Gas Permeation through Poly(*N*-*n*-alkylmaleimide) Membranes

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ABSTRACT: The permeation of oxygen and nitrogen through the membranes of poly(*N*-*n*-alkylmaleimide)s including poly(*N*-*n*-butylmaleimide) [poly(nBMI)] and poly(*N*-dodecylmaleimide) [poly(DodMI)] was investigated. These membranes from polymaleimides have been revealed to have high permeability coefficients even under their glass transition temperatures on account of facile permeation through the fused alkyl chain in the side group. The apparent diffusion coefficient was determined to be greater than $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for poly(DodMI), and the facile diffusion in the polymer was discussed.

KEY WORDS *N*-*n*-Alkylmaleimide / Poly(substituted methylene) / Glass Transition Temperature / Gas Permeability / Permeability Coefficient / Diffusion Coefficient / Mobility of Side Chain / Membrane /

Gas transport properties of polyimide films which have a variety of chemical structures have been reported on account of a high glass transition temperature and excellent thermal stability.^{1–10} We reported on the radical polymerization of *N*-alkyl-substituted maleimides and *N*-(alkyl-substituted phenyl)maleimides bearing various alkyl groups, and on the excellent thermal stability of the resulting polymers.¹¹ In the previous paper,^{12,13} we also reported that radical polymerization of *N*-*n*-alkylmaleimides (RMI) with various kinds of *n*-alkyl groups as an *N*-substituent proceeded easily to give high molecular weight polymers in high yields. The polymer membranes prepared by casting show high permeability to oxygen and nitrogen, *i.e.*, permeability coefficients (P_{O_2} and P_{N_2}) are in the range of 10^{-9} to $10^{-8} \text{ cm}^3 (\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$, although they are glassy polymers with high glass transition temperatures. It has been revealed that permeability depends on the length of the alkyl side chain, *i.e.*, P increases as the carbon

number of the side chain increases.

In this study, gas permeation through the polymer membranes of poly(*N*-*n*-butylmaleimide) [poly(nBMI), $n=4$] and poly(*N*-dodecylmaleimide) [poly(DodMI), $n=12$] as well as other poly(RMI)s (Scheme I) was investigated and the permeation mechanism is discussed.

Poly(RMI) [$n=4-18$]

Scheme 1.

EXPERIMENTAL

Materials

RMIs were prepared by the methods described in the previous paper.¹² Other reagents and solvents were used after ordinary purification.

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Polymerization was performed with 2,2'-azobisisobutyronitrile (AIBN) (0.005 mol l^{-1}) in benzene ($[\text{RMI}] = 1 \text{ mol l}^{-1}$) at 60°C . The polymer was precipitated with a large amount of methanol or ethanol, and purified by repeating reprecipitation. All polymers obtained had high molecular weight ($\bar{M}_n > 10^5$) enough to be used for subsequent measurements. Poly(nBMI) was prepared from bulk polymerization under similar conditions: $\bar{M}_n = 8.46 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.97$. The polymer membranes were prepared by casting of chloroform solution at room temperature, and drying *in vacuo* for a day.

Gas Permeability Measurements

Gas permeation measurements were carried out at 25 – 50°C by a Yanaco GTR-10 as described previously.¹² The amount of oxygen and nitrogen that permeated into the downstream side was determined by gas chromatography (Yanaco G1800T). Commercial oxygen and nitrogen, or ambient air were used as a test gas at atmospheric, reduced, or increased pressure. The thickness of the polymer membrane was measured with a micro-gage.

Determination of Coefficients

P is generally defined as the product of D and S .

$$P = D \cdot S \quad (1)$$

where D and S are the diffusion and solubility coefficients, respectively. D can be correlated to the time lag in permeation (θ) and thickness of the film (l) by the following equation.

$$D = l^2/6\theta \quad (2)$$

The apparent S is evaluated as $S = P/D$.

Other Measurements

The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were determined by gel permeation chromatography (GPC) in THF with standard polystyrenes for calibration.

Differential scanning calorimetry (DSC) was performed by a SEIKO DSC-200 or Perkin-Elmer 7 Series thermal analysis system.¹²

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the N -alkyl chain length on the permeability of oxygen and nitrogen through poly(RMI) membranes. It is clear that both P_{O_2} and P_{N_2} increase when a longer alkyl chain is introduced into the side chain of poly(RMI), suggesting that the permeation rate of the penetrants through a domain of the alkyl side chains is important compared with that through the neighborhood of the main chain of the polymaleimides. This may be due to differences in segmental motion, *i.e.*, high mobility of the alkyl side chain segments above its melting (fusion) temperature (T_f) and the frozen main chain below its glass transition temperature (T_g). It has been already reported that T_f of these poly(RMI)s is lower ($-43.0^\circ\text{C} < T_f < 19.5^\circ\text{C}$) than the temperature for permeation measurements and T_g are much higher ($97^\circ\text{C} < T_g < 185^\circ\text{C}$), according to the length of the N -alkyl chains.¹²

To clarify the permeation mechanism through these polymaleimides, P was determined by various up-stream pressures. For

Figure 1. Effect of the number of carbons (n) in the side chain of poly(RMI)s on permeability coefficients (P) for oxygen (○) and nitrogen (●) at 40°C .

Figure 2. Up-stream pressure dependence of P for poly(DodMI) (○) and poly(nBMI) (●) at 40°C.

both poly(nBMI) and poly(DodMI), it has been found that P obtained is independent of pressure in the range from 1 to 270 cmHg as shown in Figure 2. It is reasonable that poly(DodMI) with a relatively long alkyl chain in the side group does not show any dependence, because permeation may be mainly concerned with fused alkyl chains in a liquid-like state similarly to rubbery polymers. But, it is surprising that not only poly(DodMI) but also poly(nBMI) show no up-stream pressure dependence under the conditions in this study, because the latter is likely to have a relatively small volume of the flexible alkyl side chain. It is not clear whether the absence of dependence of P on pressure is due only to the alkyl side chain with high mobility, or some other contribution should be considered, e.g., free volume in the neighborhood of the less-flexible main chain.

These results suggest that transport of penetrants in poly(RMI) is likely governed by a simple solution-diffusion mechanism (eq 1), but not dual-mode models such as dual-mode sorption^{15–18} and partial immobilization model,^{19–22} represented as the follows;

$$P = k_D \cdot D_D [1 + FK/(1 + bp)] \quad (3)$$

where k_D and D_D are the coefficients of solution and diffusion for penetrant sorbed according to Henry's law, respectively. F is D_H/D_D and K is bC_H'/k_D , where D_H is the diffusion coefficient

Figure 3. Relationships between time and permeation volume of oxygen through poly(DodMI) (○) and poly(nBMI) (●) at 30°C.

according to Langmuir mode, C_H' is the hole saturation constant in the Langmuir sorption mode, b is the affinity constant of penetrant for the Langmuir site, and p is the pressure of penetrant at the up-stream side.

It has been pointed out that poly(1-trimethylsilyl-1-propyne) bearing the highest permeability coefficient among organic polymers has an exceptionally large C_H' , which is related to unrelaxed volume and is a significant factor for polymers with rigid chain structure.^{23–25} The large C_H' is the most important as well as high solubility of penetrants for excellent permeability through the polymer. P may hardly depend on pressure p when b is much small, i.e., $bp \ll 1$, as shown in eq 3.

Although it is valuable to determine the constants in eq 3, i.e., D_H , C_H' , or b in order to know the real reason for the absence of the pressure-dependence of P for polymaleimides, the permeation of poly(RMI) is tentatively treated as an ordinary solution-diffusion process by evaluating apparent D with the time-lag method (eq 2). Figure 3 shows the results of the permeation of oxygen at 30°C through poly(RMI)s with various thickness. When the membrane thickness increased, time lag of permeation was clearly observed especially in the case of poly(nBMI), where the diffusion of penetrants is slower than in poly(DodMI). P

Figure 4. Temperature dependence of (A) permeability, (B) diffusion, and (C) solubility coefficients of oxygen and nitrogen through poly(DodMI) (○) and poly(nBMI) (●). Membrane thickness: poly(DodMI), 250 μm ; poly(nBMI), 117 μm .

evaluated for membranes with different thickness agreed well within an experimental error as expected.

In Figure 4, P , D , and S for poly(nBMI) and poly(DodMI) are plotted in the temperature range from 25 to 50°C, where S is calculated from the P and D obtained. The respective

Table I. Permeability, diffusion, and solubility coefficients for poly(RMI)s^a

Polymer	n^b	Gas	Temp	$P \times 10^{10}$	$D \times 10^7$	$S \times 10^4$
			°C			
Poly(DodMI)	12	O_2	40	49.2	37.7	13.1
			30	39.9	30.3	13.2
		N_2	40	20.9	25.8	8.10
			30	16.3	22.0	7.41
		O_2	40	11.5	5.41	21.2
			30	10.1	3.65	27.8
Poly(nBMI)	4	N_2	40	4.81	2.30	20.9
			30	3.95	1.70	23.3

^a P in $\text{cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$, D in $\text{cm}^2 \text{ s}^{-1}$, and S in $\text{cm}^3 \text{ (STP) cm}^3 \text{ cmHg}^{-1}$.

^b Number of carbons in the N -alkyl chain.

coefficients at 30 and 40°C are summarized in Table I. It has been revealed that D for these poly(RMI)s are much higher than those reported for common ordinary glassy polymers,⁵ *i.e.*, $2\text{--}5 \times 10^{-6}$ and $1\text{--}7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for poly(DodMI) and poly(nBMI), respectively. The values for poly(DodMI) are close to the values for rubbery polymers such as polyisoprene. The fact that D for poly(DodMI) is much larger than that for poly(nBMI) is consistent with the model proposed previously¹²; *i.e.*, the facile transport of penetrants through the alkyl side chain with high mobility induces high permeability. The importance of the mobility of the side chains on permeability has also been pointed out by Kawakami *et al.* from their solid state NMR study.²⁶ S for poly(nBMI) is slightly larger than that for poly(DodMI), and it is opposite to the order in P and D . The difference in the length of the alkyl chain is relatively small.

In conclusion, P for poly(RMI) is independent of the pressure of penetrants on the up-stream side in the range of 1–270 cmHg, and determination of apparent D was attempted according to the solution-diffusion model (Henry's law). It has been revealed that poly(RMI) has a high diffusion constant, depending on the length of the N -alkyl chain.

It is concluded that high permeability for poly(DodMI) is due mainly to the high diffusion of the penetrant in the alkyl side chain region.

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- In our preliminary work,¹⁴ the permeability coefficients for poly(DodMI) were somewhat underestimated. The reason is not clear at present time, but the data in ref 12 and this paper are more consistent.
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