

Synthesis of Membranes of Poly(vinyl ether)s and Their Gas Permeability

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ABSTRACT: Cationic polymerizations of various vinyl ethers with cyclic substituents were performed with BF_3OEt_2 . The polymers had relatively high molecular weight (M_n : 18,900–132,000), although the polymerization of phenyl vinyl ether did not proceed. According to differential scanning calorimetry, the obtained poly(vinyl ether)s showed higher glass transition temperatures than room temperature. These poly(vinyl ether)s gave free-standing membranes both by a solution-casting method and by a hot-press method. In the membranes prepared by solu-

tion-casting, the oxygen permeability coefficients of these membranes were in the range of 0.81–6.01 barrers, and poly(2-adamantyl vinyl ether) showed the highest gas permeability among them. Gas permeability of the membranes prepared by hot-press was lower than that of the membranes prepared by solution-casting. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2339–2343, 2009

Key words: poly(vinyl ether); cationic polymerization; membrane; gas permeation

INTRODUCTION

Gas separation by polymeric membranes is considered to be an effective technology owing to energy efficiency, low operating costs, and simple procedure. Highly gas-permeable polymers have attracted much attention as novel gas-separation membrane materials.^{1–5} Gas permeability of several polymers has been investigated so far, which are glassy polymers such as substituted polyacetylenes^{6–8} and polyimides^{9–11} and rubbery polymers such as polysiloxanes^{12–14} and poly(phosphazene)s,^{15–17} although glassy polymers are easy to form into polymeric membranes compared with rubbery polymers. In nonporous membranes, amorphous polymers are suitable for materials of gas-permeable membrane because gas molecules penetrate through amorphous parts of polymer matrix. However, practical use of polymeric membranes for gas separation is limited because few current polymeric membranes have sufficient performance. Therefore, the design and synthesis of novel polymers are essential from the viewpoint of industrial issue.

A variety of poly(vinyl ether)s have been synthesized by cationic polymerization.^{18–20} Most of poly(vinyl ether)s are rubbery at room temperature, and it is difficult to be used for plastic materials. Poly-

(vinyl ether)s with relatively bulky substituents exhibit higher glass transition temperatures; e.g., T_g 's of poly(cyclohexyl vinyl ether),²¹ poly(tricyclodecyl vinyl ether),²² and poly(2-adamantyl vinyl ether)²³ are 50, 100, and 180°C, respectively. Such polymers can be used as membrane materials, and in addition they are amorphous polymers. It is known that carbon dioxide tend to interact with polar groups in the polymer membranes.²⁴ The polymer membranes with ether oxygen such as polyethylene glycol are considered to be favorable for carbon dioxide separation membrane because they have appropriate polarity,²⁵ and it has been reported that polyethylene glycol membranes exhibit high carbon dioxide permselectivity.^{26,27} Therefore, such amorphous poly(vinyl ether)s with high glass temperature are interesting as gas-separation membranes. However, there are no examples of researches about gas permeability of poly(vinyl ether)s.

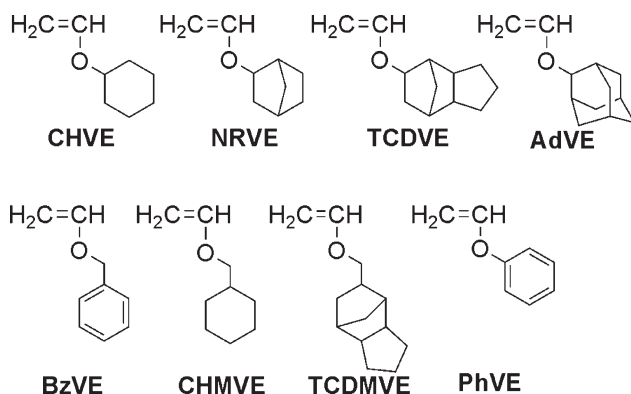
In this study, poly(vinyl ether)s with bulky cyclic substituents were synthesized by cationic polymerization to investigate possibility of their application to gas-separation membranes (Scheme 1). General properties and gas permeability of their free-standing membranes were examined.

EXPERIMENTAL

Measurements

The molecular weight distributions of polymers were measured by gel permeation chromatography (GPC) in

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Scheme 1 Structures of monomers.

chloroform (at a 1.0 mL/min flow rate) at 40°C on a Shimadzu LC-10AD chromatograph equipped with four polystyrene gel (the copolymer of styrene and divinyl benzene) columns (Shodex K-805L \times 1 and K-804L \times 3) and a Shimadzu RID-6A refractive index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from chromatograms based on a polystyrene calibration. $^1\text{H-NMR}$ (500 MHz) and $^{13}\text{C-NMR}$ (125 MHz) spectra were recorded on Jeol LA-500 instrument in CDCl_3 at room temperature. Differential scanning calorimetry (DSC) was performed with Rigaku Thermo Plus DSC 8230L. The temperature range was -50 to $+250^\circ\text{C}$, and the heating and cooling rates were $5^\circ\text{C}/\text{min}$. During the measurement, the sample was purged by nitrogen gas. Glass transition temperature (T_g) was defined as the temperature of midpoint of the change in heat capacity on second heating scan. Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus at 25°C .

Materials

Phenyl vinyl ether (PhVE) was synthesized according to the literature.²⁸ Cyclohexyl vinyl ether

(CHVE) was supplied by Maruzen Petrochemical (Tokyo, Japan), and purified by silica gel column chromatography (eluent: hexane) before use. Benzyl vinyl ether (BzVE), cyclohexylmethyl vinyl ether (CHMVE), 2-adamantyl vinyl ether (AdVE), norbornyl vinyl ether (NRVE), 8-tricyclo[5.2.1.0]decyl vinyl ether (TCDVE), and 8-tricyclo[5.2.1.0]decylmethyl vinyl ether (TCDMVE) were supplied by Maruzen Petrochemical and distilled under reduced pressure over calcium hydride. Toluene (solvent for polymerization) was distilled twice over calcium hydride.

Polymerization

Polymerizations of vinyl ethers were carried out under a dry nitrogen atmosphere in a glass tube equipped with a three-way stopcock. The reaction was initiated by addition of a prechilled solution of BF_3OEt_2 (0.5 mL in toluene) to a monomer solution (4.5 mL in toluene). Polymerization was terminated by the addition of an excess amount of ammoniacal methanol (2.0 mL). The formed polymers were isolated by precipitation into a large amount of methanol, and its yields were determined by gravimetry.

Membrane preparation

Membranes by solution-casting (thickness ca. 100–200 μm) were prepared using polymer solution in toluene (concn 1.0–1.5 wt %) onto a Teflon plate. The plate was covered with a glass vessel to slow down solvent evaporation at 20°C (ca. 3–5 days). Membranes by hot-press (200–300 μm) were prepared by molding the powdered polymers with a hot-press apparatus (As One AH-2003) at 100 – 150°C . Before gas permeability measurement, the membranes were dried under vacuum (<0.05 mmHg) for 1 h.

TABLE I
Cationic Polymerization of Vinyl Ethers^a

Monomer	[M] ₀ , M	[BF ₃ OEt ₂] ₀ , mM	Polymer ^b		
			Yield, %	$M_n \times 10^{-3c}$	M_w/M_n^c
CHVE	1.5	5.0	66	47,800	5.08
NRVE	1.3	5.0	88	113,000	3.20
TCDVE	1.4	5.0	89	36,800	5.49
AdVE	1.2	5.0	78	132,000	2.46
BzVE	1.8	5.0	82	55,400	3.39
CHMVE	0.6	4.5	88	18,900	4.73
TCDMVE	0.3	5.0	97	38,800	3.39
PhVE	1.3	5.0	0		

^a In toluene at -78°C for 30 min.

^b Methanol-insoluble product.

^c Measured by GPC.

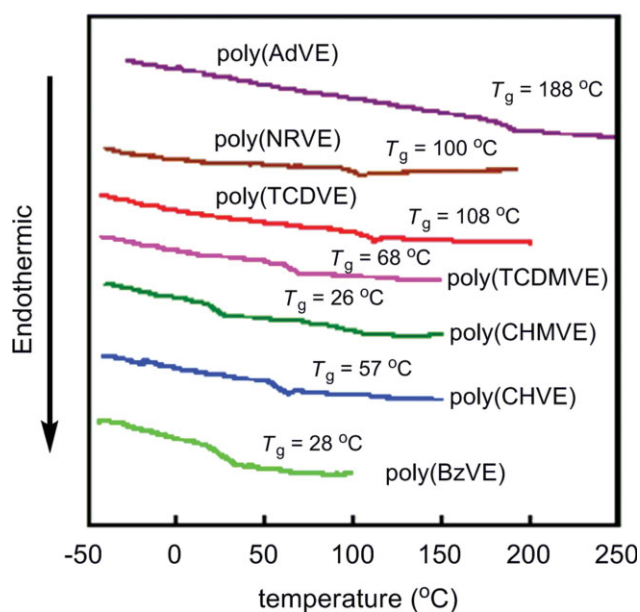


Figure 1 DSC thermograms of poly(vinyl ether)s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Density of polymer membrane

The densities of membranes were determined by hydrostatic weighing using a Mettler Toledo balance and a density determination kit. In this method, a liquid with known density (ρ_0) is needed, and the membrane density (ρ) is given by the following equation:

$$\rho = \rho_0 \times M_A / (M_A - M_L)$$

where M_A is membrane weight in air and M_L is membrane weight in the auxiliary liquid. Water was used as the auxiliary liquid.

RESULTS AND DISCUSSION

Polymerization

The polymerizations of vinyl ethers were carried out with BF_3OEt_2 in toluene at -78°C . The BF_3OEt_2 -initiating polymerization is known to produce poly(vi-

nyl ether)s with relatively high molecular weights. High molecular weight is essential for preparation of free-standing membrane, whereas it induces poor solubility of a polymer. To obtain the polymers with appropriate molecular weights, the initial monomer concentration was varied. The polymerization results are summarized in Table I. CHVE was polymerized in good yield to give a polymer with a relatively high molecular weight. The other vinyl ethers except phenyl vinyl ether (PhVE) were also polymerized in high yields to give corresponding poly(vinyl ether)s, whose molecular weights were relatively high (M_n : 18,900–132,000). The free-standing membranes of these seven kinds of poly(vinyl ether)s could be prepared by solution-casting. However, the polymerization of PhVE did not give a methanol-insoluble polymer. This is presumably due to the frequent occurrence of chain transfer reactions. It is reported that the polymerization of PhVE gave only very low-molecular weight polymers because PhVE easily induced the chain transfer reactions in the cationic polymerization.^{29,30}

Thermal properties of the polymers

Figure 1 shows DSC thermograms of poly(vinyl ether)s obtained in this study. None of all the polymers exhibited crystallization and melting of crystallites in this temperature range, and glass transitions were observed for all the polymers. Poly(vinyl ether)s with bulky cyclic substituents attached to the main chain via the ether oxygen exhibited relatively high T_g 's. For instance, the T_g 's of poly(AdVE), poly(NRVE), and poly(TCDVE) were 188, 100, and 108°C , respectively, whereas poly(CHVE) showed lower T_g of 57°C . On the other hand, the T_g 's of poly(vinyl ether)s having methylene spacer between the bulky cyclic substituents, and the ether oxygen were relatively low and in the range from 24 to 68°C .

Gas permeability of the polymer membranes

The free-standing membranes of poly(vinyl ether)s were prepared by casting toluene solution onto

TABLE II
Gas Permeability (P)^a and Selectivity of poly(vinyl ether) membranes

	$T_g, ^\circ\text{C}$	PO_2	PN_2	PCO_2	PO_2/PN_2	PCO_2/PN_2
Poly(CHVE)	57	3.69	0.99	13.6	3.73	13.7
Poly(NRVE)	100	3.55	0.96	25.0	3.70	26.0
Poly(TCDVE)	108	3.06	1.20	12.6	2.55	10.5
Poly(AdVE)	188	6.01	1.69	25.2	3.56	14.9
Poly(BzVE)	28	2.33	0.79	11.1	3.38	23.2
Poly(CHMVE)	26	1.55	0.46	5.89	3.34	12.7
Poly(TCDMVE)	68	0.81	0.13	2.85	6.23	21.9

^a In the units of $1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ (=1 barrer).

TABLE III
Gas Permeability Coefficients (P)^a, Permselectivity, and Density of Polymer Membranes

Preparation method	PO_2	PN_2	PCO_2	PO_2/PN_2	PCO_2/PN_2	Density (g/cm ³)
Poly(CHVE)						
Casting	3.69	0.99	13.6	3.73	13.7	1.027
Hot-press	0.99	0.16	3.47	6.19	21.7	1.040
Poly(NRVE)						
Casting	3.55	0.96	25.3	3.70	26.4	1.055
Hot-press	1.42	0.29	4.87	4.90	16.8	1.071
Poly(TCDVE)						
Casting	3.06	1.20	12.6	2.55	10.5	1.063
Hot-press	1.99	0.47	6.23	4.23	13.3	1.088

^a In the units of 1×10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹ (=1 barrer).

Teflon flat dish. The permeability of their membranes to oxygen, nitrogen, and carbon dioxide was examined at 25°C. Gas permeability coefficients and permselectivity of poly(vinyl ether)s in this study are summarized in Table II. The oxygen permeability coefficients (PO_2) of membranes of poly(CHVE), poly(NRVE), and poly(TCDVE) were 3.69, 3.55, and 3.06 barrers, respectively. These values are close to those of poly(tetrafluoroethylene) (PO_2 4.26 barrers) and poly(chloroprene) (PO_2 3.94 barrers),³¹ which are one of the gas-permeable glassy and rubbery polymers. Poly(AdVE) exhibited the highest oxygen permeability among poly(vinyl ether)s in this study, and its PO_2 value is 6.01 barrers and approximately twice as large as those of poly(CHVE), poly(NRVE), and poly(TCDVE). This may be mainly due to the shape of substituent. Compared with cyclohexyl, norbornyl, and tricyclodecyl groups, adamantyl group is a spherical substituent, and thus its steric repulsion seems to be effective in preventing polymer chain packing. On the other hand, poly(vinyl ether)s with methylene spacer between the bulky substituents and the ether oxygen showed lower oxygen permeability. The PO_2 values of poly(BzVE), poly(CHMVE), and poly(TCDMVE) were 2.33, 1.55, and 0.81 barrers, respectively. These findings suggest that steric repulsion of bulky substituents prevents polymer chains to pack together but methylene spacer weakens the effect of steric hindrance. The permeability to other gasses such as N₂ and CO₂ exhibited similar tendencies to the case of oxygen. The N₂ and CO₂ permeability coefficients (PN_2 and PCO_2) of poly(AdVE) were 1.69 and 25.2 barrers, respectively, which are the largest among those of these poly(vinyl ether)s. The oxygen/nitrogen and carbon dioxide/nitrogen separation factors (PO_2/PN_2 , PCO_2/PN_2) of all these polymers were in the range of 2.55–6.23 and 10.5–26.0, respectively. The membrane of poly(TCDMVE) showed the highest oxygen permselectivity and the lowest oxygen permeability among these poly(vinyl ether)s. This is

reasonable because a trade-off relationship and an upper boundary line are present.^{32,33} The carbon dioxide permselectivity of membrane of poly(NRVE) was relatively high, but it was much lower than that of poly(ethylene oxide), whose PCO_2/PN_2 value was around 50.²⁷ This is presumably due to the low polarity of poly(vinyl ether)s in this study compared with poly(ethylene oxide).

The membranes of poly(CHVE), poly(NRVE), and poly(TCDVE) could be prepared by the hot-press method. However, it was difficult to prepare the hot-press membrane of poly(2-AdVE), which exhibited the highest gas permeability, owing to its high glass transition temperature. The gas permeability of membranes prepared by the hot-press method was compared with that of membranes prepared by the solution-casting method (Table III). The PO_2 value of poly(CHVE) membrane by the solution-casting was 3.69 barrers, whereas that of membrane by the hot-press method was 0.99 barrers. Poly(NRVE) and poly(TCDVE) also showed the same tendency; i.e., gas permeability of membranes by the solution-casting was about three times as large as that of membranes by the hot-press method. Densities of membranes of poly(CHVE), poly(NRVE), and poly(TCDVE) by the solution-casting method were 1.027, 1.055, and 1.063, respectively. On the other hand, those by the hot-press method were 1.040, 1.071, and 1.088, respectively. These results indicate that preparation of membranes at higher temperatures than their glass transition temperatures induce the formation of dense structures of polymer membranes.

CONCLUSIONS

This article first revealed the gas permeation properties of membranes of poly(vinyl ether)s with various substituents. Poly(vinyl ether)s with bulky substituents attached to the main chain via the ether oxygen exhibited relatively high gas permeability. Poly(2-admanthyl vinyl ether), especially, showed high

gas permeability and its oxygen permeability coefficient was as large as 6.01 barrers. In contrast, poly(vinyl ether)s with methylene spacer between the bulky substituents and the ether oxygen showed relatively low gas permeability. Furthermore, it was found that gas permeability of poly(vinyl ether) membranes prepared by the solution-casting method was higher than that of poly(vinyl ether) membranes prepared by the hot-press method.

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