Thermal and gas permeation properties of copolymers derived from 3-methacryloxypropyltris(trimethylsiloxy)silane and adamantyl group-containing methacrylate derivatives

Shota Ando, Akihiro Yoshida, Masao Nakagawa, Kazukiyo Nagai
Department of Applied Chemistry, Meiji University, 1-1-1 Higashimita, Tama-Ku, Kawasaki 214-8571, Japan
Correspondence to: K. Nagai (E-mail: nagai@meiji.ac.jp or nagai@shikon.meiji.ac.jp)

ABSTRACT: Novel copolymer membranes derived from three types of adamantyl group-containing methacrylate derivatives and 3-methacryloxypropyltris(trimethylsiloxy)silane (SiMA) were synthesized via free radical polymerization. The thermal and permeation properties of these copolymer membranes were investigated. Copolymer membranes with less than 11.9 mol % adamantane content exhibited good membrane forming abilities that are suitable for permeation measurement. The decomposition temperature of all copolymers increased up to approximately 40–80°C with increasing adamantane content compared with poly(SiMA). Moreover, the glass transition temperature (T_g) of all copolymers increased up to approximately 46–60°C with increasing adamantane content compared with the theoretical value, which was estimated from Fox equation. 1-Adamantyl methacrylate copolymer had the highest fractional free volume among the three types of adamantly group-containing methacrylate derivatives. The gas permeability coefficient of this copolymer increased by 22–45% with increasing adamantane content compared with that of poly(SiMA). © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43129.

INTRODUCTION

Gas permeability of polymer materials is extensively investigated for its significance in various industrial and medical applications, such as fuel combustion systems.[1,2] nitrogen and oxygen generators,[3–5] hydrogen purification,[6,7] and degassing membranes for artificial gills.[8,9] High gas diffusivity and/or high gas solubility is an essential qualification to develop materials with high gas permeability. Poly(1-trimethylsilyl-1-propyne) has attracted considerable interest over the past decades despite its glassy nature, because it has the highest known permeability to gases among polymers.[10,11] This high permeability is attributed to high gas diffusivity, which is caused by having a trimethyl silyl group as bulky side chain. Numerous studies focus on polymer materials that possess pendant groups as side chains to improve gas permeability because the pendant groups be able to restrict mobility and molecular rotation of polymer main chain.[12–19]

Adamantane is a bulky diamond-like, cage-type structure that is composed of three fused cyclohexane rings arranged in a chair conformation, which results in a large structure (volume higher than 150 Å^3). This material is expected to possess high thermal stability, mechanical strength, low dielectric constant, and gas

permeation properties.[20–25] However, homopolymer permeability has not been reported because self-standing thin membranes of adamantane homopolymer are difficult to obtain given that adamantyl groups rigidize the polymer main chain. Permeation properties of adamantine that introduce other polymers, such as polyimide,[14,26–28] polyamide,[29] poly(vinyl ether),[30] cellulose,[31] and poly(sulfone),[32] are widely investigated.

In the current study, we focused on 3-methacryloxypropyltris (trimethylsiloxy)silane (SiMA), which is a silicon-containing polymer. This study aimed to improve membrane formation of adamantane-containing polymers and develop novel polymer materials with high thermal stability and high gas permeability. Poly(SiMA) shows good gas permeability based on its high free volume. Poly(SiMA) is also a rubbery polymer at room temperature because of its flexible structure.[33] Therefore, poly(SiMA) was used to improve gas permeability and support poor membrane formation of adamantane. Furthermore, adamantane and siloxane exhibited good compatibility, because introducing adamantane and siloxane with identical structures as substituents is expected to increase thermal resistance and decrease dielectric constant and photo transparency.[34–36] In our previous study, we synthesized a novel random copolymer, which comprised polyhedraloligomericilsesquioxane (POSS) with cage-type structure
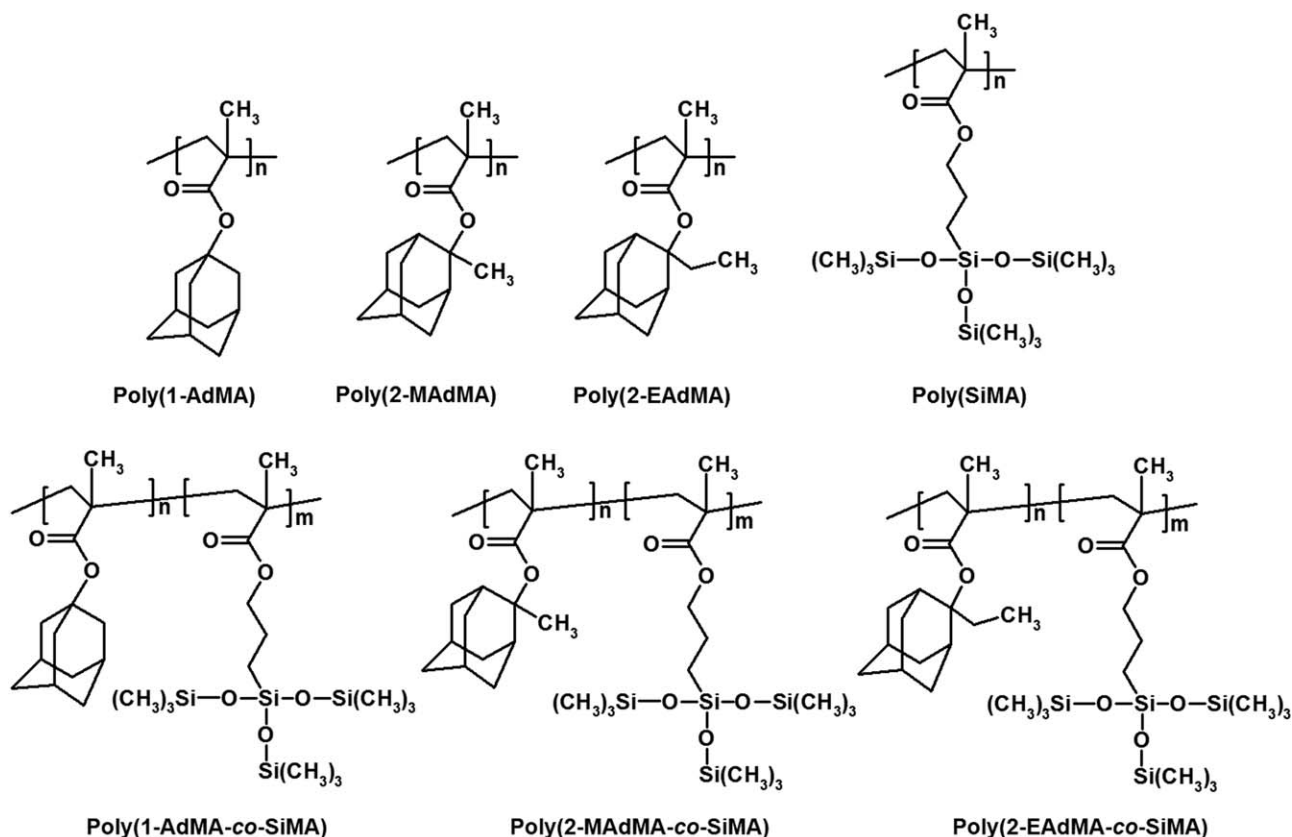
Figure 1. Chemical structures of poly(1-AdMA), poly(2-MAdMA), poly(2-EAdMA), poly(1-AdMA-co-SiMA), poly(2-MAdMA-co-SiMA), poly(2-EAdMA-co-SiMA), and poly(SiMA).

that is similar to that of adamantane and SiMA.[37] However, POSS structure is approximately 2.5 times larger than adamantane (structure diameter: POSS, 1.5 nm[38]; adamantane, 6.5–7.1 Å[39]). It is considered that the more bulky pendant group in the polymer, the membrane is the more hard and brittle because of restrict mobility of polymer chain. Thus, this POSS-containing copolymer possesses low membrane-formation capacity, and permeation measurement, which is necessary for achieving constant membrane strength, could not be performed. Therefore, we assumed that permeation properties can be measured using adamantane. Previous reports focused on the copolymerization of glassy and rubbery polymers. A glassy polymer generally shows gas permeability-related diffusivity[40,41] and has high membrane strength, such as tensile strength and dimensional stability.[42] By contrast, a rubbery polymer exhibits a gas permeability-related solubility[40,41] and has high membrane flexibility because of its primary structure, such as elasticity and stretch properties.[43] The improvements in its gas permeability and mechanical strength are expected because of the combination of each feature.[44–46] Novel copolymer membranes derived from the three types of adamantyl group-containing methacrylate derivatives and SiMA were synthesized via free radical polymerization and then characterized. The effects of adamantane content on the physical–thermal and gas permeation properties of the copolymer membranes were also investigated.

EXPERIMENTAL

Chemicals and Synthesis

The monomers used in this study were 1-adamantylmethacrylate (1-AdMA; Mitsubishi Gas Chemical, Tokyo, Japan), 2-methyl-2-adamantylmethacrylate (2-MAdMA; Mitsubishi Gas Chemical, Tokyo, Japan), 2-ethyl-2-adamantylmethacrylate (2-EAdMA; Mitsubishi Gas Chemical, Tokyo, Japan), and SiMA (Gelest, PA). 1-AdMA, 2-MAdMA, and SiMA, which are liquid at room temperature, were distilled in a vacuum condition. 2-EAdMA and α,α′-azobis(isobutyronitrile) (AIBN; Junsei Chemical, Tokyo, Japan), which are polymerization initiators, are solid at room temperature; these monomers were purified via recrystallization with methanol (Junsei Chemical, Tokyo, Japan). Polymerization was performed with AIBN. Toluene (Junsei Chemical, Tokyo, Japan) is a polymerization solvent that was distilled in a vacuum and dehydrated with well-dried molecular sieves before use. Poly(1-AdMA-co-SIMA), poly(2-MAdMA-co-SiMA), and poly(2-EAdMA-co-SiMA) were synthesized via free radical polymerization. 1-AdMA, 2-MAdMA, 2-EAdMA, and SiMA monomers with varied composition ratios (100:0 mol %, 75:25 mol %, 50:50 mol %, 25:75 mol %, 10:90 mol %, 5:95 mol %, 1:99 mol %, and 0:100 mol %) and AIBN were dissolved in toluene at 1.0 mol/L concentration and were added into tubes. The tubes were subjected to freeze–dry cycles to remove dissolved oxygen that inhibits free radical polymerization. Polymerization was performed at 80°C for 24 h. A solution-precipitation process with

Table I. Physical Properties of Each Polymer

Polymer	Adamantan monomer in feed (mol %)	Adamantan component in copolymer (mol %)	Adamantan component in copolymer (wt %)	Molecular weight (g/mol)			η (g/dL)	ρ (g/cm^3)
				$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n		
Poly(1-AdMA)	100	100	100	6.5	12.5	1.9	0.24	1.122 ± 0.001
	74.9	80.8	68.5	8.5	16.4	1.9	0.30	1.085 ± 0.001
	50.0	56.4	40.0	10.5	18.6	1.8	0.24	1.048 ± 0.001
	25.2	28.1	16.8	13.3	26.6	2.0	0.22	1.018 ± 0.001
Poly(1-AdMA-co-SiMA)	10.0	11.9	6.52	12.3	24.8	2.0	0.22	0.997 ± 0.001
	4.42	6.26	3.33	9.4	17.2	1.8	0.23	0.990 ± 0.001
	0.962	3.00	1.57	13.2	27.6	2.1	0.28	0.987 ± 0.001
Poly(2-MAdMA)	100	100	100	4.4	7.6	1.7	0.16	1.134 ± 0.001
	75.0	75.5	61.4	7.9	13.8	1.8	0.27	1.085 ± 0.001
	50.1	45.5	30.1	9.4	14.8	1.6	0.24	1.048 ± 0.001
	25.0	26.5	15.7	11.6	18.1	1.6	0.24	1.012 ± 0.001
Poly(2-MAdMA-co-SiMA)	9.98	11.7	6.40	12.4	23.5	1.9	0.29	0.991 ± 0.001
	5.00	5.76	3.08	12.8	27.5	2.1	0.27	0.987 ± 0.001
	1.02	1.10	0.57	16.5	31.5	1.9	0.21	0.983 ± 0.001
Poly(2-EAdMA)	100	100	100	1.1	2.5	2.2	0.08	1.129 ± 0.001
	75.0	51.7	35.6	2.6	4.4	1.7	0.27	1.049 ± 0.001
Poly(2-EAdMA-co-SiMA)	50.0	32.9	20.2	6.5	9.9	1.5	0.14	1.029 ± 0.001
	25.1	12.6	6.93	9.4	14.4	1.5	0.13	1.005 ± 0.001
	10.0	7.49	4.01	10.8	17.6	1.6	0.14	0.993 ± 0.001
	5.02	2.21	1.15	12.7	21.9	1.7	0.17	0.983 ± 0.001
	1.00	1.98	1.03	9.7	18.8	1.9	0.25	0.983 ± 0.001
Poly(SiMA)	0	0	0	21.0	32.0	1.5	0.58	0.982 ± 0.001

toluene and methanol was conducted for purification. The proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy of this dried polymer was measured, and the aforementioned steps were continued until impurities, such as monomers, catalysts, and solvents, were removed completely.

Membranes Preparation
Poly(1-AdMA-co-SIMA), poly(2-MAdMA-co-SiMA), and poly (2-EAdMA-co-SiMA) membranes were prepared through casting 5 wt % toluene solution of each polymer onto a Teflon Petri dish for 72 h under atmospheric pressure at room temperature. The solvent was evaporated for 48 h. ^{1}H-NMR analyses confirmed the removal of the residual solvent. The membrane thickness used varied between 200 and 240 nm.

Structural Analysis and Characterization. Characterization data were determined in the membrane state in at least three samples to confirm the reproducibility of the experimental results. ^{1}H-NMR and ^{13}C-NMR were performed on a JNM-ECA500 (JEOL, Tokyo, Japan). NMR was measured from 0.1 wt % (^{1}H–) and 0.5 wt % (^{13}C–) of chloroform-d (CDCl$_3$-d, ISO-TEC) at 30 ± 1°C. The copolymerization ratio of the copolymer was estimated from the integration on the strength ratio in the NMR spectra.

Fourier transform infrared spectrometry (FT-IR; FT/IR-4100 JASCO, Tokyo, Japan) was employed using the KBr method. The measurement conditions were as follows: resolution of 2 cm^{-1} and multiplication number of 32 at 23 ± 1°C.

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution ratio (M_w/M_n) of the polymers were determined using gel permeation chromatography (HLC-8220; Tosoh, Tokyo, Japan) with TSK-gel columns (Super AWM-H) and a detector (RI-8220). Calibration was performed under polystyrene standards at 40°C in tetrahydrofuran (Junsei Chemical, Tokyo, Japan) at a 0.300 mL/min flow rate.

The inherent viscosity (η_{inh}) of the polymers was measured with a Canon Fensuke viscometer (Yoshida Seisakusho, Tokyo, Japan). Viscosity was determined using a 0.5 g/dL toluene solution at 30°C.

Membrane density (ρ) was measured using a flotation method at 23 ± 1°C using calcium nitrate tetrahydrate (Junsei Chemical, Tokyo, Japan) or dilute methanol (Junsei Chemical, Tokyo, Japan).
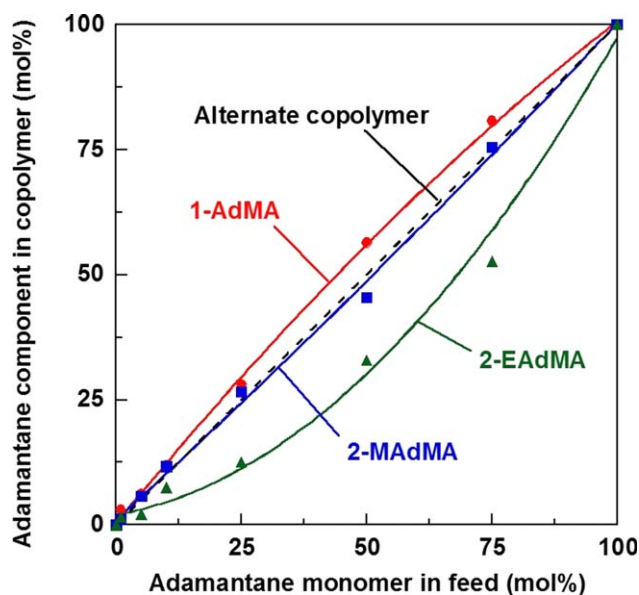
Figure 2. Copolymer composition curve of each copolymer based on the Fineman–Ross method. Dotted line represents the theoretical alternate copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Wide-angle X-ray diffraction (WAXD) measurement was performed on a Rint 1200 X-ray diffractometer (Rigaku, Tokyo, Japan) at scanning speed of 2°/min using a Cu-Kα radiation source at 40 kV and 20 mA at a dispersion angle range of 3–30°. The wavelength and mesurement temperature were 1.54 Å and 23 ± 1°C, respectively. The d-spacing, which presented the mean distance between polymer chains, was calculated from Bragg's conditions.[47]
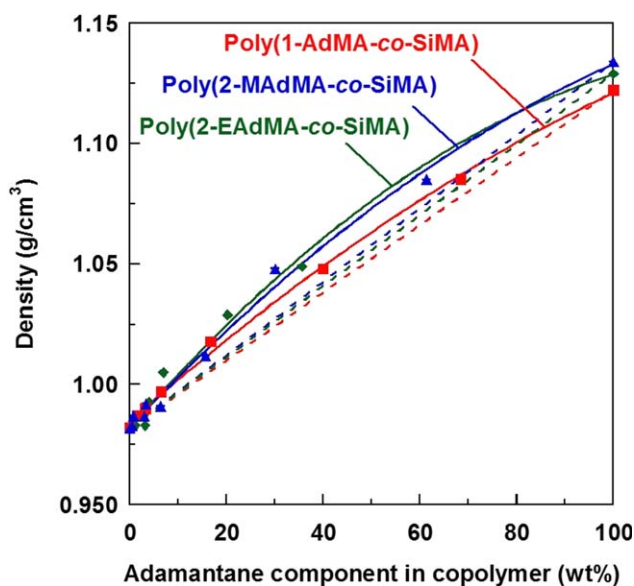
Figure 3. Membrane density of each polymer membrane as a function of adamantane content. Dotted line represents the theoretical density calculated by Eq. (5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
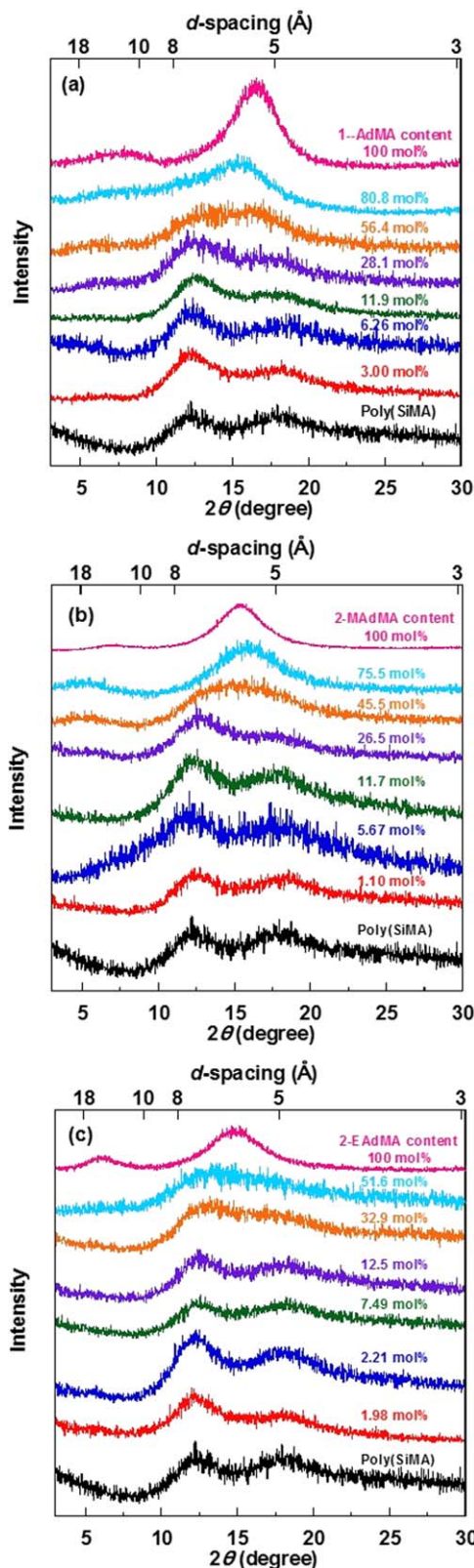
Figure 4. WAXD patterns of (a) poly(1-AdMA-co-SiMA), (b) poly(2-MAdMA-co-SiMA), and (c) poly(2-EAdMA-co-SiMA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Thermal Properties of Each Polymer

Polymers	Adamantane component in copolymer (mol %)	T5 (°C)	T10 (°C)	Td (°C) 1st (adamantane unit)	Td (°C) 2nd (main chain)	Tg (°C)	ΔCp [J/(g·°C)]
Poly(1-AdMA)	100	314 ± 2	325 ± 1	-	400 ± 1	N/A	N/A
	80.8	298 ± 5	315 ± 3	-	356 ± 2	139 ± 1	0.223 ± 0.049
	56.4	298 ± 2	312 ± 6	-	352 ± 2	101 ± 3	0.060 ± 0.022
Poly(1-AdMA-co-SiMA)	28.1	287 ± 1	301 ± 2	-	350 ± 3	51.9 ± 4.3	0.303 ± 0.140
	11.9	281 ± 3	295 ± 3	-	344 ± 5	8.5 ± 0.6	0.457 ± 0.056
	6.26	290 ± 4	302 ± 6	-	345 ± 4	4.2 ± 0.4	0.472 ± 0.034
	3.00	290 ± 6	306 ± 9	-	348 ± 5	−3.6 ± 1.3	0.220 ± 0.028
Poly(2-MAdMA)	100	232 ± 2	240 ± 1	250 ± 4	435 ± 1	141 ± 2	0.101 ± 0.011
	75.5	240 ± 3	242 ± 4	247 ± 5	397 ± 2	94.3 ± 3.1	0.306 ± 0.009
	45.5	247 ± 6	254 ± 5	257 ± 3	383 ± 1	78.2 ± 0.1	0.615 ± 0.064
Poly(2-MAdMA-co-SiMA)	26.5	268 ± 3	285 ± 2	273 ± 6	376 ± 1	36.8 ± 0.9	0.090 ± 0.008
	11.7	265 ± 4	286 ± 5	267 ± 5	359 ± 1	15.9 ± 0.7	0.077 ± 0.003
	5.76	275 ± 3	299 ± 4	-	352 ± 1	4.8 ± 0.5	0.089 ± 0.002
	1.10	263 ± 5	281 ± 6	-	340 ± 2	−5.0 ± 0.7	0.100 ± 0.009
Poly(2-EAdMA)	100	220 ± 2	222 ± 2	226 ± 1	442 ± 3	134 ± 2	0.066 ± 0.004
	51.7	235 ± 3	240 ± 1	242 ± 2	389 ± 6	75.7 ± 0.8	0.414 ± 0.036
Poly(2-EAdMA-co-SiMA)	32.9	240 ± 3	248 ± 2	246 ± 4	382 ± 4	59.6 ± 0.1	0.222 ± 0.039
	12.6	253 ± 4	290 ± 2	251 ± 5	374 ± 4	26.4 ± 1.4	0.161 ± 0.046
	7.49	289 ± 3	319 ± 3	261 ± 2	365 ± 2	6.2 ± 0.2	0.098 ± 0.006
	2.21	293 ± 4	311 ± 5	-	355 ± 2	−3.0 ± 0.3	0.070 ± 0.025
	1.98	283 ± 6	298 ± 6	-	347 ± 3	−3.2 ± 1.1	0.097 ± 0.007
Poly(SiMA)	0	281 ± 7	297 ± 3	-	320 ± 2	−6.3 ± 1.3	0.103 ± 0.088

Thermogravimetric analysis (TGA) of the membranes was performed using a Pyris 1 TGA Thermo Gravimetric Analyzer (PerkinElmer, Shelton). Approximately 1.0 mg of the polymer sample was heated from 50 to 900°C in a platinum pan at a 10°C/min heating rate under a nitrogen atmosphere at a 60 mL/min flow rate. T_5 and T_{10} were the degradation temperatures of 5 and 10 wt % weight decrease, respectively.

Glass transition temperature (T_g) was measured using a Diamond DSC (PerkinElmer, Shelton). Differential scanning calorimeter (DSC) measurements were performed up to 200°C where no pyrolysis occurred. Heat scan was performed between −100 and 200°C at a 20°C/min heating rate under a nitrogen atmosphere. A natural cooling condition was adopted. The T_g value, which was measured over the second scan, was determined as the middle point of the endothermic transition.

Gas Permeation Properties. The gas permeability coefficients (P) of pure gases, such as H_2, O_2, N_2, CO_2, and CH_4, in polymer membranes were determined at 35 ± 1°C by the constant-volume/variable-pressure method in accordance with literature.[48,49] The purities of the gases in this research are as follows: H_2, 99.99%; O_2, 99.5%; N_2, 99.99%; CO_2, 99.9%; and CH_4, 99.999%. The feed pressure was between 75 and 77 cmHg, and the permeate side was maintained in a vacuum. All permeation

data were determined for at least three samples to ensure the reproducibility of the experimental results. P was calculated from following equation:

$$P = \frac{dp}{dt} \frac{273\,V}{760\,(273+T)} \frac{1}{A} \frac{1}{p_1} l \tag{1}$$

The apparent gas diffusion coefficient (D) was determined based on membrane thickness (l) and time-lag (θ), i.e., the period within which the steady state was reached:

$$D = \frac{l^2}{6\theta} \tag{2}$$

According to the solution-diffusion mechanism, the apparent gas solubility coefficient (S) can be evaluated as follows:

$$S = \frac{P}{D} \tag{3}$$

The ideal gas permeability selectivity (α) of Gas A over Gas B was expressed as the ratio of the permeability coefficient of Gas A to that of Gas B.

$$\frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \tag{4}$$

where D_A/D_B is the gas diffusivity selectivity (the ratio of the gas diffusion coefficients of Gases A and B), and S_A/S_B is the
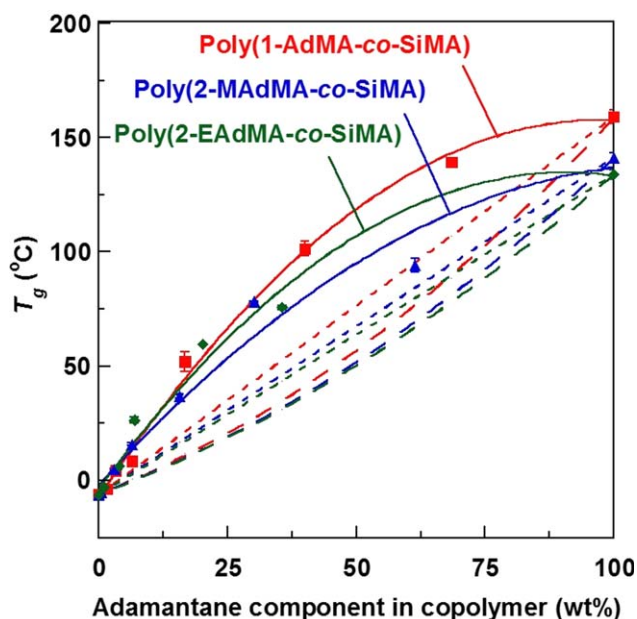
Figure 5. Glass transition temperatures (T_g) of each polymer membrane as a function of adamantane content. Dotted line and dashed line presents the theoretical T_g of simple mixing rule and fox equation calculated by Eqs. (6) and (7). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gas solubility selectivity (the ratio of the gas solubility coefficients of Gases A and B).

RESULTS AND DISCUSSION

Structural Analysis. ^{1}H-NMR, ^{13}C-NMR, and FT-IR analyses confirmed the chemical structures of poly(1-AdMA-*co*-SIMA), poly(2-MAdMA-*co*-SiMA), and poly(2-EAdMA-*co*-SiMA) (Figure 1).

Table I provide the polymer properties including the adamantane content in each copolymer that was caluculated from NMR integration ratio, molecular weight, and viscosity. The molecular weight of all synthesized polymers was more than 10,000 g/mol.

The copolymerization composition curves of poly(1-AdMA-*co*-SIMA), poly(2-MAdMA-*co*-SiMA), and poly(2-EAdMA-*co*-SiMA) are shown in Figure 2. According to the Fineman–Ross plot,[50] the reactant ratios of poly(1-AdMA-*co*-SIMA) were $r_1 = 0.688$ for poly(1-AdMA), $r_2 = 1.21$ for poly(SiMA), and $r_1 \times r_2 = 0.829$ for poly(1-AdMA-*co*-SIMA). Given that $r_1 < 1$ and $r_2 > 1$, we considered that 1-AdMA and SiMA monomers reacted in block by 1-AdMA. The reactant ratios of poly(2-MAdMA-*co*-SiMA) were $r_1 = 1.07$ for poly(2-MAdMA), $r_2 = 1.05$ for poly(SiMA), and $r_1 \times r_2 = 1.13$ for poly(2-MAdMA-*co*-SiMA). As r_1 and r_2 were nearly 1, we considered that 2-MAdMA and SiMA monomers reacted randomly. The reactant ratios of poly(2-EAdMA-*co*-SiMA) were $r_1 = 2.73$ for poly(2-EAdMA), $r_2 = 0.485$ for poly(SiMA), and $r_1 \times r_2 = 1.33$ for poly(2-EAdMA-*co*-SiMA). As $r_1 > 1$ and $r_2 < 1$, we considered that 2-EAdMA and SiMA monomers reacted in block by SiMA. These results indicate that 1-AdMA, 2-MAdMA, and 2-EAdMA have varied responses to SiMA.

Membranes Characterization

Table I summarize the membrane density. The membrane densities of poly(1-AdMA), poly(2-MAdMA), poly(2-EAdMA), and poly(SiMA) were 1.122 ± 0.001, 1.134 ± 0.001, 1.129 ± 0.001, and 0.982 ± 0.001 g/cm^3, respectively. The membrane density increased with increasing adamantane content. Simple mixing blends and copolymers estimate the density as follows[51]:

$$\rho = w_1 \rho_1 + w_2 \rho_2 \tag{5}$$

where ρ_1 and ρ_2 are the membrane densities (g/cm^3) of components 1 and 2 in the copolymer, respectively. w_1 and w_2 are the weight fraction ratios of components 1 and 2 in the copolymer, respectively. Figure 3 shows the experimental and estimated membrane densities of each copolymer as a function of adamantane content. When the density follows eq. (5), this parameter increases with increased adamantane content. The experimental values were higher than the estimated values in all copolymers.

Figure 4 presents WAXD patterns of poly(1-AdMA-*co*-SIMA), poly(2-MAdMA-*co*-SiMA), and poly(2-EAdMA-*co*-SiMA). A broad halo was observed in all copolymer membranes, which indicates the formation of an amorphous structure. Each adamantane homopolymer was observed at angles $2\theta = 14.5$–$16.4°$ (*d*-spacing = 5.4–6.1 Å) in a previous study.[52] Conversely, two broad peaks were observed at $2\theta = 12°$ (*d*-spacing = 7.4 Å) and $2\theta = 17.4°$ (*d*-spacing = 5.1 Å) in poly(SiMA). These two broad halos indicate the distance between polymer segments in a small angle, whereas that in the large angle was attributed to the intermolecular distance between long side chains.[37] Interestingly, all of the copolymers with 50 mol % adamantane showed an extended broad halo at $2\theta = 10$–$20°$, and this halo perfectly separated the two peaks at 10 mol % adamantane in common with poly(SiMA). Therefore, all of the copolymers with 10–50 mol % adamantine have *d*-spacing of adamantane polymer and poly(SiMA).

Thermal Property

The TGA results of each copolymer are shown in Table II. Poly(SiMA) exhibited one step of decomposition, whereas all adamantane polymers showed two steps of decomposition. The first decomposition of adamantine polymers corresponded to the adamantane unit decomposition, and the second decomposition was the main chain decomposition.[52] For poly(1-AdMA-*co*-SiMA), the decomposition temperature (T_d) of the copolymers was increased by approximately 20–40°C with increasing adamantane content compared with poly(SiMA). Poly(2-MAdMA-*co*-SiMA) exhibited a two-step decomposition within 100–11.7 mol % range. The first step T_d was increased up to approximately 20°C with increasing SiMA content, and the second step T_d was increased up to approximately 80°C with increasing adamantane content compared with that of poly(SiMA). Poly(2-EAdMA-*co*-SiMA) showed two-step decomposition at 100–7.49 mol % range, where the first step T_d was increased up to approximately 35°C with increasing SiMA content, and the second step T_d was increased up to approximately

Table III. Gas Permeability, Diffusivity, and Solubility Coefficient of Each Polymer Membrane

Polymer	H2	O2	N2	CO2	CH4
Gas permeability coefficient ($\times10^{-10}$ [cm^3(STP)cm/(cm^2 s cmHg)])					
Poly(1-AdMA-co-SiMA) (11.9:88.1 mol %)	495±6	259±3	101±1	1190±1	293±1
Poly(1-AdMA-co-SiMA) (3.00:97.0mol %)	400±4	225±1	88.2±0.7	989±4	254±1
Poly(2-MAdMA-co-SiMA) (11.7:88.3 mol %)	385±5	216±1	84.8±0.4	962±2	248±3
Poly(2-MAdMA-co-SiMA) (5.76:94.24 mol %)	334±3	186±1	72.6±0.2	810±1	207±1
Poly(2-EAdMA-co-SiMA) (7.49:92.51mol %)	372±6	204±1	77.8±0.3	898±1	227±2
Poly(2-EAdMA-co-SiMA) (2.21:97.79mol %)	352±4	186±8	66.0±0.2	741±5	187±1
Poly(SiMA)	342±6	207±4	84.5±0.6	932±1	240±1
Gas diffusion coefficient ($\times10^{-6}$ (cm^2/s))					
Poly(1-AdMA-co-SiMA) (11.9:88.1 mol %)	–	13.8±0.1	9.44±0.55	7.18±0.07	6.37±0.07
Poly(1-AdMA-co-SiMA) (3.00:97.0mol %)	–	6.05±0.07	4.05±0.11	3.72±0.05	3.18±0.03
Poly(2-MAdMA-co-SiMA) (11.7:88.3 mol %)	–	7.79±0.15	4.82±0.17	4.33±0.04	3.90±0.06
Poly(2-MAdMA-co-SiMA) (5.76:94.24 mol %)	–	5.49±0.05	3.28±0.18	2.78±0.04	2.56±0.07
Poly(2-EAdMA-co-SiMA) (7.49:92.51mol %)	–	8.54±0.3	5.08±0.46	4.00±0.06	3.33±0.25
Poly(2-EAdMA-co-SiMA) (2.21:97.79mol %)	–	7.03±0.42	3.71±0.08	2.97±0.06	2.96±0.08
Poly(SiMA)	–	6.90±0.34	4.20±0.09	3.90±0.04	2.40±0.04
Gas solubility coefficient [$\times10^{-4}$ (cm^3(STP)/(cm^3 cmHg)])					
Poly(1-AdMA-co-SiMA) (11.9:88.1 mol %)	–	18.8±0.2	10.8±0.7	166±2	46.1±0.6
Poly(1-AdMA-co-SiMA) (3.00:97.0mol %)	–	37.1±0.6	21.8±0.7	266±3	80.1±1.0
Poly(2-MAdMA-co-SiMA) (11.7:88.3 mol %)	–	27.7±0.1	17.6±0.1	222±2	63.6±1.6
Poly(2-MAdMA-co-SiMA) (5.76:94.24 mol %)	–	33.9±0.1	22.2±0.6	292±4	80.9±2.3
Poly(2-EAdMA-co-SiMA) (7.49:92.51mol %)	–	23.9±0.1	15.4±0.1	225±3	68.7±0.6
Poly(2-EAdMA-co-SiMA) (2.21:97.79mol %)	–	26.5±0.1	17.8±0.4	249±7	63.1±1.9
Poly(SiMA)	–	30.0±1.6	20.1±0.4	239±3	72.2±1.2

Table IV. Ideal Gas Permeability Selectivity of Each Polymer Membrane

Polymer	CO2/CH4	CO2/N2	H2/CO2	O2/N2	H2/N2	N2/CH4
Poly(1-AdMA-co-SiMA) (11.9:88.1 mol %)	4.07 ± 0.02	11.8 ± 0.1	0.42 ± 0.03	2.56 ± 0.04	4.89 ± 0.10	0.34 ± 0.03
Poly(1-AdMA-co-SiMA) (3.00:97.0mol %)	3.89 ± 0.02	11.2 ± 0.1	0.40 ± 0.03	2.55 ± 0.03	4.54 ± 0.08	0.35 ± 0.03
Poly(2-MAdMA-co-SiMA) (11.7:88.3 mol %)	3.88 ± 0.05	11.3 ± 0.1	0.40 ± 0.04	2.54 ± 0.03	4.54 ± 0.08	0.34 ± 0.04
Poly(2-MAdMA-co-SiMA) (5.76:94.24 mol %)	3.91 ± 0.01	11.2 ± 0.1	0.41 ± 0.02	2.57 ± 0.02	4.60 ± 0.05	0.35 ± 0.01
Poly(2-EAdMA-co-SiMA) (7.49:92.51mol %)	3.95 ± 0.04	11.5 ± 0.1	0.41 ± 0.04	2.62 ± 0.03	4.79 ± 0.10	0.34 ± 0.03
Poly(2-EAdMA-co-SiMA) (2.21:97.79mol %)	3.97 ± 0.05	11.2 ± 0.1	0.48 ± 0.04	2.81 ± 0.13	5.33 ± 0.07	0.35 ± 0.03
Poly(SiMA)	3.89 ± 0.02	11.0 ± 0.1	0.37 ± 0.05	2.45 ± 0.06	4.05 ± 0.10	0.35 ± 0.03

70°C with increasing adamantane content compared with that of poly(SiMA).

T_g measurement by DSC of each copolymer was observed in a single value, which indicates the synthesis of random copolymers. An increase in T_g was observed with increasing adamantane content. Thus, the adamantane content can restrict the mobility of flexible SiMA structures. T_g of polymer can be estimated from two predictive equations, namely, the simple mixing rule of mixtures in eq. (6) and the Fox equation in eq. (7).[51,53]

$$T_g = w_1 T_{g1} + w_2 T_{g2} \qquad (6)$$

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (7)$$

where T_{g1} and T_{g2} are the T_g of components 1 and 2, respectively. w_1 and w_2 are the weight fraction ratios of components 1 and 2 in the copolymer, respectively. The Fox relation is considered an ideal volume additivity equation for the T_g of compatible copolymers or polymer blends. Figure 5 indicates that the T_g of each copolymer followed the predictions of simple mixing and Fox. DSC results of each copolymer are shown in Table II. Interestingly, all of the copolymers exhibited completely different results, that is, the measured T_g was higher than the each estimated value. In the poly(1-AdMA-co-SiMA), T_g of the copolymers was increased up to approximately 60°C with increasing adamantane content compared with Fox estimated value and was increased up to approximately 42°C with increasing adamantane content compared with the simple mixing estimated value. Similarly, in the poly(2-MAdMA-co-SiMA) and poly(2-EAdMA-co-SiMA), the T_g of the copolymers was increased up to approximately 52°C, up to approximately 46°C with increasing adamantane content compared with the Fox-estimated value, and up to approximately 40°C and 38°C with increasing adamantane content compared with the simple mixing estimated value. The TGA and DSC results showed that the thermal stability of each copolymer was drastically increased by the introduction of adamantane structure. The bulky adamantane structure and pendant side chain of SiMA were suggested to be synergistically restricted by molecular rotation and molecular mobility of main polymer chain. In addition, each copolymer was assumed to consist of randomly conformed variously sized block rather than simple block or random copolymer (as estimated by Fineman–Ross method) because T_g does not fit theoretical values of simple mixing and Fox equation.

Gas Permeation Property

Tables III and IV summarize the gas permeation properties of membranes that have adequate membrane strength at 35°C: poly(SiMA) and poly(1-AdMA-co-SiMA) (11.9:88.1 mol %; 3.00:97.0 mol %), poly(2-MAdMA-co-SiMA) (11.7:88.3 mol %; 5.79:94.21 mol %), and poly(2-EAdMA-co-SiMA) (7.49:92.51 mol %, 2.21:97.79 mol %).

The P of each copolymer is presented in Figure 6 as a function of adamantane content. In the poly(1-AdAMA-co-SiMA), the P of the copolymer increased with increasing adamantane content. The rates of increase are as follows: 45% (H_2), 25% (O_2), 20% (N_2), 28% (CO_2), and 22% (CH_4). By contrast, the P of poly(2-MAdMA-co-SiMA) and poly(2-EAdMA-co-SiMA) increased after a decline in the increment of adamantane content. However, major change was not observed in poly(SiMA) compared with poly(1-AdAMA-co-SiMA).

Figure 7 presents the D of each copolymer as a function of gas critical volume: 65.0 cm³/mol (H_2), 73.4 cm³/mol (O_2), 90.1 cm³/mol (N_2), 94.1 cm³/mol (CO_2), and 98.6 cm³/mol (CH_4).[54] Figure 8 shows the S of each copolymer as a function of gas critical temperatures: 304 K (CO_2), 191 K (CH_4), 155 K (O_2), 126 K (N_2), and 33.3 K (H_2).[54] Polymer membranes generally showed a relationship between D and gas critical volume S and gas critical temperature. Similarly, all of the copolymers in this study were interrelated. The D and S values of the poly (1-AdMA-co-SiMA) (3.00:97.0 mol %) were nearly similar to those of poly(SiMA). In the poly(1-AdMA-co-SiMA) (11.9:88.1 mol %), D increased by 1.8–2.8 times and S decreased by 0.5–0.7 times compared with poly(SIMA). By contrast, the D and S of poly(2-MAdMA-co-SiMA) and poly(2-EAdMA-co-SiMA) showed no considerable change with increasing adamantane content compared with poly(1-AdMA-co-SiMA) (11.9:88.1 mol %). These results indicate that the increase in P contributed to
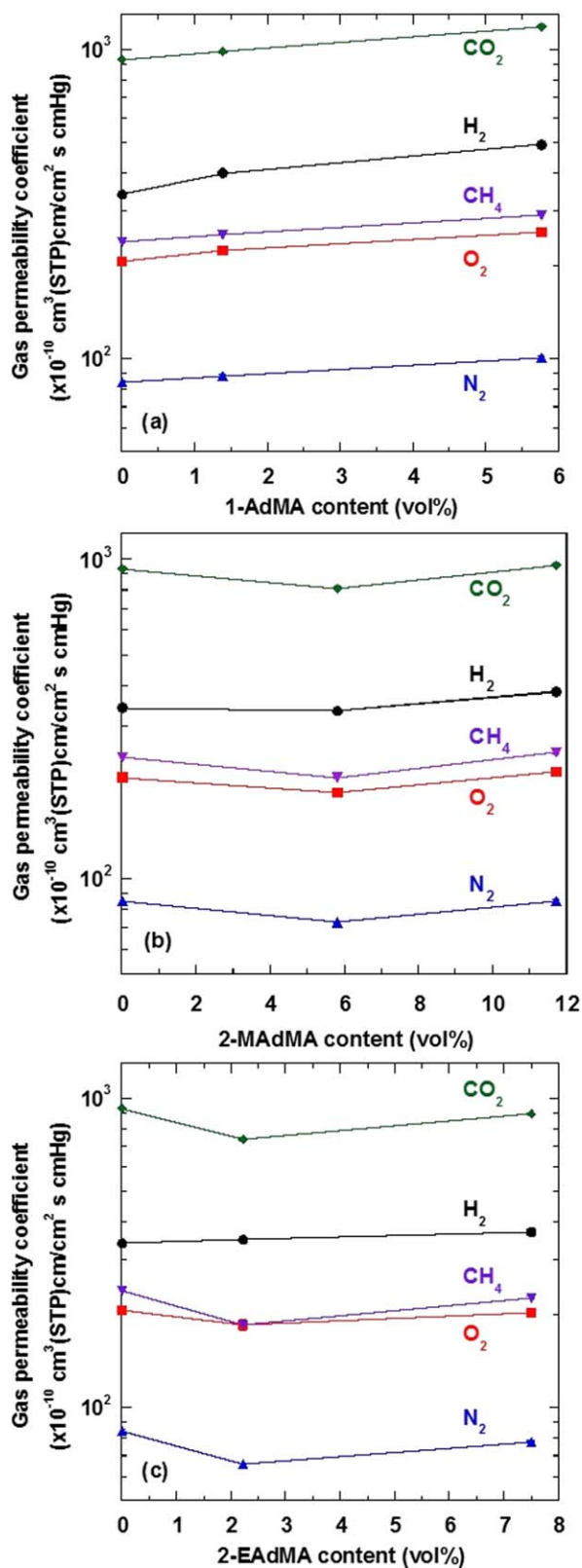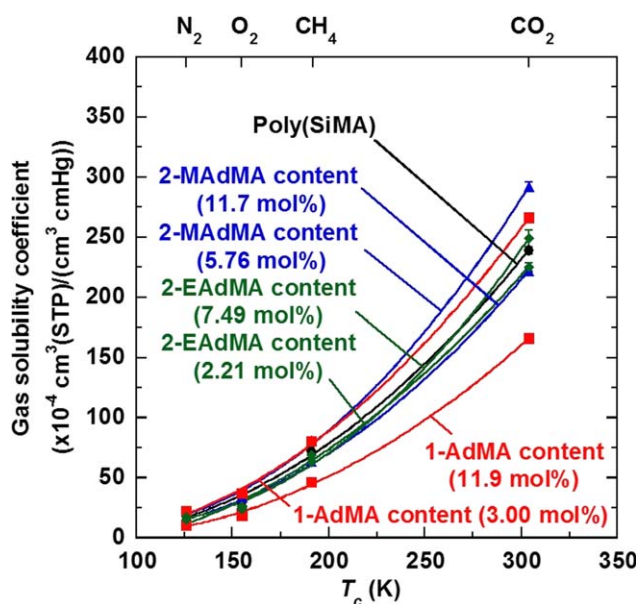
Figure 6. Gas permeability coefficients of (a) poly(1-AdMA-*co*-SiMA), (b) poly(2-MAdMA-*co*-SiMA), and (c) poly(2-EAdMA-*co*-SiMA). Gases: hydrogen (•), oxygen (■), nitrogen (▲), carbon dioxide (◆), and methane (▼). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
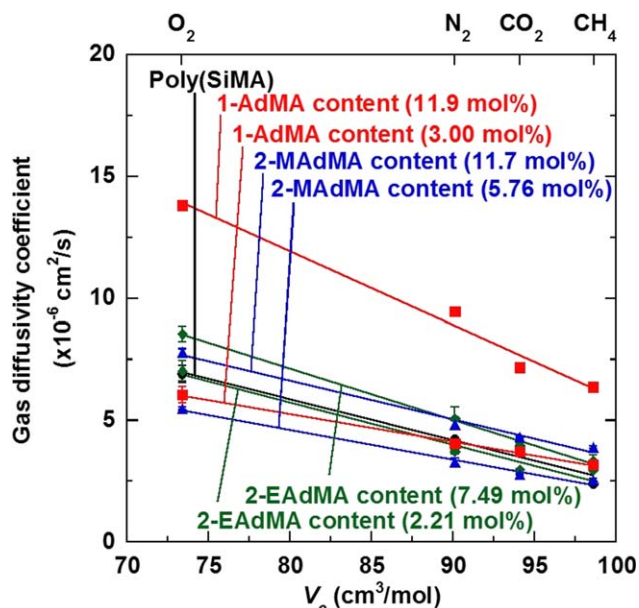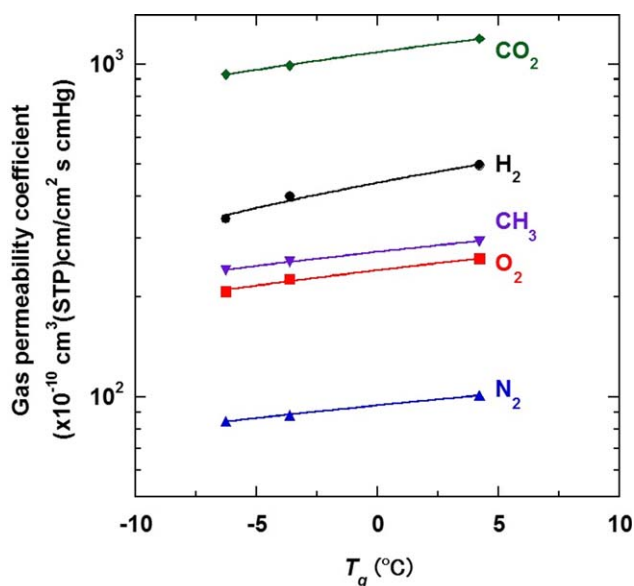

Figure 7. Gas diffusivity coefficient of each polymer membrane as a function of critical volume of each gas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

an increase in D, regardless of the small adamantane content (11.7 mol %) in 1-AdMA copolymer that has the highest fractional free volume (FFV) [FFV: poly(1-AdMA) (0.151), poly(2-MAdMA) (0.129), and poly(2-EAdMA) (0.125)[52]].

Figure 9 presents the P of poly(1-AdAMA-*co*-SiMA) as a function of T_g. The results showed a linear relationship between P and T_g of poly(1-AdAMA-*co*-SiMA). Therefore, we estimated the theoretical P and α of high-adamantane-containing poly

Figure 8. Solubility coefficient of each polymer membrane as a function of critical temperature of each gas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Gas permeability coefficient of poly(1-AdMA-*co*-SiMA) as a function of glass transition temperature (T_g). Gases: hydrogen (•), oxygen (■), nitrogen (▲), carbon dioxide (◆), and methane (▼). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

(1-AdAMA-*co*-SiMA), whose gas permeability was not measured because of membrane brittleness. We also discussed the beneficial copolymer derived from adamantane and SiMA. Table V summarizes the theoretical P and α of poly(1-AdMA-*co*-SiMA) (80.8:19.2 mol %). P in all gases of high-adamantane-containing copolymer was drastically higher than that of poly(SiMA) (H_2: 4.9 times, O_2: 3.3 times, N_2: 2.9 times, CO_2: 3.7 times, CH_4: 3.1 times). Moreover, α (except for N_2/CH_4) of high-adamantane-containing copolymer was higher than that of poly(SiMA) (CO_2/CH_4: 1.2 times, CO_2/N_2: 1.3 times, H_2/CO_2: 1.3 times, O_2/N_2: 1.1 times, H_2/N_2: 1.7 times, N_2/CH_4:
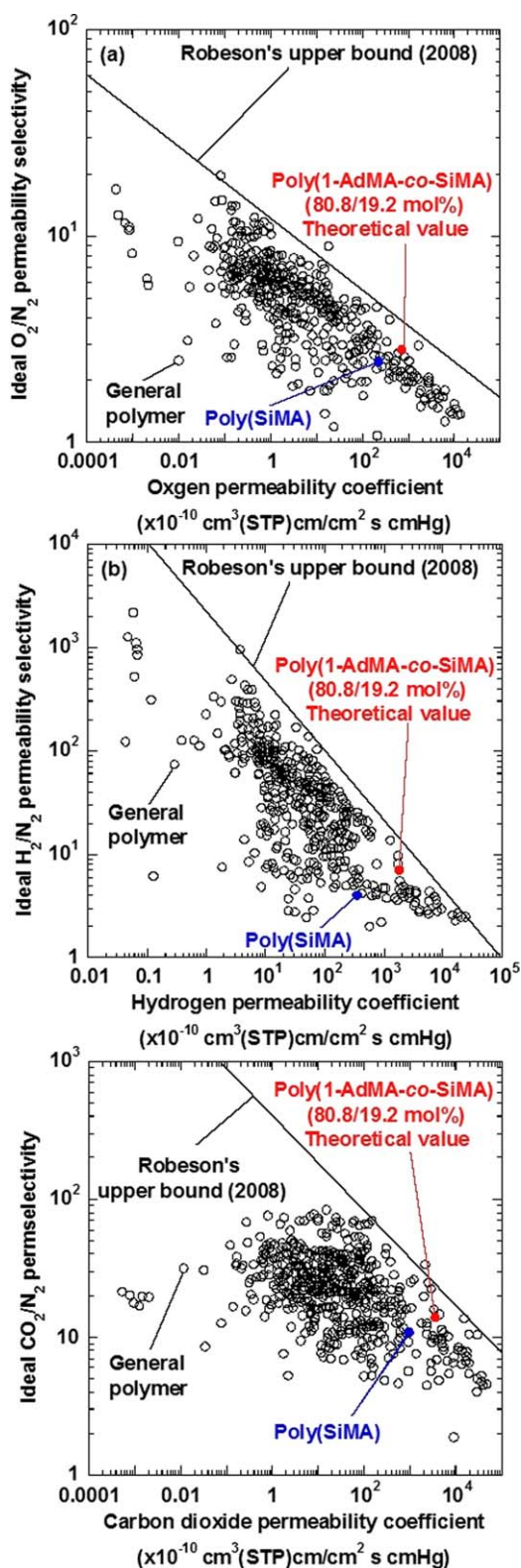
0.9 times). Figure 10 shows the O_2/N_2, H_2/N_2, and CO_2/N_2 separation performance at 35°C with other general polymers for comparison with the empirical upper bound that was cited in literature.[55] The gas separation performance of poly(1-AdMA-*co*-SiMA) (80.8:19.2 mol %) was located near the upper bound compared with that of poly(SiMA).

CONCLUSIONS

Novel copolymer membranes derived from the three types of adamantyl group-containing methacrylate derivatives and SiMA were synthesized via free radical polymerization and then characterized. The effect of adamantane content on the thermal and gas permeation properties of the copolymer membranes was investigated. Each copolymer membrane with less than 11.9 mol % adamantane exhibited good membrane-forming abilities, thereby enabling permeation measurement. Thermal property analysis showed that the T_d of all of the copolymers increased up to approximately 40–80°C with increasing adamantane content compared with the T_d of poly(SiMA). T_g values of all copolymers increased up to approximately 46–60°C with increasing adamantane content compared with the theoretical value, which was obtained using Fox equation. Gas permeation measurements showed that the P of 1-AdMA copolymer, which had the highest FFV among the three types of adamantyl group-containing methacrylate derivatives, increased by 22–45% with increasing adamantane content compared with the P of poly(SiMA). An increase in P contributed to an increase in D; therefore, 1-AdMA, which showed high FFV and T_g, had increased excess free volume and restricted polymer main chain mobility. A linear relationship was also observed between P and T_g of poly(1-AdMA-*co*-SiMA); thus, we estimated the theoretical P and α of high-adamantane-containing poly(1-AdAMA-*co*-SiMA). This material showed excellent performance for O_2/N_2, H_2/N_2, and CO_2/N_2 separation; the performance was located near the empirical upper bound cited in literature compared with that of poly(SiMA). Therefore, introducing adamantane

Table V. Gas Permeability Coefficient and Ideal Gas Permeability Selectivity of Poly(1-AdMA-*co*-SiMA) Theoretical Value and Poly(SiMA)

	Gas	Poly(1-AdMA-*co*-SiMA) (80.8:19.2 mol %) theoretical value	Poly(SiMA)
Gas permeability coefficient ($\times 10^{-10}$ (cm³(STP)cm/(cm² s cmHg)))	H_2	1753	342 ± 6
	O_2	692	207 ± 4
	N_2	245	84.5 ± 0.6
	CO_2	3443	932 ± 1
	CH_4	748	240 ± 1
	CO_2/CH_4	4.60	3.89 ± 0.02
	CO_2/N_2	14.1	11.0 ± 0.1
Ideal gas permeability selectivity	H_2/CO_2	0.51	0.37 ± 0.05
	O_2/N_2	2.83	2.45 ± 0.06
	H_2/N_2	7.15	4.05 ± 0.10
	N_2/CH_4	0.33	0.35 ± 0.03

Figure 10. Relationship between ideal gas permselectivity and permeability coefficient for theoretical value of poly(1-AdMA-*co*-SiMA) with the upper bound (2008): (a) O_2/N_2 permselectivity and O_2 permeability coefficient; (b) H_2/N_2 permselectivity and H_2 permeability coefficient, (c) CO_2/N_2 permselectivity and CO_2 permeability coefficient. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

structure with high *FFV* and T_g to silicon-containing poly (SiMA) is an effective approach to improve thermal stability and gas permeation property through enhancement of polymer rigidity.

REFERENCES

1. Tsutsumi, N.; Nishikawa, Y.; Kiyotsukuri, T.; Nagata, M. *Polymer* **1992**, *33*, 209.

2. Coombe, H. S.; Nieh, S. *Energy Conversion Manage.* **2007**, *48*, 1499.

3. Chung, T.; Kafchinski, E. R. *J. Appl. Polym. Sci.* **1997**, *65*, 1555.

4. Li, X. G.; Huang, M. R.; Lin, G.; Yang, P. C. *J. Appl. Polym. Sci.* **1994**, *51*, 743.

5. Liu, Q.; Wang, T.; Qiu, J.; Cao, Y. *Chem. Commun.* **2006**, 1230.

6. Lin, H.; Van Wagner, E.; Freeman, B. D.; Toy, L. G.; Gupta, R. P. *Science* **2006**, *311*, 639.

7. Perry, J. D.; Nagai, K.; Koros, W. J. *MRS Bull.* **2006**, *31*, 745.

8. Haramoio, H.; Kokubo, K. I.; Sakai, K.; Kuwana, K.; Nakanishi, H. *ASAIO J.* **1994**, *40*, M803.

9. Nagase, K.-I.; Kohori, F.; Sakai, K. *J. Membr. Sci.* **2003**, *215*, 281.

10. Ana, F. B.; Clara, C. C.; Miguel, P.; Susana, V.; Angel, I. *Chem. Eng. Technol.* **2015**, *38*, 658.

11. Nagai, K.; Nakagawa, T. *J Appl. Polym. Sci.* **1994**, *54*, 1651.

12. Sterescu, D. M.; Bolhuis-Versteeg, L.; van der Vegt, N. F. A.; Stamatialis, D. F.; Wessling, M. *Macromol. Rapid Commun.* **2004**, *25*, 1674.

13. Suzuki, T.; Yoshida, A.; Ando, S.; Nagai, K. *Polym. Int.* **2015**, *64*, 1209.

14. Maya, E. M.; Garcia-Yoldi, I.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. *Macromolecules* **2011**, *44*, 2780.

15. Dai, Y.; Guiver, M. D.; Robertson, G. P.; Kang, Y. S.; Lee, K. J. *Macromolecules* **2003**, *36*, 6807.

16. Katsumata, T.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Polymer* **2009**, *50*, 1389.

17. Mao, H.; Zhang, S. *J. Mater. Chem. A* **2014**, *2*, 9835.

18. Bermeshev, M.; Bulgakov, B.; Starannikova, L.; Dibrov, G.; Chapala, P.; Demchuk, D.; Yampolskii, Y.; Finkelshtein, E. *J. Appl. Polym. Sci.* **2015**, *132*, 41395.

19. Rios-Dominguez, H.; Ruiz-Trevino, F. A.; Contreras-Reyes, R.; Gonzalez-Montiel, A. *J. Membr. Sci.* **2006**, *271*, 94.

20. Matsumoto, A.; Tanaka, S.; Otsu, T. *Macromolecules* **1991**, *2424*, 4017.

21. Ishizone, T.; Tajima, H.; Torimae, H.; Nakahama, S. *Macromol. Chem. Phys.* **2002**, *203*, 2375.

22. Archibald, T. G.; Malik, A. A.; Baum, K.; Unroe, M. R. *Macromolecules* **1991**, *24*, 5261.

23. Kavitha, A. A.; Singha, N. K. *Macromol. Chem. Phys.* **2009**, *210*, 1536.

24. Nagai, K.; Freeman, B. D.; Cannon, A.; Allcock, H. R. *J. Membr. Sci.* **2000**, *172*, 167.

25. Watanabe, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *Polym. J.* **2005**, *37*, 270.

26. Ando, S.; Koyama, Y.; Miyata, S.; Sato, S.; Kanehashi, S.; Nagai, K. *Polym. Int.* **2014**, *63*, 1634.

27. Bera, D.; Bandyopadhyay, P.; Ghosh, S.; Banerjee, S. *J. Membr. Sci.* **2014**, *453*, 175.

28. Mathews, A. S.; Kim, I.; Ha, C. S. *Macromol. Symp.* **2007**, *249/250*, 344.

29. Bera, D.; Bandyopadhyay, P.; Ghosh, S.; Banerjee, S.; Padmanabhan, V. *J. Membr. Sci.* **2015**, *474*, 20.

30. Sakaguchi, T.; Koide, Y.; Hashimoto, T. *J. Appl. Polym. Sci.* **2009**, *114*, 2339.

31. Chen, J.; Zhang, J.; Feng, Y.; Wu, J.; He, J.; Zhang, J. *J. Membr. Sci.* **2014**, *469*, 507.

32. Pixton, M. R.; Paul, D. R. *Polymer* **1995**, *36*, 3165.

33. Nakagawa, T.; Nagashima, S.; Higuchi, A. *Desalination* **1993**, *90*, 183.

34. Ohshita, J.; Hino, K.; Inata, K.; Kunai, A.; Maehara, T. *Polymer* **2007**, *48*, 4301.

35. Tsai, C. W.; Wu, K. H.; Yang, C. C.; Wang, G. P. *React. Funct. Polym.* **2015**, *9192*, 11.

36. Pai, Y. M.; Weber, W. P. *Appl. Organomet. Chem.* **1987**, *1*, 171.

37. Kanehashi, S.; Tomita, Y.; Kawakita, H.; Sato, S.; Miyakoshi, T.; Nagai, K. *J. Appl. Polym. Sci.* **2013**, *129*, 2036.

38. Wu, J.; Mather, P. T. *J. Macromol. Sci. Part C: Polym, Rev.* **2009**, *49*, 25.

39. Harry, R. A. Introduction to Materials Chemistry; Wiley: Hoboken, **2008**.

40. Yampolskii, Y.; Pinnau, I.; Freeman, B. D. Materials Science of Membranes for Gas and Vapor Separation; Wiley: England, **2006**.

41. Freeman, B. D. *Macromolecules* **1999**, *32*, 375.

42. Haward, R. N.; Young, R. J. The Physics of Glassy Polymers; Springer: Netherlands, **1997**.

43. Ward, I. M.; Sweeney, J. Mechanical Properties of Solid Polymers, 3rd ed.; Wiley: United Kingdom: **2012**.

44. Arnold, M. E.; Nagai, K.; Freeman, B. D.; Spontak, R. J.; Betts, D. E.; DeSimone, J. M.; Pinnau, I. *Macromolecules* **2001**, *34*, 5611.

45. Lee, H. J.; Han, S. H.; Nam, S. Y. *J. Membr. Sci.* **2015**, *485*, 10.

46. Rubin, A.; Rebutin, N.; Gerard, P.; Gauthier, C. *Mater. Lett.* **2014**, *135*, 184.

47. Komatsuka, T.; Nagai, K. *Polymer J. (Tokyo, Japan)* **2009**, *41*, 455.

48. Komatsuka, T.; Kusakabe, A.; Nagai, K. *Desalination* **2008**, *234*, 212.

49. Kanehashi, S.; Gu, H.; Shindo, R.; Sato, S.; Miyakoshi, T.; Nagai, K. *J. Appl. Polym. Sci.* **2013**, *128*, 3814.

50. Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259.

51. Akiba, C.; Watanabe, K.; Nagai, K.; Hirata, Y.; Nguyen, Q. T. *J. Appl. Polym. Sci.* **2006**, *100*, 1113.

52. Kanehashi, S.; Konishi, S.; Takeo, K.; Owa, K.; Kawakita, H.; Sato, S.; Miyakoshi, T.; Nagai, K. *J. Membr. Sci.* **2012**, *427*, 176.

53. Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

54. Poling, B. E. The Properties of Gases and Liquids; McGraw-Hill: New York, **2001**.

55. Robeson, L. M. *J Membr. Sci.* **2008**, *320*, 390.