxygen gas permeability in water and the permeability in air: (●) aminophosphazene; (○) aryloxyphosphazene

Also, membranes of various thicknesses were prepared with $[NP(OCH_2CF_3)_2]_n$ and $[NP(NEt)(NHBu^n)]_n$, and the oxygen gas permeabilities of these membranes were also determined under water. The results are shown in *Figure 2*, where the relation between oxygen permeability ($Dk \times 10^{-11}$ cm^2 s^{-1} mmHg^{-1}) and the reciprocal of the membrane thickness ($1/L$) is given.

Using the technique described by Magatani[8], Refojo[9], Huang[10] and Ng[11], the straight line from a $1/Dk$ vs. $1/L$ plot can be extrapolated to zero, yielding the oxygen gas permeability value in the dry condition. The three straight lines shown in *Figure 2* are extrapolated to zero, and the results calculated from the point of intersection are summarized in *Table 2*. The different values given can be compared with the value shown in the dry condition in *Table 2* or the paper previously described by Kajiwara[1].

Also, Rogers[12] reported that the oxygen gas permeability coefficient of polymers measured under gas/gas conditions is independent of sample thickness. On the other hand, Ng[11] and Huang[10] reported that, with silicone rubber and poly(4-methylpent-1-ene) membranes, the oxygen permeability coefficient in water was found to increase asymptotically with sample

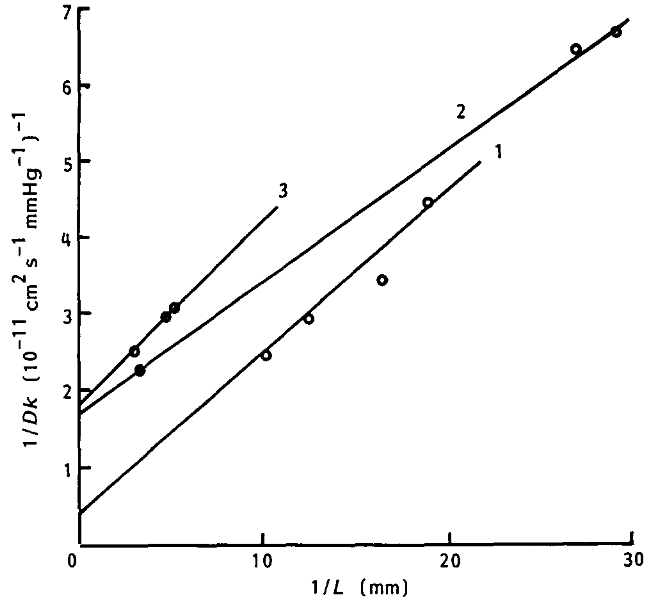

Figure 2 The relation between $1/Dk$ and $1/L$: (1) $[NP(OCH_2CF_3)_2]_n$; (2) $[NP(NEt_2)(NHBu^n)]_n$; (3) pressed membrane of (2)

Table 2 Oxygen gas permeabilities of poly(organophosphazene) membranes under air or wet conditions

$(NPRR')_n$		Dk ($cm^2\ s^{-1}\ cmHg^{-1}$)	
R	R'	Air	Wet
OCH_2CF_3	OCH_2CF_3	2.0×10^{-9}	2.0×10^{-10}
NEt_2	$NHBu^n$	2.8×10^{-7}	52.6×10^{-8}
NEt_2	$NHBu^{n\,a}$		83.3×10^{-8}

[a] Pressed membrane

thickness. A difference between the oxygen gas permeability coefficient in water and that in dry conditions appears in these experimental results. It seems that the difference in behaviour is due to the additional resistance to oxygen permeation at the boundary between water and the membrane, described by Refojo[9].

Oxygen gas permeability and properties of poly(organophosphazenes)

To understand the factors that affect the oxygen gas permeability value, the relation between those values and the properties of poly(organophosphazenes) are determined by measurement of the glass transition temperature or the dielectric constant, as previously reported by Murakami[7]. The results obtained are given in *Figures 3* and *4*, respectively.

Using poly(organophosphazene) membranes, if oxygen gas permeability follows the solution–diffusion mechanism, the glass transition temperature of the membranes and the diffusion constant are the important factors, and an approximately linear relation with a positive slope exists between them, as described by Kajiwara[13]. As shown in *Figure 3*, in the case of poly(organophosphazenes), there is a random relation between oxygen gas permeability and glass transition temperature of the polymers. That is, there is no linear relation between them. Also, Volkov[14] and Sanders[15] proposed that a polymer with a higher glass transition temperature would have a higher oxygen gas permeability value. It is found from *Figure 4* that the oxygen gas permeability of a polymer under dry conditions changes in a random fashion as a function of dielectric constant. On the other hand, the oxygen gas permeability of poly(aminophosphazenes) is related to the dielectric constant. That is, the permeability in water increases on decreasing the dielectric constant of the polymer. However, the permeability of poly(aryloxyphosphazenes) is not dependent on the dielectric constant. Consequently, the dielectric constant of the polymer should have an influence on the oxygen gas permeability in water. To prepare a polymer having the highest oxygen gas permeability in water, the dielectric constant should be considered. In other words, in the case of poly(organophosphazenes), the polymer having the lowest dielectric constant should have the highest oxygen gas permeability and should be used as a soft contact lens without water, if it is transparent. The dielectric constant of the polymer is one of the advantageous effects of oxygen gas permeability increase.

Measurement of water absorption and crystallinity of poly(organophosphazene) membranes

The saturated water absorption of the membranes determined is less than 6.0%. To increase the oxygen gas

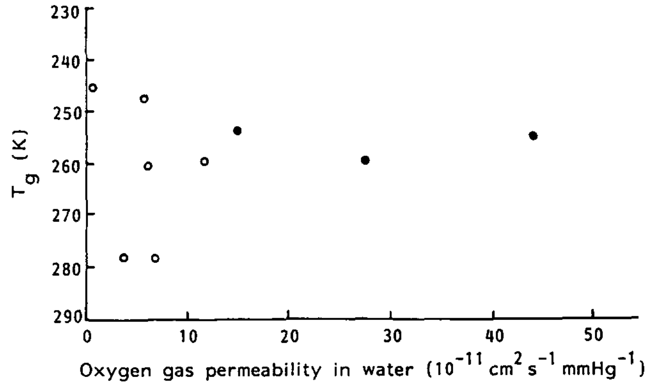

Figure 3 The relation between T_g and oxygen gas permeability of poly(organophosphazene) membranes in water: (●) aminophosphazene; (○) aryloxyphosphazene

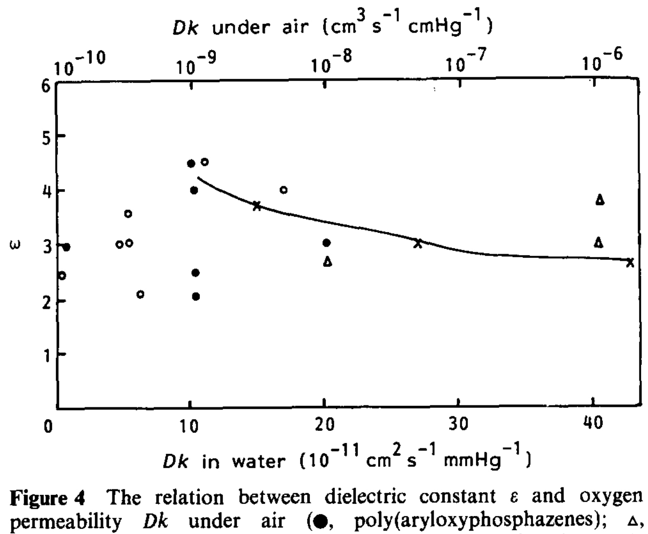

Figure 4 The relation between dielectric constant ε and oxygen permeability Dk under air (●, poly(aryloxyphosphazenes); △, poly(aminophosphazenes)) or water (○, poly(aryloxyphosphazenes); ×, poly(aminophosphazenes))

permeability value Dk of a contact lens, water was necessarily introduced into them. However, recently the problem of amoeba has occurred owing to water present in the contact lens. Consequently, it is preferable to prepare a contact lens having a higher oxygen gas permeability value and no water. It is found that a membrane prepared using poly(diethylaminobutylaminophosphazene) has an oxygen gas permeability value of $Dk = 55.2 \times 10^{-11}$ cm^2 s^{-1} mmHg^{-1} and a water absorption of less than 6%. It seems that water has no influence on oxygen gas permeability in water. Also, the crystallinity of the membrane is important for oxygen gas permeability as well as for water absorption. The crystallinity of the membrane is determined by X-ray diffraction analysis. It is found that membranes are amorphous solids, as no crystals are detected in them.

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