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# $CO_2$ selective membranes Prepared from Hyper-branched Graft Polymers by Atom Transfer Radical Polymerization

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We prepared a novel gas separation membrane having both high $CO_2$ permselectivity and high mechanical strength from a hyper-branched graft polymer synthesized using atom transfer radical polymerization (ATRP) method. A macro-initiator for ATRP was prepared by copolymerization of methyl methacrylate and chloromethylstyrene. The graft polymers were obtained by grafting poly(ethylene glycol)methyl ether methacrylate (POEM) on the macro-initiator by ATRP changing POEM content, $C_p$, in the polymers. Self-standing membranes were prepared by casting a tetrafydrofuran solution of the polymers obtained. The permeation experiment at 308K shows that permeability coefficient of $CO_2$ through the membrane of $C_p$ =72wt% is $1.0\times10^{-8}$ $cm^2$ (STP) $cm^{-1}$ $s^{-1}$ $cmHg^{-1}$, and separation factor of $CO_2/N_2$ is 53. The maximum tensile strength of the membrane obtained from a stress-strain curve is 2.7 MPa. These data indicate that the membrane obtained from the hyper-branched graft polymers has an enough performance for $CO_2/N_2$ gas separation.

Key words: $CO_2$, Separation, Membrane, Hyper branch, Graft polymer, Atom transfer radical polymerization

## 1. INTRODUCTION

The greenhouse effect is one of the important issues in the world. A comparison of the relative greenhouse effect of each gas reveals that nearly two-thirds of the total greenhouse effect can be attributed to carbon dioxide. Therefore, a most relevant approach to prevent global warming is regulating $CO_2$ gas emission. Membrane separation is one of the key technologies to regulate $CO_2$ gas emission with reduced energy consumption.

There have been many studies on $CO_2$ selective membranes [1-18]. Ion-exchange or liquid membranes using facilitated transports mechanism of $CO_2$ [1,2] have shown high permselectivity. However, they have not been applied on a commercial scale because of their characteristic shortcomings. Solid polymeric membranes such as fluorine-containing polyimides have also been studied [5-11]. However, these polyimides have a low permeability ratio of $CO_2$ over $N_2$. For practical application, it is necessary to develop membrane materials having a much higher performance: e.g. $P_{CO_2}$ >100 Barrer (1 Barrer = $10^{-10}$ $cm^2$ (STP) $cm^{-1}$ $s^{-1}$ $cmHg^{-1}$) and a permeability ratio of $CO_2$ over $N_2$, $P_{CO_2}/P_{N_2}$ >70 [12]. Okamoto *et al.* have reported the excellent performance of $CO_2/N_2$ separation by poly(ether imide) segmented copolymers [13-15], for example, $P_{CO_2}$ = 140 Barrer and $P_{CO_2}/P_{N_2}$ >70 at 298 K [15]. They also have reported excellent gas permeation properties through a membrane using high molecular weight branched

polyethers: $P_{CO_2}$ = 770 Barrer and $P_{CO_2}/P_{N_2}$ =46 at 308 K [16].

For practical applications of a $CO_2$ selective membrane in industrial use, both high $CO_2$ perm-selectivity and high mechanical strength are needed. In this study, we prepared such a high performance membrane for $CO_2$ separation from a hyper-branched graft polymer using atom transfer radical polymerization (ATRP) method.

## 2. EXPERIMENTAL

### *2.1 Synthesis of the macroinitiator for ATRP*

A macro-initiator for ATRP was prepared by copolymerization of methyl methacrylate (MMA) and chloromethylstyrene (CMS) by a conventional radical polymerization in toluene solvent using 2,2'-azobis isobutyronitrile as an initiator.

### 2.2. *Synthesis of a hyper branched graft polymer using ATRP*

The graft polymers were obtained by grafting poly(ethylene glycol) methyl ether methacrylate, referred to herein as poly[(oxyethylene)$_9$ methacrylate] (POEM, *Mn*= 475g/mol: Aldrich), macromonomer on the macro-initiator in 1-methyl-2- pyrrolidinone solvent by ATRP using CuCl and 4,4'-dimethyl-2,2'-dipyridyl as catalyst.

### *2.3. Preparation of $CO_2$ selective membranes*

A $CO_2$ selective membrane was prepared by casting a tetrafydrofuran solution of the polymer obtained on Teflon sheet and by drying it at 30°C for 4 h.

### *2.4 Permeation experiments for $CO_2$ and $N_2$ gas.*

Permeability coefficients $P$ and the diffusion time lag $\theta$ were measured by a vacuum time-lag method at 1 atm and 308 K. The apparent diffusion coefficient $D$ was calculated from the following equation:

$$D = \frac{d^2}{6\theta} \quad (1)$$

where $d$ is the membrane thickness. The apparent solubility coefficient $S$ was evaluated from $S=P/D$.

### *2.5 Measurement of the mechanical strength of the membranes*

The mechanical strength of the membranes was determined with a table model testing machine (SHIMADZU, EZ-Test500N). In the static stress-strain curves, specimens with a nominal 20-mm-gauge length and 0.2-mm thickness were deformed in tension at a constant strain rate of 10 mm/min at 25 °C, and stress-strain data were determined to failure.

## 3. RESULTS AND DISCUSSION

The POEM content, $C_p$, calculated from NMR and the tensile strength and Young's modulus obtained from the stress-strain curve of the membranes are listed in Table 1. Both the tensile strength and Young's modulus decrease with increasing $C_p$. The tensile strength at $C_p$ =72wt% is 2.7 MPa. This means that the sample membranes have enough strength for a membrane for gas separation.

**Table 1** Characteristics of sample membranes
$R_{MI}$ : MMA/CMS mole ratio in the macro initiator, $Dd$ : membrane thickness, $C_p$ : POEM content from NMR data, $\sigma$ : tensile strength, $E$ : Young's modulus

| Sample | $R_{MI}$ [-] | $Dd$ [$\mu$m] | $C_p$ [wt%] | $\sigma$ [MPa] | $E$ [MPa] |
|---|---|---|---|---|---|
| M1 | 43 | 72.0 | 22 | 41 | 1400 |
| M2 | 140 | 165 | 47 | 4.1 | 15 |
| M3 | 150 | 155 | 72 | 2.7 | 0.29 |

Figure 1 shows the permeability coefficient of $CO_2$ and $N_2$ gases as a function of $C_p$. The value of the permeability coefficient of $CO_2$ gas increases with increasing $C_p$ while that of $N_2$ gas is almost independent

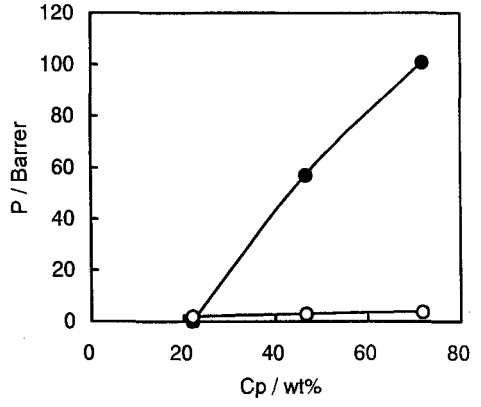


**Fig.1** Permeability coefficient of $CO_2$ and $N_2$ gases as a function of POEM content, $C_p$, in the membranes. ●: $CO_2$. ○: $N_2$.

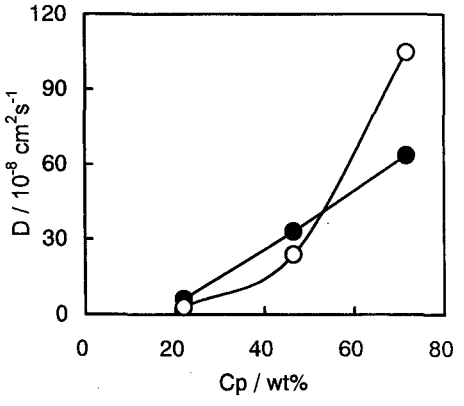


**Fig.2** Diffusion coefficient of $CO_2$ and $N_2$ gases as a function of POEM content, $C_p$, in the membranes.

of $C_p$. The value of the permeability coefficient of $CO_2$ gas is 100 Barrer when $C_p$ is equal to 72 wt%.

Figure 2 shows the diffusion coefficient of $CO_2$ and $N_2$ gases as a function of $C_p$. The diffusion coefficient of $CO_2$ gases has almost the same values as that of $N_2$ gases. The value of the diffusion coefficient of both the gases increases with $C_p$.

Figure 3 shows the solubility coefficient of the two gases as a function of $C_p$. The solubility coefficient of $CO_2$ gas is 83 times higher than that of $N_2$ gas when $C_p$ = 73 wt% although the solubility coefficient of $CO_2$ gas has less value when $C_p$ = 22 wt%. The high solubility coefficient of the membrane with high POEM content

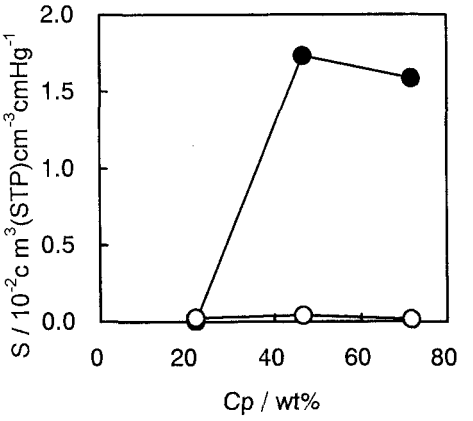


**Fig.3** Solubility coefficient of $CO_2$ and $N_2$ gases as a function of POEM content, $C_p$, in the membranes. ●: $CO_2$. ○: $N_2$.

will due to the high affinity of $CO_2$ molecules to the POEM segments. This result indicates that the high permeability coefficient of $CO_2$ through the membrane is due to the high solubility of $CO_2$ in the membrane.

## 4. CONCLUSIONS

We prepared a novel $CO_2$ selective membrane from a hyper-branched graft polymer synthesized by graft polymerization of MMA main chain on POEM graft chains, changing POEM content. The permeability coefficient of $CO_2$ through the membrane increases with increasing POEM content and has a value of $1.0\times 10^{-8}$cm$^3$(STP)cm/(cm$^2$scmHg), when $C_p$ = 72 wt%. The separation factor of $CO_2/N_2$ also increases with increasing $C_p$ and is 53 when $C_p$ = 72 wt%. The high permeability of $CO_2$ gas is due to the high solubility coefficient of $CO_2$ in the POEM domain. The tensile strength of the membrane decreases with increasing $C_p$ and is 2.7 MPa when $C_p$ = 72 wt%. Both the high $CO_2$ permeability and high mechanical strength may come from the microphase-separated structure consisting of rubbery POEM segments and glassy PMMA segments. These results indicate that the membrane obtained from

the hyper-branched graft polymers will have an enough performance for $CO_2/N_2$ gas separation.

## 5. ACKNOWLEDGMENT

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