PEGBEM 고분자를 기반으로 한 가지형 공중합체 제조 및 기체분리막에의 응용

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Synthesis of Comb Copolymer Based on PEGBEM and Application to Gas Separation Membrane

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Introduction

With significantly increasing CO_2 emission to atmosphere in around world, the global warming effect and green-house gas effect have been considered as one of the most threatening problem causing abnormal climate and destroying our daily life. To solve this problem, enormous studies were conducted and several gas separation technology was developed such as adsorption, absorption and cryogenic distillation. Among them, membrane science exhibited advantages in regard of cost-effectiveness, eco-friendliness and operating process and so on.

Specifically, membrane consisted of polymer matrix can be used as alternative separation technology due to its facile and economic fabrication process and high scalability to large size unlikely to conventional free standing membrane. Furthermore, its separation performance could be enhanced by incorporating other materials such as multi-dimensional carbon, metal-organic frameworks (MOFs), zeolite and other inorganics.

Theory

In the case of CO_2 separation to other inert gases such as He, N_2 and etc. of polymer composite membrane, CO_2-philicity of polymer is crucial as gas molecules are separated by difference of solubility between gas and polymer matrix. Based on Lewis acid-base theory, polar groups such as ether and ester is essential to obtain CO_2-philic copolymer as they could act as electron-donor to CO_2 molecule which generally acts as electron-acceptor resulting interaction between them and high CO_2 solubility.

So to realize high CO_2 separable membrane, obtaining CO_2-philic polymer is important. Furthermore, when consider economic and environmental aspect, polymeric composite membrane is very attractive option due to its exceedingly thin selective layer than conventional free standing membrane. Besides that, in the majority cases, the polymer consisting free-standing structure are prepared in complex and harsh condition resulting low scalability.

Experimental

In this study, we synthesized several polymer to prepared polymer composite membrane with poly(ethylene glycol) behenyl ether methacrylate (PEGBEM). This PEGBEM contains a bunch of ester and ether which are mentioned as major CO_2-philic functional group. All obtained polymers was synthesized via free-radical polymerization which is more economic and eco-friendly process. At first, poly(oxyethylene methacrylate) (POEM) was copolymerized with PEGBEM with AIBN initiator. When polymerization was conducted, sequential methylene chain of PEGBEM could be stacked resulting somewhat crystallinity giving mechanical strength. The sample containing relatively high PEGBEM contents exhibited solid and crystalline phase and on the other hand, amorphous liquid state by relatively high contents of POEM which is totally amorphous monomer. The overall synthesize scheme and optical photos of obtained comb copolymer are summarized in Figure 1.

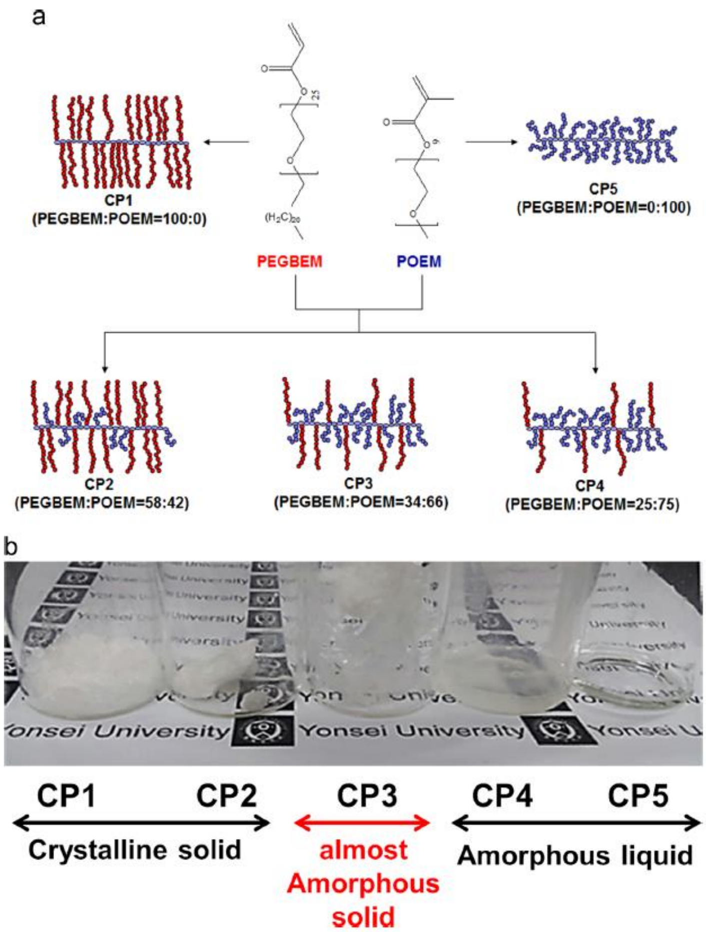

Fig. 1. Polymerization scheme and (b) optical photos of PEGBEM-g-POEM comb copolymers.

The obtained PEGBEM-g-POEM copolymer exhibited hydrophilic state with alcohol soluble property. In the regard of composite membrane, such alcohol soluble property is essential as common organic solvent such as THF, DMF or NMP can dissolve polysulfone substrate destroying micro-porous structure giving it low gas separation performance.

Not only PEGBEM-g-POEM copolymer, poly(1-trimethylsilyl-1-propyne) (PTMSP) was also applied with PEGBEM. PTMSP is well known as highly permeable polymer matrix with high free volume, glassy property and hydrophobicity. However, to much high permeability, its separation performance is quite low when compared with other polymer matrix. To enhance its separation perforamcne PEGBEM was treated via facile annealing process. Its chemical scheme for preparation is summarized in Figure 2. At first, PTMSP solution was prepared with 2.5 wt% in cyclohexane and coated onto polysulfone substrate. Then, PEGBEM solution containing AIBN initiator and allyamine was casted on PTMSP composite membrane. The PEGBEM casted PTMSP membrane directly was moved to 50 ^{o}C oven for free radical polymerization to obtain PEGBEM treated PTMSP membrane.

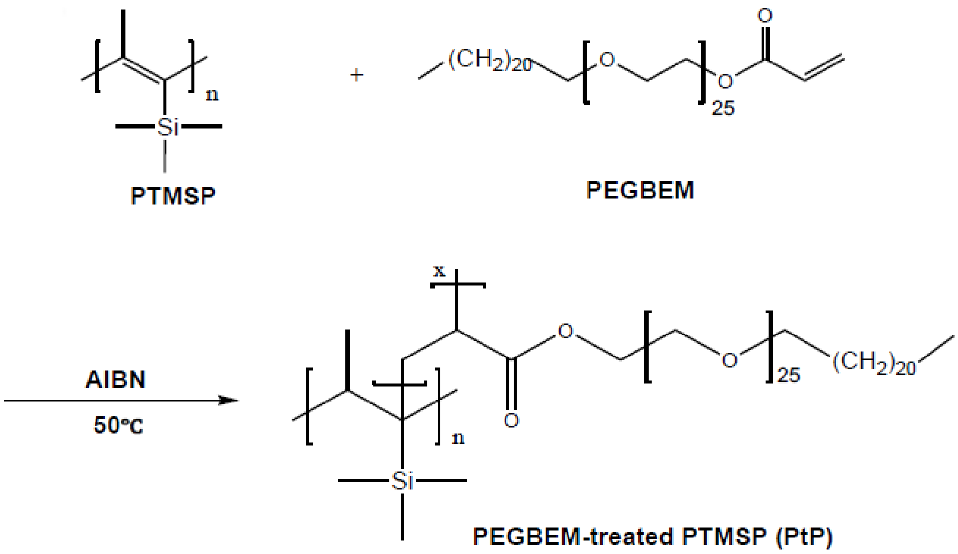

Fig. 2. Polymerization scheme of PEGBEM treated PTMSP

Results and Discussion

The successful polymerization was confirmed by FT-IR, NMR, TGA, DSC, GPC and XPS for PEGBEM-g-POEM and PtP. As shown in Figure 3, moderately formed crystallinity derived by methylene chain of PEGBEM was confirmed via XRD. From that, at low contents of PEGBEM, high gas permeation was observed in both N_2 and CO_2 resulting low CO_2/N_2 selectivity (CP4 and CP5 with 16.8 and 1.7 CO_2/N_2 selectivity). On the contrary, at high contents of PEGBEM (CP1 and CP2), too much high crystalline phase, low CO_2 permeance was obtained with 1.3 and 15.9 CO_2 GPU. At moderately controlled sample (CP3), the highest CO_2/N_2 selectivity (84.7) was obtained with 21.9 CO_2 GPU. When compared with Robeson upper bound curve (2008), such CO_2/N_2 separation performance was very closed to upper bound curve implying its potentiality to be used as useful matrix for CO_2 separation membrane.

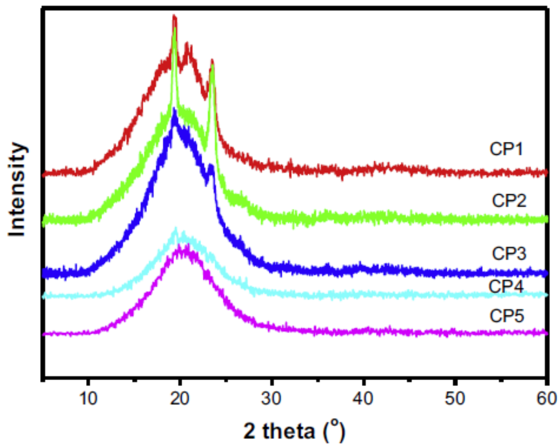

Fig. 3. XRD results of PEGBEM-g-POEM copolymer

Besides that, PEGBEM treated PTMSP exhibited lamellar structure which was confirmed by SAXS and cross-sectional TEM measurement as shown in Figure 4. Such oriented micro-structure gave membrane high CO_2 selective performance resulting 166.9 CO_2 GPU and 77.2 CO_2/N_2 selectivity. Furthermore, when calculating permeability from thickness of PtP composite membrane and CO_2 permeance, high CO_2 separation performance was obtained overpassing Robsen upper bound.

When allyamine was not contained PEGBEM treatment solution, polymerization of PEGBEM was conducted discriminately resulting too much high crystalline phase onto PTMSP surface with low gas permeation performance. Also role of other components such as PTMSP and annealing time also was investigated.

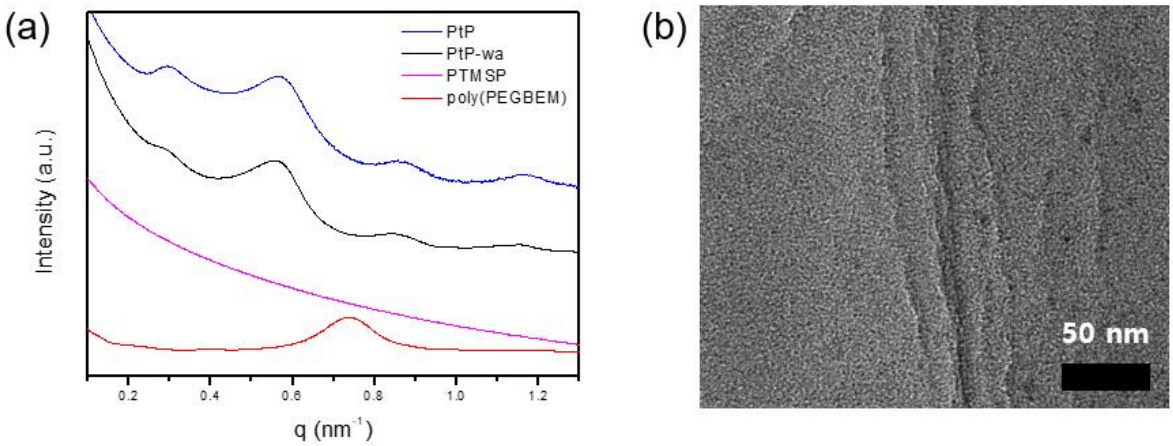

Fig. 4. (a) SAXS result of PtP, PtP-wa (with out allyamine), PTMSP and poly(PEGBEM) and (b) cross-sectional TEM images of PtP

References
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