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# Oxygen gas permeability in water and the properties of poly(organophosphazene) films

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$[NP(NR_2)(NHR)]_n$ and $[NP(NR_2)(NHR)_{1-x}(OCH_2CH_2COOCH=CH_2)_x]_n$ type polymers were prepared by the reaction of $(NPCl_2)_n$ with various secondary or primary amines and 2-hydroxyethylacrylate. Membranes were prepared by casting, the mixing mill technique and ultraviolet radiation. The oxygen gas permeability of the membranes and the mechanical properties of the membranes were determined using a film oxygen gas permeater and an Instron tester. It was found that $[NP(\text{Di-}n\text{-hexylamine})(n\text{-butylamine})]_n$ had the highest oxygen gas permeability value; $Dk = 116 \times 10^{-11}$ cm$^3$ ml cm$^{-2}$ s$^{-1}$ mm Hg$^{-1}$. Also, it was found that the oxygen gas permeability of poly (aminophosphazenes) was not directly related to the dielectric constant and mechanical properties of the membranes in wet conditions (water).

## Introduction

The oxygen gas permeability of many polymers has been determined under dry [1] or wet [2] conditions. For example, silicon polymer and silicon–methylacrylate [3] copolymers (60%–70% silicon and 30%–40% methylacrylate) have been tested for oxygen gas permeability under wet conditions, yielding $79 \times 10^{-11}$ and $10 \times 10^{-11}$ cm$^3$ ml cm$^{-2}$ s$^{-1}$ mmHg$^{-1}$ for the polymer and copolymer, respectively. At present, soft polymer membranes having higher oxygen gas permeabilities are required for applications such as contact lenses or $O_2/N_2$ gas separation membranes. For separation using poly (organophosphazenes), Krieev in [4] was the first to describe the gas permeability of oxygen, nitrogen and argon using a poly(diamyloxyphosphazene) membrane. Patents pertaining to gas separation with poly (organophosphazene) membranes have since been proposed by many companies [5]. These patents and Krieev's investigation concerned gas permeability under dry conditions. The present paper describes oxygen gas permeability in water or wet conditions and the mechanical properties of some poly (organophosphazene) films.

## 2. Experimental procedure

### 2.1. Preparation of hexachlorocyclotriphosphazene $(NPCl_2)_3$ and polydichlorophosphazene $(NPCl_2)_n$

$(NPCl_2)_3$ was synthesized by the method given by Saito and Kajiwara [6], in which $(NPCl_2)_3$ was prepared by the reaction of 500 g of phosphorus pentachloride and 200 g ammonium chloride using 1500 ml tetrachloroethane or chlorobenzene. Pure trimer was obtained by repeated fractional vacuum distillation.

Linear polydichlorophosphazene $(NPCl_2)_n$ was prepared by the method reported by Kajiwara [7], in which 5 g $(NPCl_2)_3$ and 0.1 g 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 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 completed, the polymer– oligomer mixture was dissolved in 200 ml dry tetrahydrofuran (THF). To remove the oligomer, THF solution was added to 500 ml $n$-heptane or ethanol. After the polymer had precipitated, the precipitate was separated, dissolved in THF and reprecipitated. This purification procedure was repeated several times and the purified polymer was then dissolved in 100 ml of THF.

### 2.2. Preparation of poly(organophosphazenes)

Various poly (organophosphazenes) such as $(NPR^1R^2)_n$ were formed with amine compounds. The preparation of typical poly (organophosphazenes) is described below.

#### 2.2.1. *Synthesis of* $[NP(NEt_2)(NHBu\text{-}n)]_n$

A solution of $(NPCl_2)_n$ dissolved in THF was added dropwise over 2 h to a stirred solution of diethylamine in 100 ml THF. The reaction was allowed to proceed at 25 °C for 24 h. Then, $n$-butylamine and triethylamine dissolved in 50 ml 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 *n*-heptane. Purification was effected by precipitation of the polymer three times from solution in dilute aqueous sulphuric acid into dilute acetic acid in ethanol and into methanol which contained a trace of triethylamine. The polymer was then dried under vacuum over $P_2O_5$.

### 2.2.2. *Preparation of poly(organophosphazene) films*

Some 5 or 10 g $(NPR^1R^2)_n$ was dissolved in 100 g 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. In addition, after Irga-Cure 184 was added to $[NP(\text{Di-}n\text{- butylamine})(NHBu\text{-}n)_{1-x}(OCH_2CH_2COOCH = CH_2)_x]_n$ dissolved in THF, the solution was kept at room temperature. The films obtained were irradiated with 160 W cm$^{-1}$ for 30 s.

### 2.3. Determination of oxygen gas permeability and the mechanical properties of poly(organophosphazene) films

The dimensions of the films were 15 mm diameter by 0.2 mm thick. The oxygen gas permeability of the films in water were determined with a film oxygen permeater of Seikaken type at 20 °C. Oxygen gas permeability, *Dk*, was also estimated from equations 1 and 2, respectively.

$$K = 14.2\ p/i\,l\,760 \tag{1}$$

$$Dk = K\ i'\,l'\,760/p' \tag{2}$$

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

The mechanical properties of poly (organophosphazene) films were determined with Instron tester using equation 3

$$K = L\,E/2\,l \tag{3}$$

where $K$ is the index of strength, $L\,(g)$ the fracture load, $E$ (%) the fracture elongation and $l$(μm) the thickness of the film.

## 3. Results and Discussion

### 3.1. Oxygen gas permeability, *Dk*, and dielectric constant, ε′ of poly(aminophosphazene) films $[NP(NR_2)(NHBu\text{-}n)]_n$

In general, poly(aminophosphazene) films are a transparent but poly(alkoxyphosphazene) and poly(phenoxyphosphazene) films are opaque. *Dk* values of $(NPR^1R^2)$ are shown in Table I. It is seen from Table I that the *Dk* value increases with an even number of *n* in $(CH_2)_n$ groups and the film having the highest *Dk* value consisted of di-*n*-hexylamine in comparison to other poly(organophosphazenes). It was observed in the previous paper [8] that *Dk* values of poly(aminophosphazenes) in water were related to the dielectric constant, ε′, of the polymer, i. e., *Dk* increased with decreasing ε′ of the polymer. However, the *Dk* values of poly(aryloxyphosphazenes) are not dependent on ε′. Therefore, ε′ of the five films prepared in this study were determined, and the results are given in Table I.

It was found that ε′ of the polymers increased with frequency, but no relation between *Dk* values and ε′ was found in this work.

### 3.2. Oxygen gas permeability, *Dk*, and the mechanical properties of poly(aminophosphazenes) film $[NP(\text{Di-}n\text{-hexylamine})(NHR)]_n$ prepared in a mixing mill

To obtain poly(aminophosphazene) films with higher *Dk* values in comparison to $[NP(\text{Di-}n\text{-hexylamine})(NHBu\text{-}n)]_n$ film, $[NP(\text{Di-}n\text{-hexylamine})(NHR)]_n$ type polymers were prepared with $[NP(\text{Di-}n\text{-hexylamine})Cl]_n$ and primary amines such as *n*- propyl amine. However, it was impossible to prepare a film by the casting method except $[NP(\text{Di-}n\text{-hexylamine})(NHBu\text{-}n)]_n$. Then, to increase the strength of the film, the polymer was treated in a mixing mill used in the rubber industry. However, films cannot be prepared with this technique using $[NP(\text{Di-}n\text{-hexylamine})(NHPr\text{-}n)]_n$ polymer. The film made in the mixing mill can be mounted on a sample holder to determine the *Dk* value. Thus the intermolecular action of the polymer is stronger than that of the polymer not treated in the

TABLE I Oxygen gas permeability, *Dk*, and dielectric constant ε′ of poly(aminophosphazene) films $[NP(NR_2)(NHBu\text{-}n)]_n$

| $[NP(NR_2)(NHBu\text{-}n)]_n$ | Dielectric constant, ε′ | | | $Dk(10^{-11}\ cm^3\,cm\,cm^{-2}\,s^{-1}\,mmHg^{-1})$ |
|---|---|---|---|---|
| $NR_2$ | 30 Hz | 330 Hz | 3 KHz | |
| Di-*n*-ethylamine | 3.6 | 4.2 | 4.6 | 55.2 |
| Di-*n*-propylamine | 3.3 | 3.7 | 4.1 | 40.3 |
| Di-*n*-butylamine | 4.1 | 4.5 | 4.9 | 86.8 |
| Di-*n*-amylamine | 3.3 | 3.5 | 3.6 | 64.4 |
| Di-*n*-hexylamine | 3.8 | 3.9 | 4.1 | 116.0 |
| Di-*n*-octylamine | – | – | – | – |

TABLE II. Oxygen gas permeability and the mechanical properties of poly(organophosphazene) films [NP(Di-$n$-hexylamine) (NHR-$n$)]$_n$ prepared by mixing mill treatment

| [NP(Di-$n$-hexylamine) (NHR-$n$)]$_n$ NHR-n | $Dk$ ($cm^3\,cm\,cm^{-2}\,s^{-1}\,mmHg^{-1}$) | Mechanical property | | |
|---|---|---|---|---|
| | | $F$ (g) | $E$ (%) | $K$ |
| Propylamine | | | | |
| Butylamine | 124.3 (116)[a] | 66.0 | 6.5 | 1 |
| Amylamine | 109.5 | 64.5 | 7.6 | 1 |
| Hexylamine | 126.3 | 52.1 | 7.7 | 1 |
| Octylamine | 102.9 | 26.7 | 9.2 | 1 |

$F$ = Fracture load, $E$ = fracture elongation, $K$ = index of strength.

[a] No mixing mill treatment.

TABLE III Oxygen gas permeability, $Dk$, and the mechanical properties of poly(organophosphazene) films [NP(Di-$n$-butylamine) (NHBu-$n$-)$_{1-x}$ ($OCH_2$-$CH_2COOCH = CH_2$)$_x$]$_n$

| $x$ | Radiation (s) | $Dk$ ($10^{-11}\,cm^3\,cm\,cm^{-2}\,s^{-1}\,mmHg^{-1}$) | $F$ (g) | $E$ (%) |
|---|---|---|---|---|
| 0 | | 86.8 | 366 | 10.5 |
| 0.07 | 0 | 40.2 | 234 | 4 |
| | 4 | 25.0 | 230 | 3 |
| | 4 × 4 | 25.0 | 232 | 3 |
| 0.13 | 0 | 30.8 | 257 | 6 |
| | 4 | 24.7 | 285 | 5 |
| | 4 × 4 | 42.6 | 302 | 4 |
| 0.27 | 0 | 27.2 | 269 | 6 |
| | 4 | 22.1 | 307 | 4 |
| | 4 × 4 | 23.6 | 319 | 4 |

mixing mill. $Dk$ values and mechanical properties of the films are shown in Table II.

It is seen from Table 2 that [NP(Di-$n$-hexylamine)-($n$-hexylamine)]$_n$ film has the highest $Dk$ value. Also, for [NP(Di-$n$-hexylamine)($n$-hexylamine)]$_n$, the $Dk$ value increased after mixing mill treatment. However, there was no relation between $Dk$ value and the mechnical properties, such as fracture load and fracture elongation.

## 3.3. The relation between oxygen gas permeability, $Dk$, and the mechanical properties of [NP(Di-$n$-butylamine)-(NHBu-$n$)$_{1-x}$ ($OCH_2CH_2COOCH = CH_2$)$_x$]$_n$ films by ultraviolet radiation

As di-$n$-hexylamine in secondary amines is very expensive, the cheaper di-$n$-butylamine is selected. In addition, to increase the strength of the film, 2-hydroxyethlacrylate group ($CH_2 = CHCOOCH_2\ CH_2O$) was bonded to the side chain. The prepared polymer [NP(Di-$n$-butylamine)(NHBu-$n$)$_{1-x}$($OCH_2CH_2CO$-$OCH = CH_2$)$_x$]$_n$ type was treated with ultraviolet radiation. $Dk$ value, diening strength and elongation of the films before or after ultraviolet radiation were determined, and the results are summarized in Table III.

It is seen from Table III that the $Dk$ value of the film before or after ultraviolet radiation decreased with increasing 2-hydroxy-elthylacrylate in comparison with the original film. On the other hand, diening strength and elongation of the films before or after ultraviolet radiation decrease in comparison with those of the original film.

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