

## 올레핀 촉진수송용 고분자 전해질막의 내구성에 대한 Brij98의 효과

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### Effect of Brij98 on Durability of Silver Polymer Electrolyte Membranes for Facilitated Olefin Transport

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**요 약:** 은 고분자 전해질은 올레핀/파리핀 혼합물 분리에 매우 효과적인 분리막 재료이다. 이는 고분자 매트릭스에 녹아 있는 은이온이 올레핀과 선택적, 가역적 반응을 통해 올레핀만을 분리막속으로 통과시키기 때문이다. 그러나 이러한 은 고분자 전해질 분리막은 실제 공정에 응용되기에는 다소 약한 장시간 운전 성능 안정성을 보인다. 즉 분리 성능이 시간이 지남에 따라 점차 감소되는데 이는 은이온이 은 나노입자로 환원되기 때문이다. 따라서 본 연구에서는 poly(vinyl pyrrolidone) (PVP)와 AgBF<sub>4</sub>로 이루어진 고분자 전해질막의 안정성을 향상시키고자 비이온 계면활성제인 C<sub>18</sub>H<sub>35</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>20</sub>OH (Brij98)를 첨가제로 사용하였다. 분리막속에서 은이온의 은 나노입자로의 환원현상을 원자전자 현미경과 자외선 분광학을 이용하여 분석하였다. 그 결과 Brij98이 첨가된 분리막의 경우 은 나노입자의 성장이 늦춰졌으며, 프로판/프로펜 선 택도가 장시간 유지됨을 알 수 있었다.

**Abstract:** Silver polymer electrolytes are very promising membrane materials for the separation of olefin/paraffin mixtures. Olefin molecules are known to be transported through reversible complex formation with silver ions entrapped in polymer matrix. However, they have poor long-term stability, which is very important for the industrial application; the selectivity through the membrane decreases gradually with time mostly due to the reduction of silver ions (Ag<sup>+</sup>) into silver nanoparticles (Ag<sup>0</sup>). In this study, the stability of silver polymer electrolyte was investigated for poly(vinyl pyrrolidone) (PVP) and AgBF<sub>4</sub> system containing a surfactant, i.e. C<sub>18</sub>H<sub>35</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>20</sub>OH (Brij98) as a stabilizer. The reduction behavior of silver ions to silver nanoparticles in PVP was also investigated by atomic force microscopy (AFM) and UV-visible spectroscopy. It was found that the growth of silver nanoparticles was slower and selectivity of polymer electrolyte for propylene in propylene/propane was maintained longer time when Brij98 was added as a stabilizer.

**Keywords:** facilitated olefin transport, polymer electrolyte, membrane stability, silver, surfactant

## 1. Introduction

Olefins such as ethylene or propylene are the most important feedstock in petrochemical industries and their separation from olefin/paraffin gas mixtures has

been currently performed by cryogenic distillation processes. Since it needs high capital investment and enormous operation cost, alternative energy-saving separation technology is urgently demanding. Membrane separation technology has been proposed as a possible alternative to distillation due to low cost and simple operation. However, the separation of olefin/paraffin

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mixtures via conventional polymeric membranes has not been very effective because of the indiscernible physico-chemical properties of olefins and paraffins such as molecular size and solubility [1-3].

Facilitated olefin transport membranes have been paid much attention due to their high separation properties. Among various kinds of facilitated transport membranes [4-8], the polymer electrolyte membranes consisting of silver ions dissolved in a polymeric solvent have received much attention because of their excellent separation performance in solid state [9-30]. The propylene permeance through the poly(2-ethyl-2-oxazoline) (POZ) [11,12,15], poly(vinyl pyrrolidone) (PVP) [14,17,20] or poly(ethylene oxide) (PEO) [21-23] membranes containing  $\text{AgBF}_4$  was as high as 40~50 GPU (1 GPU= $10^{-6}$  cm<sup>3</sup> (STP)/(cm<sup>2</sup> sec cmHg)), while the propane permeance was extremely low as 0.003 GPU. Thus, the pure gas selectivity of propylene over propane was more than 10,000, but the mixed gas selectivity is approximately 50 due to plasticization of membranes [14,16]. This exceptional performance enhancement is achieved primarily due to 1) extremely high loading of silver salts in the polymer matrix, which is possible by the interaction between silver ions and carbonyl oxygens of polymer matrices [25], and 2) a fast reversible reaction of silver ions with olefin [26].

In a series of previous studies, we obtained results that shed light on the mechanism of facilitated olefin transport through silver polymer electrolyte membranes [14-16,27]. First, the coordinative interaction between silver ion and polymeric ligand induces the dissolution of silver salts in a polar polymer solvent. Its intensity and silver salt concentration in the polymer matrix determine the concentrations of ionic constituents such as free ion, ion pair and higher-order ionic aggregates. It is spectroscopically observed that all three silver ionic constituents are converted into free ions under an olefin environment, suggesting that the most effective olefin carrier is the free silver ion [14]. On these experimental findings, a new mechanism for the com-

plexation reaction between propylene and silver salt in silver polymer electrolytes was proposed [14].

Second, in facilitated olefin transport through silver polymer electrolytes, a threshold concentration was observed at the silver mole fraction of approximately 0.25 for  $\text{AgBF}_4$  or  $\text{AgCF}_3\text{SO}_3$  dissolved in POZ or PVP, below which facilitated transport was not observed [15,16]. However, the propylene permeance increased nearly linearly with the silver concentration at silver concentrations above the threshold concentration. The existence of the threshold concentration may be attributable to the coordination behavior of silver ion with polymeric ligand as well as olefin. For POZ or PVP/ $\text{AgBF}_4$  or  $\text{AgCF}_3\text{SO}_3$  systems [15], it was found that 1) the most favorable coordination number of silver ion under a propylene environment was 3, and 2) the interaction between silver ion and amide carbonyl oxygen was marginally stronger than that between silver ion and olefin. It was thus proposed that a silver ion can act as an olefin carrier only when it has vacant coordination sites, i.e., when the number of amide carbonyl oxygens coordinated to the silver ion is less than 3. It was further found that the threshold concentration for facilitated olefin transport was strongly dependent on the relative strength of the interactions of silver ion with the carbonyl oxygen and with olefin [16]. The threshold concentration is high when the former interaction is slightly stronger than the latter, and is low when the latter is stronger than the former. This is the first report on the importance of the coordination behavior of metal ion in determining the activity of silver ion as olefin carrier, and the presence of the threshold concentration for facilitated transport membranes in solid state.

Third, the reaction mechanism between silver ion and olefin can be elucidated by calculating the theoretical structure of a silver-polymer complex in the gas phase and the electronic energies of its reaction step with olefin [27]. The reaction between silver ion and olefin is proposed to occur by two steps; the first is to form a silver-olefin complex as an intermediate, and the second

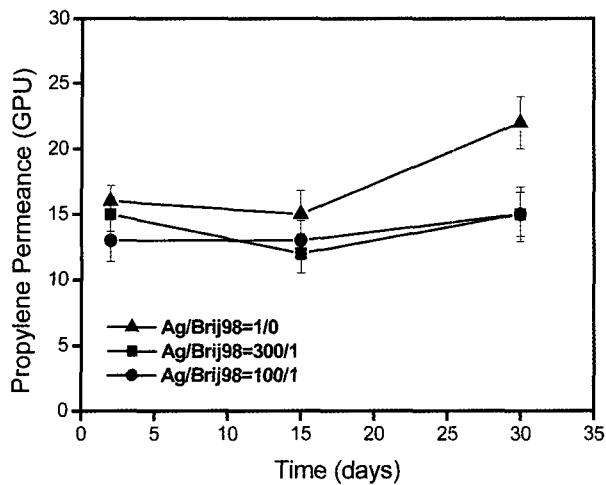


Fig. 1. The propylene permeance of PVP/AgBF<sub>4</sub> and PVP/AgBF<sub>4</sub>/Brij98 membranes as a function of time.

is the exchange of the complexed-olefin in the intermediate with a new olefin. The first complexation step is irreversible and slow, whereas the second exchange step is rapid and reversible, which appears to be the key step in determining facilitated olefin transport. Note that the second step is only observed when a concentration gradient is present, but not in a homogeneous system.

Despite the extensive research on facilitated olefin transport phenomena in the polymer/silver complex membranes, the long-term stability of membrane performance has been relatively insufficiently explored [28]. One of the several problems to be solved for the commercialization is the gradual decrease of membrane performance mostly due to the reduction and aggregation of silver ions.

Among the various polymer electrolytes containing silver salts, PVP/AgBF<sub>4</sub> membranes were chosen for this study because PVP has been reported to be used for polymer/salt complexes as well as silver reducing agent [31-35]. In order to improve long-term stability in dry polymer membranes containing silver salts, we have employed nonionic surfactant, polyoxyethylene (20) oleyl ether (Brij98) as a stabilizer. The nonionic surfactant was chosen to eliminate the effect of extra ionic species on membrane properties. Before examining the effects of the added Brij98 surfactant to the PVP/

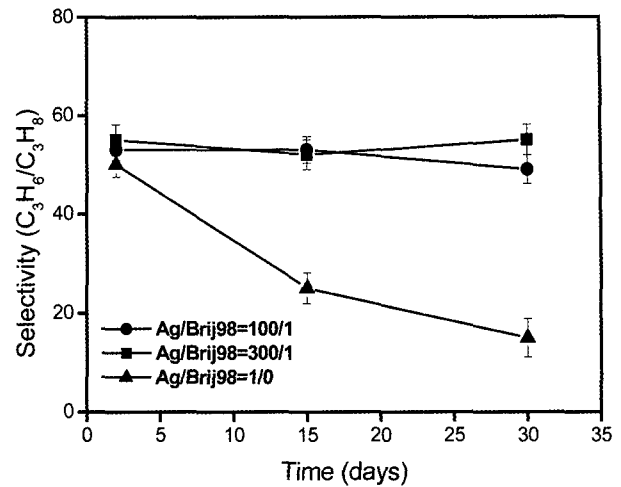


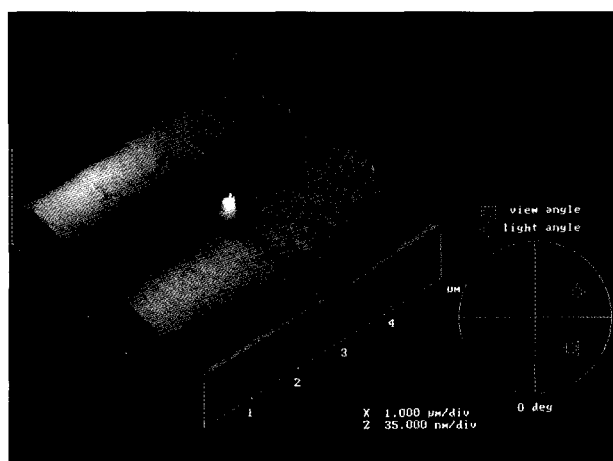
Fig. 2. The mixed gas selectivity of PVP/AgBF<sub>4</sub> and PVP/AgBF<sub>4</sub>/Brij98 membranes as a function of time.

AgBF<sub>4</sub> system, the miscibility between PVP and Brij98 was tested using differential-scanning calorimetry (DSC). A single T<sub>g</sub> was seen for all the polymer-surfactant complexes, which indicates a homogeneous system. The clarity of solution formed from the PVP/Brij98 also supports the homogeneity of these polymer/surfactant systems. The selectivity and permeance of membrane against time for the separation of propylene from propylene/propane mixtures were investigated in the presence and absence of Brij98 in the membrane.

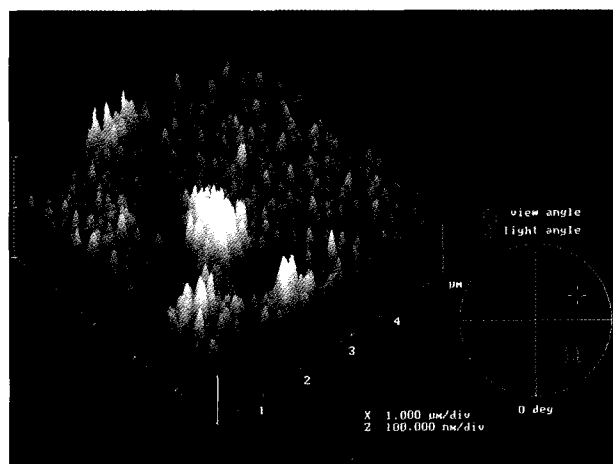
## 2. Experimental

### 2.1. Materials

Silver tetrafluoroborate (AgBF<sub>4</sub>) (98%), and polyoxyethylene(20) oleyl ether (Brij98, C<sub>18</sub>H<sub>35</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>20</sub>OH) were purchased from Aldrich Chemical Company (Milwaukee, WI). Poly(vinylpyrrolidone) (PVP) (Mw=1,000,000 g/mol) was purchased from Polyscience. All chemicals were used as received. A micro-porous polysulfone (PSf) membrane was provided by Saehan Industry (South Korea). Average and maximum pore sizes of PSf were estimated ca. 7 and 20 nm, respectively, by the liquid displacement method.



0 min UV



60 min UV

**Fig. 3.** AFM images of PVP/AgBF<sub>4</sub> membranes with various UV irradiation time.

### 2.2. Preparation of PVP/AgBF<sub>4</sub> and PVP/AgBF<sub>4</sub>/Brij98 Electrolytes

The silver salt (AgBF<sub>4</sub>) was dissolved in the 20 wt% PVP aqueous solution or in the 20 wt% PVP aqueous solution containing Brij98 by stirring for 2hr. The molar ratio of carbonyl oxygen in PVP to silver ion in the solution was kept as 1:1 (In this paper “PVP/AgBF<sub>4</sub>=1/1” corresponds to a 1:1 molar ratio of carbonyl oxygen atoms to silver atoms). The molar ratio of AgBF<sub>4</sub> to Brij98 was fixed to 100:1 or 300:1. The polymer/salt mixed solution was then coated on a micro-porous support membrane to make composite membrane using a RK Control Coater (Model 101, Control Coater RK Print-Coat Instruments LTD, UK). The

membrane was dried in a convection oven under N<sub>2</sub> environment and in a vacuum oven at room temperature for 2 days. The thickness of the support PSf layer and the top polymer electrolyte layer were approximately 100 μm and 1μm, respectively.

### 2.3. Characterization

Gas permeation experiments were carried out using a constant pressure/variable volume method. The mixed gas separation properties were investigated with mixture gas (50/50 vol% of propane/propylene) at room temperature. The feed pressure and the permeated pressure were 40 psig and atmosphere, respectively. Volumetric gas flow rates were determined with a soap-bubble flow meter. The composition of permeated gas was analyzed by gas chromatography equipped with thermal conductivity detector. The unit of the gas permeance without considering membrane thickness is GPU, where 1 GPU=1×10<sup>-6</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup>sec cmHg.  $\alpha = (y_i/y_j)/(x_i/x_j)$  is used as the mixed gas selectivity ( $x_i$  or  $x_j$  and  $y_i$  or  $y_j$  are mole fraction of component  $i$  or  $j$  in feed and in permeate).

Atomic force microscopy (AFM) measurements were carried out using a scanning probe microscope (Nanoscope IIIa, Digital Instruments). Tapping mode was employed at the cantilever's resonance frequency using a probe and cantilever unit.

For UV absorption of silver particles in PVP the methanol solution containing PVP/AgBF<sub>4</sub> (1:1) and PVP/AgBF<sub>4</sub>/Brij98 (100:100:1) were cast onto a quartz window and dried under N<sub>2</sub> atmosphere. The samples were dried in vacuum at room temperature at least for 48 hours. UV-visible spectra were measured with spectrophotometer (Hewlett Packard) in the range between 190 and 900 nm. For UV irradiation, a 8W lamp (VL-4. LC) supplied by Vilber Lourmat, France, was used. The sample was exposed to UV radiation at a distance of 7 cm from the lamp under N<sub>2</sub> atmosphere. The intensity at 240 nm was 2070 μW/cm<sup>2</sup>.

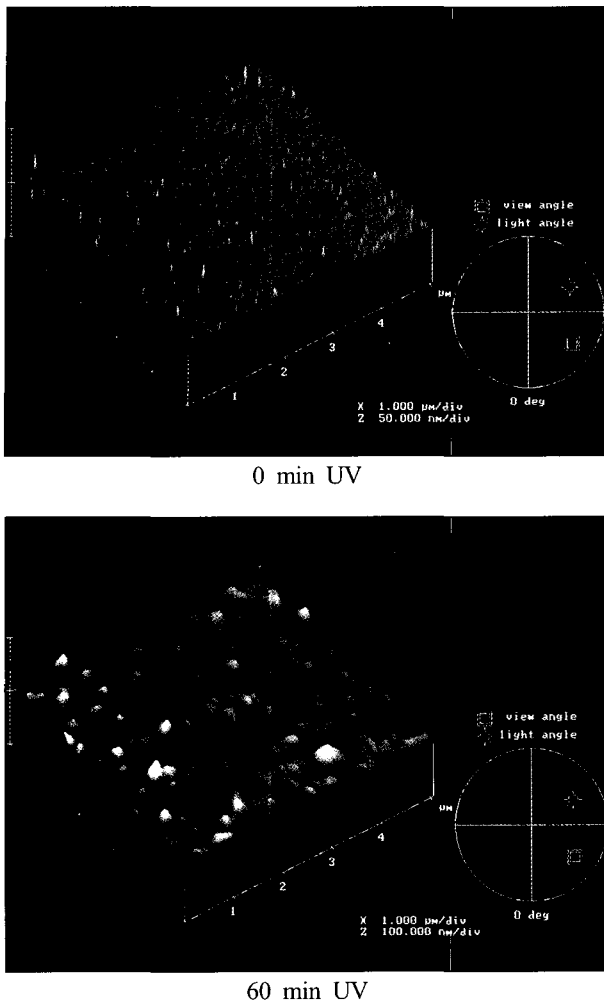


Fig. 4. AFM images of PVP/AgBF<sub>4</sub>/Brij98 membranes with various UV irradiation time.

### 3. Results and Discussion

#### 3.1. Mixture Gas Selectivity and Permeance

The separation of a propane/propylene mixture (50/50, v/v) was performed to evaluate the effect of Brij98 on long-term stability of PVP/AgBF<sub>4</sub> membrane. The actual selectivity was determined by the ratio of mole fractions of the gas components in permeate streams. Figs. 1 and 2 show the propylene permeance and mixed gas selectivity, respectively, through PVP/AgBF<sub>4</sub> and PVP/AgBF<sub>4</sub>/Brij98 membranes with varying the concentration of Brij98. As shown in these figures, there were no significant differences in facilitating performance for those membranes at first. With increasing time, how-

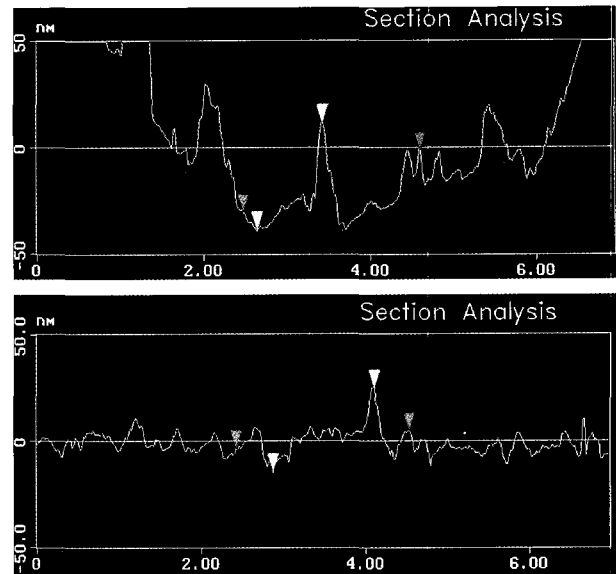


Fig. 5. AFM Section analysis of 60 min UV irradiated PVP/AgBF<sub>4</sub> (top) and PVP/AgBF<sub>4</sub>/Brij98 (bottom).

ever, the selectivity decreased as an order of magnitude through the PVP/AgBF<sub>4</sub> membrane is observed. Meanwhile, the selectivity and permeance for the membranes containing Brij98 remained nearly constant up to 30 days no matter what the concentration of Brij98 is.

#### 3.2. AFM Images

Several authors reported that the polymers containing amide group play an important role in the protection of the synthesized silver particles, but it has also been found to act as a reducing agent [31-35]. The ligands of C-N and C=O in PVP is known to take part in electronic density in the  $p\pi-d\pi$  hybrid orbital of silver ions, thus reducing them to silver atoms [35]. In this part, the effect of Brij98 on the reduction of silver ions in the PVP/AgBF<sub>4</sub> membrane was investigated by AFM analysis to elucidate the long-term stability of membranes.

UV irradiation (240 nm) was used to reduce silver ions artificially and it worked as a catalyst. UV was irradiated for 0 and 60 min on the surface of PVP/AgBF<sub>4</sub> or PVP/AgBF<sub>4</sub>/Brij98 membranes. Fig. 3 and 4 depict the AFM images for each sample. The AFM image of the PVP/AgBF<sub>4</sub> membrane showed very

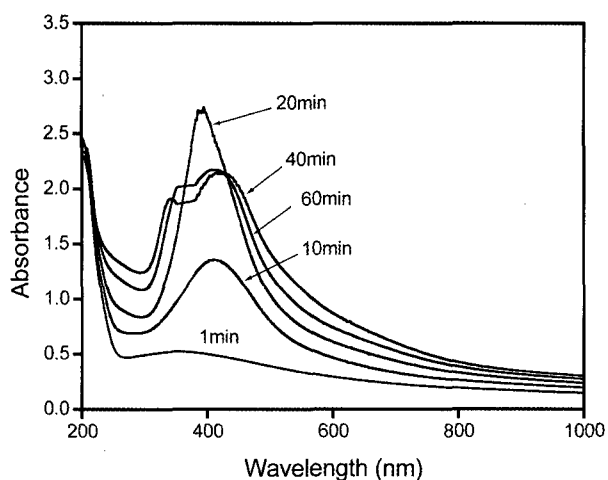


Fig. 6. UV absorbance of PVP/AgBF<sub>4</sub>=1/1 with increasing UV irradiation time.

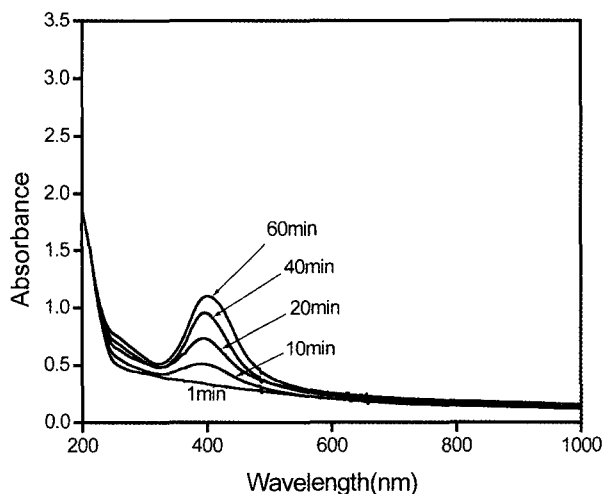


Fig. 7. UV absorbance of PVP/AgBF<sub>4</sub>/Brij98 = 100/100/1 with increasing UV irradiation time.

smooth surface at first. However, after UV irradiation for 60 min, the AFM images exhibited rapid reduction and aggregation of silver ions. In the presence of Brij98, however, the small-sized silver nanoparticles were observed on the membrane surface without growth or aggregation of nanoparticles with increasing UV irradiation time. This strongly represents that Brij98 plays an important role in preventing the rapid reduction of silver ions. This result becomes clearer by comparing the cross section analysis of 60 min-irradiated PVP/AgBF<sub>4</sub> and PVP/AgBF<sub>4</sub>/Brij98 membranes

(Fig. 5). Severe fluctuation was observed in PVP/AgBF<sub>4</sub> membrane, indicating that the silver ions are prone to be reduced and aggregated easily. On the contrary, the fluctuation of the membrane containing Brij98 was much lower under the same UV irradiation time. The stabilization of membranes may be explained by the adsorption of surfactant molecules onto the surface of small-sized silver nanoparticles and by putting the surfactant molecules among polymer chains, consequently preventing the aggregation of silver nanoparticles.

### 3.3. UV-visible Spectroscopy

To confirm this correlation between Brij98 and particle formation, UV was taken on those two different samples, PVP/AgBF<sub>4</sub> and PVP/AgBF<sub>4</sub>/Brij98 (Figs. 6 and 7). An intense absorption peak around 410 nm is generally observed and attributed to the surface plasmon excitation of silver nanoparticles [31-33]. The measurement of extinction spectra of silver nanoparticles dispersed in media allows the rapid analysis of particles size and size distribution. The general trend is that the absorbance peak shifts toward longer wavelengths as nanoparticles become bigger [36,37], which is well studied theoretically by Henglein [38]. In addition, the height of this peak gives direct information about the metallic silver concentration in the medium because UV absorbance follows the Lambert-Beer law ( $A = \epsilon lc$ ). The 410 nm peak height is directly proportional to the quantity of Ag<sup>0</sup> present in media. Thus, we can estimate the rate of reduction of AgBF<sub>4</sub> by following its evolution during the reaction.

The absorption spectra were obtained for each sample with increasing photo-reduction time using 254 nm light. When the UV light of 254 nm wavelength is irradiated into the PVP/AgBF<sub>4</sub> membrane, silver nanoparticles started to be formed within 1 minute. From 1 min to 20 min, the number of silver nanoparticles increased quickly, and then the number of silver nanoparticles decreased with further irradiation due to the aggregation of silver nanoparticles. The aggregation

causes a decrease in the intensity of the main peak around 410 nm and results in peak shift to the long-wavelength side. On the contrary, silver nanoparticles in PVP/AgBF<sub>4</sub>/Brij98 were slowly formed at the same condition. Surfactant has both hydrophilic part and hydrophobic part in a molecule. Surfactants molecules will adsorb at the interface formed between two phases spontaneously due to their unique molecular structure. When surfactant molecules exist in the solid polymer electrolytes, they would adsorb onto the surface of silver atoms and form surfactant films, which hampers the coalescence and growth of particles in membrane as shown above.

#### 4. Conclusions

The selectivity of propylene over propane through PVP/AgBF<sub>4</sub> polymer electrolyte membranes decreased gradually with time mostly due to the reduction of silver ions into silver atoms, followed by the growth of silver particles through the coalescence. In order to minimize the growth rate of silver nanoparticles, a nonionic surfactant, Brij98, was introduced, which resulted in a longer durability of the separation performance. The surfactant molecules in membrane hampered the growth of silver atoms or nuclei into large silver particles by the formation of surfactant film on the surface of silver atoms or nuclei.

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