JOURNAL OF MATERIALS SCIENCE 23 (1988) 1360–1362

Gas permeability of poly(organophosphazenes)

MEISETSU KAJIWARA
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

The gas permeability and oxygen-to-nitrogen selectivity were determined for some poly(organophosphazenes). It was found from the data that the membrane having the highest gas permeability was $[NP(NHPr^n)(NEt_2)]_n$, which had 1.5×10^{-6} cm^3 (cm cm^{-2}) s^{-1} (cm Hg)$^{-1}$ to oxygen or 2.2×10^{-6} cm^3 (cm cm^{-2}) s^{-1} (cm Hg)$^{-1}$ to nitrogen. On the other hand, the membrane having the highest oxygen-to-nitrogen selectivity of about 3 had the formula $[NP(OC_6H_4Cl\text{-}p)_2]_n$. Also, the selectivity did not depend on the glass transition temperature of the membranes. The membrane prepared from $[NP(OC_6H_4CH_3\text{-}p)_2]_n$ had a negative activation energy for oxygen and nitrogen permeability.

1. Introduction

Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, has been polymerized in bulk and/or solution, using radiation or plasma methods. Linear polydichlorophosphazene $(NPCl_2)_n$ prepared using various polymerization methods is soluble in some organic solvents such as benzene or tetrahydrofuran (THF). However, $(NPCl_2)_n$ is unstable to moisture or water, and by its hydrolysis phosphoric acid, hydrogen chloride and ammonia are finally produced. Therefore, the chlorine atoms in $(NPCl_2)_n$ have been substituted by nucleophilic reagents such as alcohol, phenol or amine. The poly(organophosphazenes) prepared have many useful properties.

As an example, one of them has good fuel, acid and base resistance. Also, special elastomers for O-rings, lip-seals, arctic fuel hoses, gaskets, vibration damping equipment and coated fabrics have been developed by the Firestone Tire and Rubber Company [1]. Furthermore, biocompatibility testing of some poly(organophosphazenes) has shown them to be as compatible with rat muscle tissue as Silastic^R silicone rubber [2], and poly(bismethylaminophosphazene) has been used as a carrier molecule for anticancer drugs [3, 4]. The properties of the various poly(organophosphazenes) are reported by many researchers [5, 6]. Bitterova [7] reported the gas permeabilities of oxygen, nitrogen and argon using poly(organophosphazene) such as $[NP(OC_8H_{17})_2]_n$. However, there are no available data about the gas permeability and selectivity of poly(organophosphazenes). This report describes the gas permeability of poly(organophosphazene) membranes.

2. Experimental procedure

2.1. Materials

$(NPCl_2)_3$ was prepared by the method of Saito and Kajiwara [8]. The melting point of purified $(NPCl_2)_3$ was 112° C. $(NPCl_2)_n$ was prepared by the method of Kajiwara and Shiomoto [9]. The chlorine substitution reaction in $(PNCl_2)_2$ was carried out using CF_3CH_2ONa, C_6H_5ONa, p-ClC_6H_4ONa, p-$CF_3C_6H_4ONa$, p-$CH_3C_6H_4ONa$, m-$CH_3C_6H_4ONa$, NH_2Pr^n, $NHEt_2$ or other compounds in THF solvent by refluxing for 24 h under dry N_2. When the substitution reaction was complete, the solution was filtered off to remove the sodium chloride or the alkylamine hydrochloride. The filtrate was concentrated under vacuum and the polymer was precipitated by adding the solution to methanol. Filtration was again carried out and the purification of the polymer was repeated two or three times by precipitation. 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 spread on a glass substrate and a protective covering was put over it. The substrate was kept at room temperature and the solvent was slowly evaporated for several hours until a membrane was formed. The membranes thus prepared were dried further under reduced pressure at 50° C for 10 h.

2.2. Measurement of gas permeability

The oxygen and nitrogen permeabilities of $(NPR_2)_n$ membranes were determined using an instrument manufactured by the Yanagimoto Co. The dimensions of the $(NPR_2)_n$ membranes were 8 cm × 8 cm × 15 to 120 μ, and the gas permeabilities were determined over the temperature range of 20 to 100° C.

3. Results and discussion

3.1. Oxygen and nitrogen permeabilities

Oxygen and nitrogen permeabilities and oxygen-to-nitrogen selectivities for some poly(organophosphazenes) membranes are shown in Table I. Also, the oxygen and nitrogen permeabilities are given in Fig. 1.

As is apparent from Table I or Fig. 1, membranes with a high oxygen permeability exhibit low selectivity, and those with high selectivity exhibit low permeability. Silicone rubber, which has the highest oxygen permeability of any reported polymeric membrane, has an oxygen-to-nitrogen selectivity of about 2, which means that the maximum oxygen concentration that can be produced in a single pass through the membrane is only about 35%. It is found from Table I that the $[NP(OC_6H_4Cl\text{-}p)_2]_n$ membrane has an

0022–2461/88 $03.00 + .12

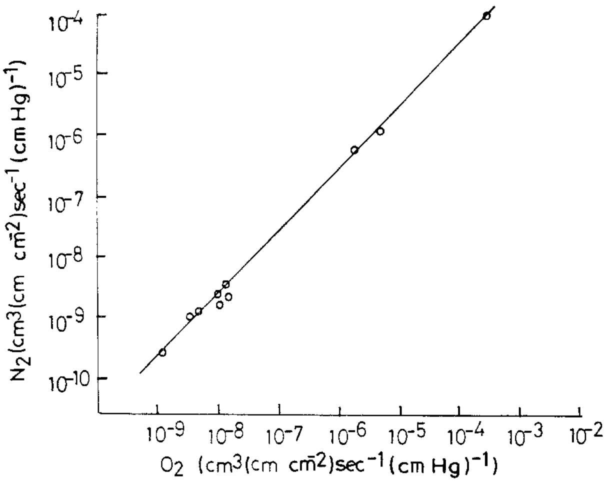

Figure 1 The relation between oxygen and nitrogen permeabilities.

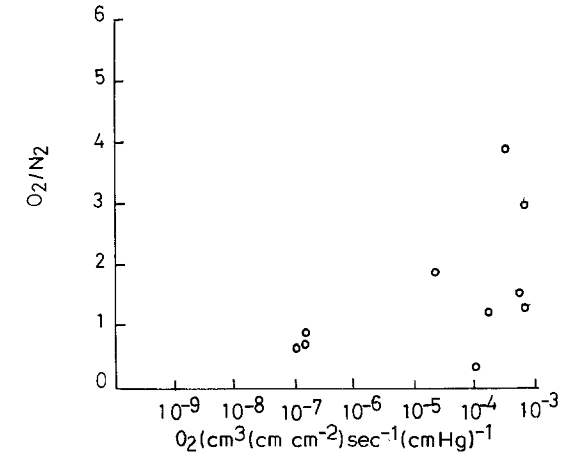

Figure 2 The relation between O_2/N_2 selectivity and oxygen permeability.

oxygen-to-nitrogen selectivity of about 3, and the selectivity is higher than for silicone rubber.

3.2. The relation between oxygen-to-nitrogen selectivity or polymer chain motion and gas permeability

The relation between the oxygen-to-nitrogen selectivity and oxygen permeability is given in Fig. 2. In general, an approximately linear relation with negative slope exists between the oxygen-to-nitrogen selectivity and the oxygen permeability in the case of the previous polymers such as silicon rubber, polystyrene, ethylcellulose, polyvinyl chloride and polyethylmethacrylate. However, using $(NPR_2)_n$-type membranes, this linear relation is not found. Also, it is said that gas permeability follows the solution–diffusion mechanism using the well-known polymers. Using poly(organophosphazenes) membranes, if gas permeability follows the solution–diffusion mechanism, the glass transition temperature of the polymer membrane and diffusion constant should be the important factors, and an approximately linear relation having a positive slope should exist between them. The relation between glass transition temperature of the polymers and oxygen or nitrogen permeability is shown in Fig. 3.

As gas molecules pass through the interstices of the polymer chain, the rate is higher if the molecular structure is not rigid or the polymer has a high free volume; that is, a polymer having a lower glass transition temperature has higher gas permeabilities. As shown in Fig. 3., however, this linear relation is not shown between the glass transition temperature and oxygen or nitrogen permeabilities.

3.3. Activation energy of oxygen or nitrogen permeability with $(NPR_2)_n$ membranes

Oxygen and nitrogen permeabilities over various temperatures were measured. Typical Arrhenius plots are shown in Fig. 4 and the activation energy as calculated is summarized in Table II. The covalent radii of the oxygen and nitrogen molecules are about 0.145 and 0.147 nm, respectively; however, different activation energies are calculated. In particular, in the case of the membrane of $[NP(OC_6H_4CH_3\text{-p})_2]_n$, oxygen and nitrogen permeabilities decreased with increasing temperature. That is, oxygen and nitrogen are more easily passed through the membrane with decreasing temperature. It is difficult to explain why the negative activation energy results from gas permeability when using $[NP(OC_6H_4CH_3\text{-p})_2]_n$ membranes.

4. Summary

Poly(organophasphazenes) were prepared by the reaction of polydichlorophosphazene with nucleophilic reagents, and the gas permeability and selectivity of poly(organophosphazenes) membranes were investigated.

1. It was found that membranes with high oxygen selectivity exhibit low selectivity.

TABLE I Oxygen and nitrogen permeabilities and selectivities for poly(organophosphazenes)

R in $(NPR_2)_n$	Temperature (°C)	Permeability (10^{-3} cm³ (cm cm⁻²) sec⁻¹ (cm Hg)⁻¹)		Selectivity O_2/N_2
		O_2	N_2	
OCH_2CF_3	27	20.0	16.2	1.2
OC_6H_5	25	75.0	56.5	1.3
$OC_6H_4CH_3$-p	20	341.0	183.0	1.9
$OC_6H_4CH_3$-m	25	7.6	5.1	1.5
OC_6H_4Cl-p	25	8.0	2.7	3.0
$OC_6H_4CF_3$-p	20	11 800	13 500	0.9
$OC_6H_4CH_2CH_3$-p	24	11.6	37.0	0.3
$NHPr^n$	28	13 600	18 600	0.7
$NHPr^n$, NEt_2	26	14 700	21 700	0.7
$NHBu^n$	25	47.0	12.0	3.9

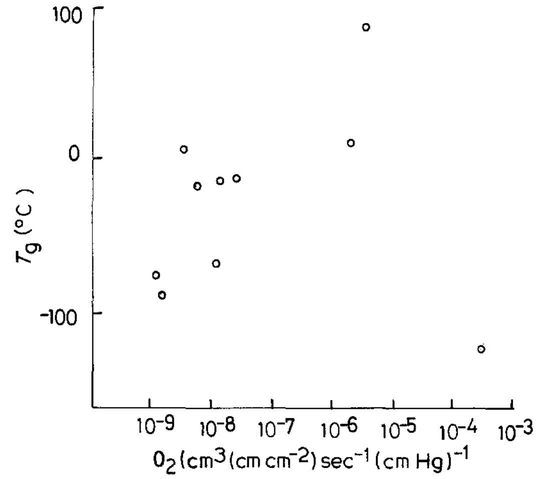

Figure 3 The relation between glass transition temperature of the membranes and oxygen permeability.

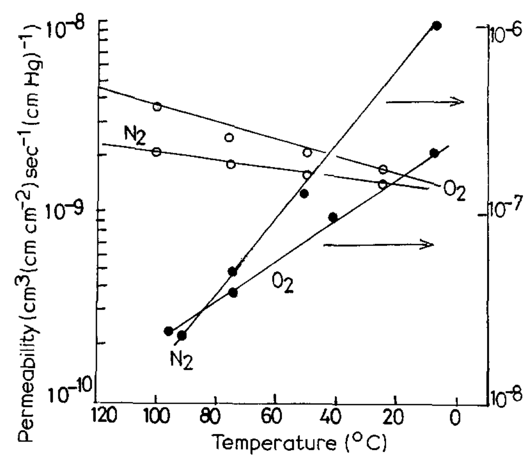

Figure 4 Arrhenius plots of oxygen and nitrogen permeabilities for (○) $[NP(OC_6H_4CH_3\text{-m})_2]_n$, (●) $[NP(OC_6H_4CH_3\text{-p})_2]_n$.

2. The $[NP(OC_6H_4Cl\text{-p})_2]_n$ membrane had the highest oxygen-to-nitrogen selectivity, and the selectivity was higher than for silicone rubber.

3. Using poly(organophosphazenes) membranes, the linear relation normally observed for other polymers between the oxygen-to-nitrogen selectivity and oxygen permeability was not found. Also, the usual linear relation (negative slope) between the glass transition temperature and the permeability was not shown.

4. In the case of the $[NP(OC_6H_4CH_3\text{-p})_2]_n$ membrane, a negative activation energy was found for oxygen and nitrogen permeabilities.

TABLE II Activation energies for oxygen and nitrogen permeabilities

R in $(NPR_2)_n$	Activation energy, Δ(kcal mol^{-1})*	
	O_2	N_2
$OC_6H_4CH_3$-p	−7.5	−7.4
$OC_6H_4CH_3$-m	3.5	3.4
OC_6H_4Cl-p	11.8	7.6
$OC_6H_4CH_2CH_3$-p	8.4	10.0

*1 cal = 4.1868 J.

References

1. S. H. ROSE, *J. Polym. Sci. B* **6** (1968) 837.
2. A. WILSON, Army Natick Laboratories Technical Report TR 75-38-CE (1974).
3. H. R. ALLCOCK, R. W. ALLEN and J. P. O'BRIEN, *J. Chem. Soc. Chem. Commun.* (1976) 717.
4. H. R. ALLCOCK, W. J. COOK and D. P. MACK, *Inorg. Chem.* **11** (1972) 2584.
5. H. R. ALLCOCK, R. L. KUGEL and E. G. STROH, *ibid.* **11** (1972) 1120.
6. R. E. SINGLER, E. L. HAGNAUER, N. S. SCHNEIDER, B. R. LALIBERTE, R. E. SACHER and R. W. MATTON, *J. Polym. Sci., Polym. Chem.* **12** (1973) 433.
7. F. A. BITTIROVA, V. V. KIREEV and A. K. MIKITAEV, *Vysokomol. Soedin, Ser. B* **23**(1) (1981) 30.
8. H. SAITO and M. KAJIWARA, *Kogyo Kagaku Zasshi* **66** (1963) 618.
9. M. KAJIWARA and K. SHIOMOTO, *Polym. Commun.* **25** (1984) 93.

Received 26 May
and accepted 24 July 1987