Preparation of well-defined hyper-branched polymers and the CO₂ separation performance

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Abstract

Polyoxyethylene (POE) exhibits great potential for selective CO₂ permeation and is tethered onto poly(methyl methacrylate) (PMMA) or poly(styrene-*r*-acrylonitrile) (PSt-*r*-PAN)) by atom transfer radical polymerization (ATRP) of POE methacrylate (POEM) to endow preferential CO₂ permeability. The polymer backbones are first prepared from corresponding monomers and 4-(chloromethyl)styrene (Cl-St) with various mixture ratios by free radical polymerization. The POE grafting is then carried out by chain propagation of POEM from the Cl-St moiety by ATRP. The introduction of Cl-St to a polymer backbone is readily controlled when the monomer ratio was less than 2 mol%, and thus the average distance of POE graft chains can be tuned along the polymer backbone. ATRP also defines the length of the POE graft chains. CO₂ separation properties over N₂ of the well-defined hyper-branched polymers are investigated by comparing permeability of CO₂ and N₂ pure gases. The gas permeabilities increase with increase of POE content, and the resulting CO₂/N₂ selectivity is also enhanced in comparison to the pristine polymers and 35 and 40 for PMMA-based and PSt-*r*-PAN-based hyper-branched copolymers, respectively. Higher POE content indeed gives higher diffusion coefficient for both of CO₂ and N₂, but the CO₂ and N₂ diffusivities are almost the same. Thus the gas permeation progresses under solubility control. The CO₂ permeability is 135 Barrer with the CO₂/N₂ selectivity 42, when the POE content is 76 wt% of PSt-*r*-PAN-based hyper-branched copolymer.

Keywords: CO₂; gas separation membrane; hyper-branched polymer; microphase separation; poly(oxyethylene)

Introduction

Self-assembly of block copolymers (BCPs) results in the formation of microphase-separated structures [1-3], which provide a unique platform for structuring materials on nanometer scale. The nano architectures in microphase separation of BCPs are readily tunable and hold potential in various fields of materials science and applications. BCPs have been widely investigated for membrane materials for gas separation, such as packaging, permselective membranes, protective coating and fibers, since Odani et al. first reported the gas permeation and diffusion properties of styrene-butadiene-styrene triblock copolymers in 1975 [4], and basic researches on interplay between nanostructures and gas separation properties have been made in the following decade [5-9].

Besides BCPs have been intensively investigated as membrane materials for CO₂ removal from light gases [10-18], graft copolymers have also drawn attention due to synthetic feasibility, resulting in cost reduction, in comparison to BCPs. Effective POEM grafting on to polymer backbones have reported [19,20], and incorporation of POEM grafted poly(dimethylsiloxane) in poly(amide-*b*-ethylene oxide) (PEBAX) enhances the CO₂ separation performance drastically [20].

CO₂ is the major species of greenhouse gas, and CO₂ Capture and Storage (CCS) is one of the promising approaches to suppress CO₂ emission and to mitigate global warming and climate change [21,22]. Effective CO₂ separation technologies should be developed for implementation of the CCS. Liquid amine scrubbing is the most widely studied technology to capture CO₂ at the CO₂ mass emission sources, such as thermal power stations [23]. However, the CO₂ regeneration process is energy intensive. With monoethanol amine, the required CO₂ capture energy is determined to be 4.0 GJ/t-CO₂ [24], which has to be decreased to a half for implementation of this technology. In comparison to the solution absorption technologies, membrane separation can significantly reduce the CO₂ capture energy. Difference in chemical potential or partial pressure between feed and permeate side of membranes drives the separation, and additional energy, such as heating, is basically not required. Thus, membrane separation can be possible candidate in CO₂ capture as a next generation technology.

Among various polymeric materials investigated for CO₂ capture, POE or poly(ethylene glycol)

has been well known to present excellent CO₂ solubility and used for a CO₂-philic segment of BCPs [25-27]. Most of POE-containing BCPs are classified into poly(ether-ester)s and poly(ether-amide)s [27]. POEs with a few thousands in molecular weight are semicrystalline and are often incorporated into the polymer backbones. However, the chain flexibility is limited even though POE has a low glass transition temperature at ca. -60 °C. As shown in Fig. 1, we design and synthesize hyper-branched polymers with a well-defined chemical structure by tethering a relatively shorter POE chain (average oxyethylene unit: 5) onto PMMA or PSt-*r*-PAN backbone containing Cl group by ATRP of POEM. ATRP manner can readily control the graft chain length or POE fraction in the BCPs [28]. Microphase separation between POE and the polymer backbones would give amorphous POE domains with higher chain flexibility than those composed of POE blocks along a polymer backbone. Higher CO₂ separation performance can be also expected in comparison to BCPs containing POE blocks in the polymer backbones. Herein, we describe the detail chemical synthesis of the hyper-branched polymers and effect of chemical structure on the gas permeability.

Fig. 1. Synthetic scheme (left) and schematic drawing (right) of hyper-branched polymers.

Experimental

Materials

MMA, Cl-St, and POEM (average Mn: 300) were purchased from Sigma-Aldrich (MO, USA).

AN was obtained from TCI (Tokyo, Japan), and St, 2,2'-azodiisobutyronitrile (AIBN), copper (I) chloride (CuCl), and 4,4'-dimethyl-2,2'-dipyridyl (bpy) were from Wako (Osaka, Japan). An inhibitor of monomers was removed by passing through a basic alumina (MP Biomedicals, Eschwege, Germany) right before use. Other organic and inorganic chemicals were analytical grade reagents and used without further purification.

Macroinitiator synthesis

For a hyper-branched polymer preparation, MMA or St and AN were first copolymerized with Cl-St, from which POEM was grafted by ATRP, to give a polymer backbone as a macroinitiator. Typical example is as follows. MMA (40 mL, 376 mmol) and Cl-St (1.0 mL, 7.1 mmol) were dissolved in 20 mL toluene. The monomer solution was applied onto a basic alumina column to remove an inhibitor right before the polymerization. To the resulting solution was added AIBN (346 mg, 2.1 mmol), where the monomers to initiator ratio was 90 by mol. Molecular oxygen in the reaction mixture was excluded by N₂ bubbling for 30 min at ambient conditions, which was followed by heating at 70 °C for 1 h under stirring. The polymer fraction was collected by reprecipitation in methanol. This purification process was repeated to eliminate unreacted monomers from the precipitate. Formation of the macroinitiator was confirmed by ¹H NMR, and the yield and recovery were 33.6 g and 87 %, respectively. The Cl-St unit incorporated was 2.0 mol%. δ_H (600 MHz; CDCl₃): 7.4-6.6 (Ar), 4.54 (ClCH₂), 3.60 (OCH₃), 2.1-0.8 ppm (CCH₃ and polymer backbone) for PMMA macroinitiator; 7.3-6.9 (Ar), 4.54 (ClCH₂), 3.1-1.2 ppm (polymer backbone) for PSt-*r*-PAN macroinitiator.

Hyper-branched polymer synthesis

POE graft chain propagation was initiated from Cl moiety of the macroinitiators above prepared by ATRP of POEM [28,29]. In brief, PMMA macroinitiator (3.00 g, Cl-S: 2.0 mol %), CuCl (70 mg, 0.71 mmol), and bpy (222 mg, 1.42 mmol) were added to 20 mL NMP (*N*-methylpyrrolidone). POEM (2.73 g, 9.1 mmol) was dissolved in 10 mL NMP, and an inhibitor was removed by passing through a basic alumina column. The resulting solution was added to the

macroinitiator suspension. Molecular oxygen in the reaction mixture was removed by N₂ bubbling for 30 min, and then the reaction mixture was kept at 90 °C for 48 h under stirring. After the ATRP reaction, the resulting polymer was precipitated in petroleum ether/ethanol (5/1 by vol.) with trace HCl, and the unreacted POEM was separated. The precipitate was then dissolved in toluene, and the solution was applied onto a basic aluminum column to remove Cu on the active chain end. The polymer was then collected by reprecipitation in petroleum ether. Introduction of POEM was confirmed by ¹H NMR, and the POE fraction was 30.7 wt%. The yield and recovery were 3.4 g and 59 %, respectively.

δ_H (600 MHz; CDCl₃): 7.3-6.9 (Ar), 4.08 (COOCH₂CH₂), 3.8-3.5 (COOCH₃ and CH₂CH₂O), 3.38 (CH₂OCH₃), 2.1-0.6 ppm (Ar- CH₂CH₂, CCH₃ and polymer backbone) for PMMA-*g*-POEM; 7.4-6.6 (Ar), 4.08 (COOCH₂CH₂), 3.8-3.5 (CH₂CH₂O), 3.38 (CH₂OCH₃), 2.1-0.7 ppm (Ar- CH₂CH₂, CCH₃ and polymer backbone) for PSt-*r*-PAN-*g*-POEM.

Characterization of hyper-branched polymers

Progress of polymerizations and chemical structures of the polymers were confirmed by ¹H NMR on a JNM-EX270 FT (JEOL, Tokyo, Japan) and an Avance III HD 600 (Bruker, MA, USA). Molecular weight and the polydispersity of macroinitiators were determined by size exclusion chromatography (SEC). The SEC measurement of the polymers developed by ATRP was not carried out due to the hyper-branched structure, which did not provide precise information of molecular weight in comparison to liner polymer architecture. The SEC system consisted of a Hitachi L-6000 pump (Hitachi, Tokyo, Japan) and a RI-2031 plus intelligent RI detector (JASCO, Tokyo, Japan). A KD-805 (Shodex, Tokyo, Japan) was used in a 860-CO column oven (JASCO). THF was used as an eluent at a flow rate of 0.8 mL/min and at 40 °C. The molecular weight was calibrated with PMMA standards (Sigma-Aldrich). Thermal properties of the hyper-branched polymers developed were studied on a Hitachi High-Technologies X-DSC7500 (Tokyo, Japan). The thermal history was first quenched at 150 °C, and the second heating was recorded with a heating rate of 10 °C/min from -75 to 150 °C to find heat transitions. Mechanical properties of the hyper-branched polymers were analyzed by tensile testing on a Shimadzu EZ Test with a 500 N load cell (Shimadzu) to measure

maximum strength and Young's modulus at 25 °C. The displacement rate of cross head was 7 mm/min. Hyper-branched polymers were dissolved in THF (0.9 g-polymer/mL) and cast on a Teflon dish. The solvent was first evaporated at 30 °C for a couple of hours and then eliminated in a vacuum oven. The thickness of the film was 0.2 mm. Each specimen was obtained from the resulting polymeric film with a custom dogbone-shaped cutter (JIS K6251, 2 mm wide and 35 mm long).

Gas permeation test of hyper-branched polymers

The polymeric membranes of the hyper-branched polymers were prepared by the same solution casting method above described. The CO₂ and N₂ permeabilities of the polymeric membranes were measured by a vacuum time-lag method at 1 atm and 35 °C. Fig. 2 shows experimental setup of the gas permeation system. The polymeric membrane was placed on a porous rubber support in a custom-made stainless steel cell with an effective membrane area A of 18.86 cm². The permeation system was first evacuated to remove residual air and gases at 50 °C, and then the test gas was led to the feed side. The upstream pressure p_0 was kept at 1 atm and 35 °C. The increase in downstream pressure p of the permeation chamber was monitored with a Baratron 122A absolute pressure transducer (MKS, MA, USA) as a function of time, which showed a liner relationship at the steady state. A slop of the plot p vs. t at the steady state gave a gas permeability P using the following equation (1).

$$P = \frac{273}{76} \frac{Vl}{ATp_0} \frac{dp}{dt} \quad (1)$$

where V , l , and T are volume of the downstream chamber (22.93 cm³), membrane thickness (0.2 mm), and absolute temperature (308 K), respectively.

The apparent diffusion coefficient D_{app} is determined from the time-lag θ , which is the period of time to reach the steady state and the intercept in x-axis of the plot p vs. t , with the following equation (2) [30]. The apparent solubility coefficient S_{app} can be then calculated from P and D_{app} by equation (3). The ideal separation factor of a membrane for gas A over gas B $\alpha(A/B)$ is given by equation (4).

$$D_{app} = \frac{l^2}{6\theta} \quad (2)$$

$$S_{app} = \frac{P}{D_{app}} \quad (3)$$

$$\alpha(A/B) = \frac{P_A}{P_B} \quad (4)$$

Fig. 2. Schematic diagram of gas permeation system used in this study.

Results and discussion

Macroinitiator synthesis

Macroinitiators from MMA and Cl-St or St/AN and Cl-St were prepared by free radical polymerization with AIBN. In both of the macroinitiator polymerizations, white powder-like polymer was obtained by reprecipitation. The result of the polymerizations is summarized in Table 1 for PMMA and Table 2 for PSt-*r*-PAN macroinitiators. The free radical polymerization is carried out under various reaction stoichiometries and conditions, and gives copolymers containing Cl moiety with enough high molecular weight more than 50 kDa in M_w to process polymeric membranes. The monomer to initiator ratio was increased to obtain a higher molecular weight polymer. With SAC9 and 10, the M_w s exceeded 100 kDa, although the yields were below 50 %. Introduction of Cl moiety to both of the polymer backbones was close to identical to the feed ratio of Cl-St to other monomer(s) as shown in Fig. 3, which indicated that Cl moiety was distributed statistically along the polymer backbones. Thus the average distance of graft chains formed in the following ATRP will be controlled.

Table 1. Results of PMMA macroinitiator synthesis by free radical copolymerization.

<Table 1>

Table 2. Results of PSt-*r*-PAN macroinitiator synthesis by free radical copolymerization.

<Table 2>

Fig. 3. Cl-St introduction in (a) PMMA and (b) PSt-*r*-PAN macroinitiator syntheses as a function of Cl-St feed ratio.

Hyper-branched polymer synthesis

ATRP is now most accessible polymerization strategy for living polymerization [28], and POEM was polymerized from Cl moiety on the macroinitiator backbones. CuCl and bpy were used to initiate the reaction, and the stoichiometry was Cl moiety:CuCl:bpy = 1:1.2:2.4 by the molar ratio [29]. The propagation of POEM graft chain was confirmed by ^1H NMR. The peak of chloromethyl protons at 4.54 ppm disappeared, and the triplet resonance of methylene protons at 4.30 ppm adjacent to ester linkage shifted to 4.08 ppm and became broader by polymerization. After removing Cu on the active chain end, the polymers were translucent or transparent depending on the POEM fraction. The results of ATRP were listed in Table 3 for PMMA-*g*-PPOEM and Table 4 for PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers. Weight fraction and degree of polymerization (DP) of POEM increased with the feed ratio, however, POEM was not quantitatively incorporated in comparison to Cl-St copolymerization with MMA or St/AN in Fig. 4. The reason would be explained by only a few mol% introduction of Cl-St monomer unit in the polymer backbone. The steric hindrance suppressed the POEM propagation even when the reaction period was extended to 48 h in PMMA-*g*-PPOEM hyper-branched polymers.

In the case of PMMA-*g*-PPOEM hyper-branched polymers in Fig. 4a, the POEM propagation was conducted onto 4 macroinitiators with various Cl moiety ratios. However, the POEM weight fraction in the resulting polymers was related to merely the feed POEM ratio and independent of Cl moiety ratio examined. While the number of points was not many, the similar tendency was also found with PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers in Fig. 4b. The POEM weight fraction was ranged from 30 to 80 for PMMA-*g*-PPOEM and 40 to 80 wt% for PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers, which would be enough to form a POE domain upon microphase separation between POE and the polymer backbones. For MCP18 (Cl-St: 0.96 mol%; POEM: 77.3 wt%) in Table 3, the average graft chain distance on the PMMA backbone and the average graft chain length were 100 MMA and 120 POEM repeating units, respectively.

Table 3. Results of PMMA-*g*-PPOEM hyper-branched polymer synthesis.

<Table 3>

Table 4. Results of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymer synthesis.

<Table 4>

Fig. 4. Plots of POEM weight fraction in (a) PMMA-*g*-PPOEM and (b) PSt-*r*-PAN-*g*-PPOEM hyper-branched polymer syntheses as a function of POEM feed ratio to macroinitiators with various Cl moieties introduced. Open circle: 0.88 (MC3 backbone); open triangle: 2.0 (MC1); open cube: 0.87 (MC7); open diamond: 0.96 (MC8); filled circle: 1.28 (SAC3); filled triangle: 1.57 (SAC1); and filled cube: 2.34 (SAC12) mol% of Cl moiety.

Thermal and mechanical properties of hyper-branched polymers

Physical properties of materials define or limit the use of them, and thermal and mechanical properties of the hyper-branched polymers developed were studied by DSC and tensile testing. The second heating of DSC curves of PMMA-*g*-PPOEM hyper-branched polymer (POEM: 47.7 wt%) and the PMMA backbone was described in Fig. 5. The polymer backbone has a clear glass transition temperature T_g at 110 °C, corresponding to that of pristine PMMA. On the contrary, while T_g of POE was seen at around -60 °C, the hyper-branched polymer did not show that of the polymer backbone. Partial mixing between POE and backbone polymer with various ratios would result in making the grass transition behavior unseen. This result indicated existence of a POE domain upon the microphase separation. DCS measurement of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers was

also conducted under the same experimental conditions and suggested POE domains as shown in Fig. S1 in the Electronic Supplementary Information (ESI).

Small-angle X-ray scattering (SAXS) with synchrotron radiation was also tried for detail analysis of the microphase separation. The Fourier-space measurement gives information of average structural length of phase separation. However, scattering peaks derived from the microphase separation was not found clearly, which might be due to small difference in the electron density between POE and the other polymer fractions as shown in Fig. S3 in the ESI. The detail phase-separated structure remained unknown by the SAXS experiment. However, DSC results exhibited formation of the POE domain upon microphase separation. The previous study also supports this discussion. A POEM tethering poly(vinyl chloride) hyper-branched polymer forms solid-state polymer electrolytes by complexation with LiCF_3SO_3 , which show high ionic conductivity [31]. A POE domain upon the microphase separation provides a channel for Li^+ to facilitate the migration through the polymer electrolytes.

Fig. 5. DSC thermographs of 2nd heating of PMMA-g-PPOEM hyper-branched polymer (POEM: 47.7 wt%, bold) and the PMMA backbone (plain) at a heating rate of 10 °C/min.

Tensile testing was performed to find the maximum strength σ_m and Young's modulus E of the hyper-branched polymers from the S-S curves, and effect of POEM weight fraction on the mechanical properties was studied. A hyper-branched polymer was dissolved in THF, and polymeric

films with controlled thickness (0.2 mm) were prepared by the solution casting. The resulting films were transparent and cut into a dumbbell shape for tensile testing. The results were summarized in Table 5 for PMMA-*g*-PPOEM and Table 6 for PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers. For both of the polymers, the σ_m and E went down with increase in POEM weight fraction as expected. With PMMA-*g*-PPOEM, the copolymer developed from MC7 showed higher mechanical properties than the copolymers from MC1 and MC3. The Cl moiety ratio of MC3 and MC7 was 0.87 mol%, thus the difference would not result from the Cl moiety ratio but would be due to molecular weight of the polymer backbones. The M_w of MC3 was the highest among the three polymer backbones, which resulted in the highest polymer chain entanglement to give the highest mechanical properties. On the other hand, the Cl moiety ratio of polymer backbones SAC3 and 12 were 1.3 and 2.3 mol%, respectively, while those M_w s were similar. SACP 1, 2, and 8 showed similar mechanical properties. POEM weight fraction determined the physical properties of the hyper-branched polymer rather than the Cl moiety or distance between PPOEM graft chains, although the data points were not many.

Table 5. Mechanical properties of PMMA-*g*-PPOEM hyper-branched polymers.

<Table 3>

Table 6. Mechanical properties of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers.

<Table 4>

Gas permeation properties of hyper-branched polymers

CO₂-philic POE was tethered onto PMMA and PSt-*r*-PAN backbones with various weight fractions to improve gas permeability, and CO₂ and N₂ gas permeation of the resulting hyper-branched polymers were investigated by a vacuum time-lag method at 1 atm and 35 °C with a permeation system depicted in Fig. 2. Fig. 6 displayed the gas permeabilities and CO₂ selectivity over N₂ of PAMAM-*g*-PPOEM hyper-branched polymer membranes determined from the ratio of the permeabilities. The gas permeabilities increased with increase of POEM fraction in the hyper-branched polymer, and it was found that the Cl moiety ratio among tested afforded little influence on the gas permeability.

When the POEM fraction was 67.3 wt% (MCP16), the polymeric membrane exhibits $1.01 \times$

10^{-8} cc(STP)cm²/(cm² s cmHg) in CO₂ permeability, which was corresponded to 101 Barrer ($1 \text{ Barrer} = 1 \times 10^{-10} \text{ cc(STP)cm}^2/(\text{cm}^2 \text{ s cmHg})$), and the CO₂ selectivity was 38. The increase of POE fraction gave rise to the CO₂ selectivity, although the deviation was not negligible. This would result from a higher CO₂ solubility of the polymeric membrane. Effects of the POEM fraction on apparent diffusion and solubility coefficients were also determined to figure out an origin of the increase in CO₂ separation performance as presented in Fig 7 and 8.

Fig. 6. Gas permeabilities (upper) and CO₂ selectivity over N₂ (bottom) of PAMAM-g-PPOEM hyper-branched polymers as a function of POEM weight fraction determined by a vacuum time-lag method at 1 atm and 35 °C. Circle: MC3 backbone; diamond: MC1; cubic: MC7. Upper: filled and open symbols are CO₂ and N₂ permeabilities, respectively.

Fig. 7 represented that the D_{app} of CO_2 and N_2 , determined from the time-lag θ , went up with increase of POEM fraction. The average oxyethylene unit of POEM was 5, and the POE did not have crystalline nature. The POE thus flew above the glass transition temperature, while polymer backbones were in a glassy state. Thus, the gas molecules could readily diffuse into the POE domain in comparison to the polymer backbone domain. However, the kinetic diameter of CO_2 (3.30 Å) is close to that of N_2 (3.64 Å) [37], and the diffusion coefficients gave similar profiles for both of the gasses. The results told that the preferential CO_2 permeation observed did not progress by diffusion control mechanism.

Fig. 7. Apparent diffusion coefficient (upper) and diffusion selectivity (bottom) of

PAMAM-*g*-PPOEM hyper-branched polymers as a function of POEM weight fraction determined by a vacuum time-lag method at 1 atm and 35 °C. Circle: MC3 backbone; diamond: MC1; cubic: MC7. Upper: filled and open symbols are CO₂ and N₂ permeabilities, respectively.

Fig. 8. Apparent solubility coefficient (upper) and solubility selectivity (bottom) of PAMAM-*g*-PPOEM hyper-branched polymers as a function of POEM weight fraction determined by a vacuum time-lag method at 1 atm and 35 °C. Circle: MC3 backbone; diamond: MC1; cubic: MC7. Upper: filled and open symbols are CO₂ and N₂ permeabilities, respectively.

On the contrary, the S_{app} of CO₂, determined from the P and D_{app} , was much higher than that of N₂ over the POEM fraction between 30 to 70 wt% in Fig. 8. The high CO₂ selectivity observed was

derived from the difference in the solubility coefficient. A dipole-quadrupole interaction between CO₂ and ether oxygen of oxyethylene group helped enhancement of the CO₂ solubility of the polymeric membranes [32].

Gas permeation properties of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers were also examined by the same operation conditions aforementioned, and the results were shown in Fig. 9, 10, and 11. As can be seen, higher POEM fraction also gave higher CO₂ and N₂ permeabilities of the PSt-*r*-PAN-*g*-PPOEM membranes in Fig. 9. The CO₂ selectivity over N₂ was around 40 over the POEM fractions examined. As a tendency, the CO₂ permeability of PMMA-*g*-PPOEM membranes was greater than that of PSt-*r*-PAN-*g*-PPOEM membranes. However, the highest CO₂ permeability was 1.35×10^{-8} cc(STP)cm²/(cm² s cmHg) or 135 Barrer with the selectivity of 42 in PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers, when the POEM fraction was 76.0 wt% (SACP1).

The D_{app} was determined from a time-lag θ with eq. 2 as well in Fig. 10. The gas diffusivity also increased with increase of the POEM fraction, which meant that the gases passed most likely through the POE domain rather than the polymer backbone domain. The difference in molecular size between CO₂ and N₂ were small as mentioned above [33], and thus the both of diffusion coefficients were close in Fig. 10. On the other hand, the S_{app} of CO₂ was about two-order higher than that of N₂ in Fig. 11, and this provided the higher permselectivity of CO₂ over N₂.

Fig. 9. Gas permeabilities (upper) and CO_2 selectivity over N_2 (bottom) of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers as a function of POEM weight fraction determined by a vacuum time-lag method at 1 atm and 35 °C. Circle: SAC3 backbone; diamond: SAC1; cubic: SAC12. Upper: filled and open symbols are CO_2 and N_2 permeabilities, respectively.

Fig. 10. Apparent diffusion coefficient (upper) and diffusion selectivity (bottom) of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers as a function of POEM weight fraction determined by a vacuum time-lag method at 1 atm and 35 °C. Circle: SAC3 backbone; diamond: SAC1; cubic: SAC12. Upper: filled and open symbols are CO₂ and N₂ permeabilities, respectively.

Fig. 11. Apparent solubility coefficient (upper) and solubility selectivity (bottom) of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers as a function of POEM weight fraction determined by a vacuum time-lag method at 1 atm and 35 °C. Circle: SAC3 backbone; diamond: SAC1; cubic: SAC12. Upper: filled and open symbols are CO₂ and N₂ permeabilities, respectively.

For both of PMMA-*g*-PPOEM and PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers, the gas permeation study revealed that introduction of POEM elevated diffusivity of CO₂ and N₂. Due to the higher solubility of CO₂ than N₂ in the polymeric membranes, the CO₂ permeability was greater than the N₂ one to give a high CO₂ selectivity. In this study, the Cl moiety introduction was only a couple of mol%, and it was assumed that the introduction did not change the gas permeability of PMMA and PSt-*r*-PAN polymer backbones. The CO₂ and N₂ permeabilities of pristine PMMA was $0.78 \times$

10^{-10} and 0.039×10^{-10} cc(STP)cm²/(cm² s cmHg), or 0.78 and 0.039 Barrer, respectively, providing a 20 in CO₂ selectivity over N₂ [34]. The gas permeability was enhanced by the introduction of POE, and a higher CO₂ selectivity of PMMA-*g*-PPOEM than the polymer backbone suggested preferential permeation of CO₂ through POE domain. For PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers, the St/AN ratio was 54/46 by wt%. The AN content was not exactly the same, however, Chiou et al. reported that the CO₂ and N₂ permeabilities of PSt-*r*-PAN (AN: 28 wt%) were 2.8×10^{-10} and 0.1×10^{-10} cc(STP)cm²/(cm² s cmHg), or 2.8 and 0.1 Barrer, respectively [35]. As well as PMMA, the POEM tethering gave rise to the gas permeabilities, especially CO₂ in the case of PSt-*r*-PAN polymers. The solubility coefficients calculated were apparent values and seemed to be independent of the POEM fraction in the hyper-branched polymer. Due to limited availability of experimental apparatus, sorption experiment was not examined to obtain the solubility coefficients directly. A part of POE would be miscible to the polymer backbone, and the CO₂ solubility of the resulting polymeric mixture would be higher than the polymer backbones. As a result, the S_{app} would not change much over the POEM introduction range in the gas sorption on the membrane surface. The DSC curves in Fig. 5 and S1 did not show the T_g s of the pristine polymer backbones at ca. 100 °C clearly, which would be because of phase mixing with a part of POE. SAXS study of the hyper-branched polymers did not show peaks derived from microphase separation (Fig. S1), which would support partial mixing between POE and the polymer backbones to form a continuous phase with a higher CO₂ solubility.

Conclusion

PMMA and PSt-*r*-PAN are widely used polymers and known to show preferential CO₂ permeation over N₂. However, for example to use in post-combustion CO₂ capture, the CO₂ permeability should be enhanced. A CO₂-philic polymer, POE, was introduced by tethering comb like POE structure to PMMA and PSt-*r*-PAN by ATRP of POEM to improve CO₂ permeability of the polymers. The ATRP was initiated from Cl moiety of Cl-St unit copolymerized with MMA or St/AN by free radical polymerization. The distance of the graft chain and the chain length (or POEM

weight fraction) were readily controlled. The resulting hyper-branched polymers with a well-defined chemical structure represented an enhanced CO₂ permeability with higher CO₂ selectivity over N₂ in comparison to the corresponding backbone polymers. The CO₂ permeability exceeded 100 Barrer with a higher POEM weight fraction. The POE introduction increased the S_{app} of CO₂ of the polymeric membranes and also improved the CO₂ diffusivity drastically in the membranes. Further improvement of CO₂ permeability is required for post-combustion CO₂ capture. However, the results obtained revealed that the POE introduction was effective to improve the CO₂ separation properties and that the chemical structure of the hyper-branched polymers defined the gas separation performance.

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Table 1. Results of PMMA macroinitiator synthesis by free radical copolymerization.

Run	Feed		Copolymer		Yield/%	M_w /kDa	M_w/M_n
	MMA/mmol	Cl-St/mmol	Cl-St/mol%	Cl-St/mol%			
MC1	376	7.1	1.85	2.00	87.1	58	1.95
MC2	376	5.0	1.30	1.40	61.0	80	1.71
MC3	376	3.5	0.93	0.87	81.2	70	1.85
MC4	376	3.5	0.93	0.72	64.9	89	1.78
MC5	376	3.5	0.93	0.73	87.5	59	1.99
MC6	376	3.0	0.79	0.81	72.1	75	1.86
MC7	751	5.0	0.66	0.87	45.8	93	1.95
MC8	751	7.1	0.93	0.96	70.3	55	2.25
MC9	751	14.2	1.85	1.90	67.8	62	2.28

Polymerization was conducted in 20 mL toluene with monomers/initiator ratio of 90 at 70 °C for 1 h.

The composition and molecular weight were determined by ^1H NMR and SEC, respectively.

Table 2. Results of PSt-*r*-PAN macroinitiator synthesis by free radical copolymerization.

Run	Feed			Copolymer		THF/mL	M/I	Yield/%	M_w /kDa	M_w/M_n
	St/mmol	AN/mmol	Cl-St/mmol	Cl-St/mol%	Cl-St/mol%					
SAC1	224	365	11.9	1.98	1.6	90	200	81.5	68	2.19
SAC2	49.8	80.9	1.29	0.98	0.24	20	200	86.8	66	2.18
SAC3	49.8	80.9	2.60	1.95	1.3	20	200	85.5	69	2.09
SAC4	49.8	80.9	3.90	2.90	2.9	20	200	88.9	71	2.09
SAC5	83.8	30.5	2.41	2.06	1.8	20	180	53.4	86	1.72
SAC6	83.8	30.5	3.47	2.94	2.8	20	180	53.6	50	1.72
SAC7	83.8	30.5	3.47	2.94	2.7	20	180	53.9	82	1.79
SAC8	83.8	30.5	4.74	3.98	3.5	20	180	54.0	84	1.79
SAC9	224	365	11.9	1.98	1.9	90	670	48.7	110	1.77
SAC10	224	365	18.1	2.98	3.2	90	670	49.5	110	1.83
SAC11	227	366	12.4	2.04	1.2	90	200	90.1	70	2.15
SAC12	227	366	18.4	3.01	2.3	90	200	85.5	71	2.16
SAC13	227	366	12.0	1.99	1.7	90	200	78.6	68	2.13
SAC14	227	366	18.4	3.01	3.0	90	200	82.5	72	2.16
SAC15	227	366	6.01	1.00	0.71	90	200	58.5	67	2.11
SAC16	227	366	24.8	4.01	4.2	90	300	66.1	80	2.03

Polymerization was conducted at 60 °C for 24 h.

The composition and molecular weight were determined by ^1H NMR and SEC, respectively.

Table 3. Results of PMMA-g-PPOEM hyper-branched polymer synthesis.

Run	Macroinitiator			Feed of POEM		NMP/mL	Time/h	Yield/%	DP of POEM	POEM
	Sample	Amount/g	Cl/mmol	Amount/mmol	Fraction/wt%					Fraction/wt%
MCP1	MC3	3.00	0.26	5.25	34.4	30	46	41.9	8.5	18.1
MCP2		3.01	0.26	8.75	46.6	30	46	55.0	24.1	38.5
MCP3		3.02	0.26	14.0	58.2	30	46	52.5	29.0	43.0
MCP4		2.99	0.26	19.3	65.9	30	48	48.1	36.6	48.8
MCP5		3.00	0.26	28.0	73.7	25	48	91.1	82.0	68.0
MCP6	MC1	3.00	0.59	9.10	47.6	30	48	59.2	7.4	30.7
MCP7		3.00	0.59	12.6	55.8	30	48	54.1	10.0	37.5
MCP8		3.00	0.59	19.6	66.2	30	48	58.7	17.7	51.4
MCP9		3.00	0.59	28.0	73.7	30	48	66.7	23.5	58.5
MCP10	MC7	1.50	0.13	6.30	55.8	15	32	62.7	21.4	35.8
MCP11		1.50	0.13	9.45	65.4	15	32	60.2	35.2	47.8
MCP12		1.50	0.13	12.6	71.6	15	32	55.7	46.3	54.6
MCP13		1.50	0.13	15.8	75.9	15	32	75.2	79.1	67.3
MCP14		1.50	0.13	18.9	79.1	15	32	74.9	92.9	70.7
MCP15	MC8	3.00	0.29	6.30	38.7	30	27.5	70.8	5.6	13.8
MCP16		3.00	0.29	19.3	65.8	30	27.5	54.7	21.8	38.5
MCP17		3.00	0.29	31.5	75.9	30	27.5	68.0	53.5	60.6
MCP18		3.00	0.29	43.8	81.4	30	27.5	72.8	119	77.3

Polymerization was conducted at 90 °C, and the composition was determined by ^1H NMR.

Table 4. Results of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymer synthesis.

Run	Macroinitiator			Feed of POEM		NMP/mL	Yield/%	DP of POEM	POEM
	Sample	Amount/g	Cl/mmol	Amount/mmol	Fraction/wt%				Fraction/wt%
SACP1	SAC3	0.90	0.16	8.41	73.7	9.0	90.4	60.6	76.0
SACP2		2.60	0.46	22.7	72.4	26	82.4	49.6	72.2
SACP3		3.05	0.54	12.3	54.6	30	51.8	7.6	32.9
SACP4		3.05	0.54	19.3	65.4	30	50.4	13.8	46.9
SACP5	SAC1	2.97	0.52	22.8	69.7	30	48.7	24.9	61.4
SACP6		3.05	0.54	8.75	46.3	30	58.0	9.3	37.4
SACP7		3.02	0.53	35.0	77.7	30	58.4	49.8	76.1
SACP8	SAC12	3.01	0.53	24.5	70.9	30	65.3	27.1	72.0
SACP9		3.00	0.52	35.0	77.8	30	68.7	34.6	76.7

Polymerization was conducted at 90 °C for 20 h, and the composition was determined by ¹H NMR.

Table 5. Mechanical properties of PMMA-*g*-PPOEM hyper-branched polymers.

Polymer	Macroinitiator	POE fraction/wt%	σ_m /MPa	E /MPa
MCP3	MC3	43.0	4.75	104
MCP4		48.8	2.25	21.4
MCP5		68.0	0.92	0.73
MCP7	MC1	37.5	5.65	148
MCP8		51.4	1.82	11.6
MCP9		58.5	0.70	0.55
MCP10	MC7	35.8	7.29	281
MCP11		47.8	6.51	259
MCP12		54.6	3.72	185
MCP13		67.3	1.23	3.97

Table 6. Mechanical properties of PSt-*r*-PAN-*g*-PPOEM hyper-branched polymers.

Polymer	Macroinitiator	POE fraction/wt%	σ_m /MPa	E /MPa
SACP1	SAC3	76.0	1.01	2.78
SACP2		72.2	1.48	2.40
SACP3	SAC1	32.9	27.5	664
SACP4		46.9	11.2	328
SACP5		61.4	10.9	282
SACP8	SAC12	72.0	0.82	0.13

Graphical Abstract