Changes in Facilitated Transport Behavior of Silver Polymer Electrolytes by UV Irradiation[†]

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Abstract : Silver species other than the silver ion were formed by UV irradiation on polymer electrolyte membranes containing silver salts and their effect on complexation behavior between the silver and olefin was investigated through the separation performance of olefin/paraffin mixtures. The ideal propylene/propane separation factor reached 350 and the separation coefficient was ca. 15 due to the high loading amount of silver ions into poly(2-ethyl-2-oxazoline) (POZ) without UV irradiation. On UV irradiation either in air or under nitrogen, the silver-POZ membranes became yellow-brown initially due to the formation of colloidal silver particles, and finally black and metal-like luster. Even when Ag^+ was converted, to some extent, to Ag^0 by UV irradiation in air at the early stage, the separation coefficient of olefin/paraffin mixtures was maintained. This suggests that silver species other than the silver ion is active for olefin carrier for facilitated transport. Meanwhile the steady decrease of the separation coefficient was observed in the silver/POZ membranes irradiated under N_2. It is suggested that the reduction of silver ions in POZ goes through a different photoreduction mechanism with UV irradiation depending on the environment.

Keywords : silver polymer electrolytes, reduction, facilitated transport, UV irradiation.

Introduction

Silver ions have been known to react reversibly with olefin molecules to make silver-olefin complexes[1]; olefin molecule donates π electrons to the empty s orbitals of silver ions to form σ-bonds. Back donation of electrons from the occupied d orbitals of silver ions into the empty antibonding orbitals of olefin molecules results in π-bonding.[2] Because of such *reversible* and *specific* interaction of silver ions with olefins, silver ions can act as olefin carriers, resulting in facilitated olefin transport. Paraffins are, however, unable to form complexes with silver ions and permeate only through Fickian transport. Therefore the facilitated olefin and the low paraffin permeabilities results in high separation performance of the olefin/paraffin mixtures. Many investigators have studied olefin/paraffin separations by facilitated transport with various

membranes.[3-5] In general, the facilitated transport phenomena have been typically observed in supported liquid membranes or ion exchange membranes containing silver ion carrier together with water.[3] Despite extensive research on olefin/paraffin separations by facilitated transport membranes in the liquid state,[3] this technology has not been applied to industrial applications mostly due to the operational instability by the evaporation of the liquid media.

One method to overcome the stability problem,[3] liquid-free solid solvent has been introduced.[4,5] Polymers containing electron donor group dissolve silver salts with low lattice energy via coordination bonds to form polymer electrolytes. Silver ions confined to the polymer electrolyte membrane form reversible complexes with unsaturated hydrocarbon molecules, which act as olefin carriers for facilitated transport. The solid polymer electrolyte membranes containing silver salts showed facilitated olefin transport where either poly(2-ethyl-2-oxazoline) (POZ) or poly(vinyl pyrrolidone)[5] was used for a polymer solvent to dissolve silver salts. Silver ions in polymer electrolytes are labile and can be easily converted to others photo-chemically, and thus there will be

various silver species in polymer electrolytes including silver ions, silver metals etc when the silver-polymer electrolyte is under photoreduction condition.

Therefore, the extent of the interaction between the carriers and olefin molecules varies depending upon the silver species, (i.e., Ag^+ and/or Ag^o), as well as the environment of silver, such as ligands, counter ions, matrix *etc*. In this study, the reaction of silver salts dissolved in a polar polymer solvent of POZ is accelerated by UV irradiation, and the irradiation effect on the facilitated propylene transport and on the separation performance of propylene/propane mixtures is investigated.

Experimental

Poly(2-ethyl-2-oxazoline) (POZ) ($M_w = 5 \times 10^5$) and silver triflate ($AgCF_3SO_3$) were purchased from Aldrich Chemical Co. All chemicals were used as received.

Polymer electrolyte solution was prepared by dissolving a silver salt in 20% (w/w) aqueous polymer solution. The mole ratio of silver ion to carbonyl oxygen of POZ was fixed to 1:1. The solution was coated onto asymmetric microporous substrate from Seahan Industries Inc., Seoul, Korea using a RK Control Coater. After evaporation of water in a convection oven at 40 °C under nitrogen, the membrane was dried completely in a vacuum oven for a day at room temperature. The thickness of the top polymer electrolyte layer was ca. 1 μm. Free standing $AgCF_3SO_3$/POZ films of 1 μm thickness were prepared for UV-VIS spectroscopy.

For UV irradiation, a 8 W lamp (VL-4.LC) supplied by Vilber Lourmat, France, was used. The sample was taken into the chamber and exposed to UV radiation at a distance of 7 mm from the lamp. The intensity at $\lambda = 253.7$ nm was 2070 μW/cm^2. The irradiation time for the experiments was varied. All samples were stored in vacuum before characterization. The UV-VIS absorption spectra were measured by a spectrophotometer from Hewlett Packard working in a spectral range between 190 and 900 nm. The surface morphologies were characterized by a scanning electron microscopy (SEM, Hitachi S-2500). The measurements of Ag^+ concentrations were carried out with a Microprocessor ion analyzer 901 (Orion Research) equipped with a silver ion selective electrode 94-16 (Orion Research) and a reference electrode 90-02 (Orion Research).

The dry and pure gases, propane (99.5%) and propylene (99.0%) were used for the permeation experiments. The pure gas permeation properties were measured by a soap-bubble flow meter. The unit of the gas permeance is GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/(cm^2 s cmHg). Mixed gas (50:50 vol% of propylene/propane mixture) separation properties of the membranes were evaluated by gas chromatography (Hewlett Packard G1530A, MA) equipped with a TCD detector. The ideal separation factor defined as the ratio of

the pure propylene to pure propane permeabilities is obtained from pure gas permeance and the separation coefficient defined as $(y_i/y_j)/(x_i/x_j)$ is obtained from mixed gas experiments, where x_i and y_i are the mole fractions of component i in feed and in permeate, respectively. The ratio of the permeate to the feed flow rates was always less than 2%.

Results and Discussion

The UV absorbance of $AgCF_3SO_3$ dissolved in POZ at a 1:1 mole ratio of silver ions to carbonyl oxygens of POZ with varying UV irradiation time in air and N_2 environments are shown in Figure 1(a) and 1(b), respectively. The characteristic peak at around 400 nm was observed for all samples after irradiation, attributable to the surface plasmon excitation of silver metal particles.[6] Organic free radicals with highly negative redox potential such as ketyl radicals were known to be involved into the reduction of silver ions to colloidal silver particles.[7] Thus it suggests that similar reactive radical species may also be involved in our reaction system to form Ag^o particles.

From Figure 1, four observations may be made. First, the peak intensity was increased and reached the maximum with the irradiation time. Second, the position of the absorption maximum was changed to small extent in the sample irradiated in air (Figure 1(a)), meanwhile it was shifted from 400 to 425 nm under N_2 (Figure 1(b)). Third, the maximum intensities of the absorbance for the sample irradiated under N_2 are greater than those of prepared in air for the same irradiation time. Forth, the onset time for the spectrum broadening is longer for the sample irradiated under N_2.

The spectral position of the silver plasmon absorption band has been known to depend on the combination of the particle size and shape, the surface composition of the particles and the dielectric constant of the matrix. According to the theory of the light absorption by small metal particles,[8] the wavelength of the maximum absorption is inversely proportional to the square root of the density of free electrons in the particles. The red shift of the surface plasmon absorption band would be due to the electron losing on Ag particles. After 5 hrs exposure in air (or 7 hrs under N_2), the intensity of the maximum absorption peak is decreased and the spectrum becomes remarkably broadened with the irradiation time. The fact that the absorption peak shifts toward a longer wavelength and becomes broadened upon UV irradiation,[9] represents a broad size distribution and subsequent agglomeration processes of Ag^o to form silver cluster. When irradiation was continued for more than several hours, the irradiated surface of the film gradually became metallic luster. The details of silver species and their complexation with olefins are under investigation in this laboratory.

The surface images of the films were presented in Figure 2. Silver particles were observed for all samples which were not detected for the pristine sample and the number of particles
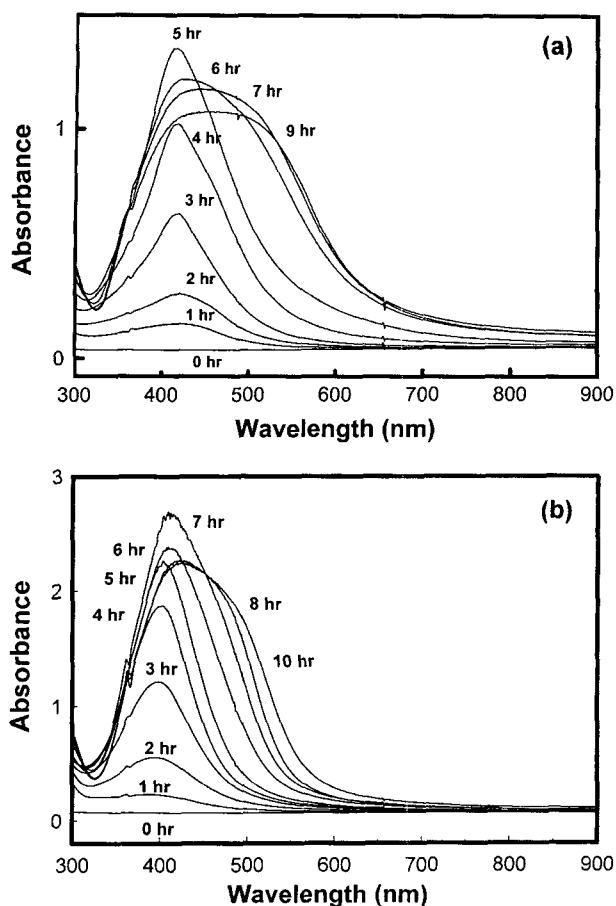
Figure 1. Time evolution of the UV-visible spectra of silver/POZ free standing film irradiated (a) in air and (b) under N_2.

increased with the irradiation time.[10] Moreover it is intriguing that the distortion of the surface morphology is significant for the sample irradiated in air for 7 hrs. Although it is not clear why the UV spectra and the surface morphologies are different when the same samples were irradiated in air and under N_2, it would be expected that the difference may be owing to the presence of water and oxygen trapped in the membrane. In the case air environment, it was found that the membrane absorbed large amount of water from air to become soft in a very short time (normally less than 1 minute). It suggests the water molecules absorbed from air would act as a plasticizer, which enhances the segmental motion of the polymer and consequently promotes migration of silver to make the particle size bigger. However, the water sorption in the dry N_2 environment is very limited, prohibiting rapid increase in the size and agglomeration of particles and consequently resulting in rather uniform surface structure as demonstrated in Figure 2.

Both of propane and propylene permeances through the POZ membrane were very low and were not detected being below the practical lower limit of the bubble flow meter (less than 0.1 GPU). However, the permeance of propylene increased up to 35 GPU at the 1 : 1 mole ratio of silver ions to carbonyl oxygens of POZ.[5] The increase of the propylene permeance is consistent with the mathematical model proposed by Kang et al. to interpret the facilitated transport behavior in solid state.[11] Meanwhile the propane permeance through the film was less than 0.1 GPU. The ideal separation factors for propylene/propane, defined by the ratio of permeance of propylene to the one of propane, is at least 350 for the membrane of the mole ratio of silver to carbonyl
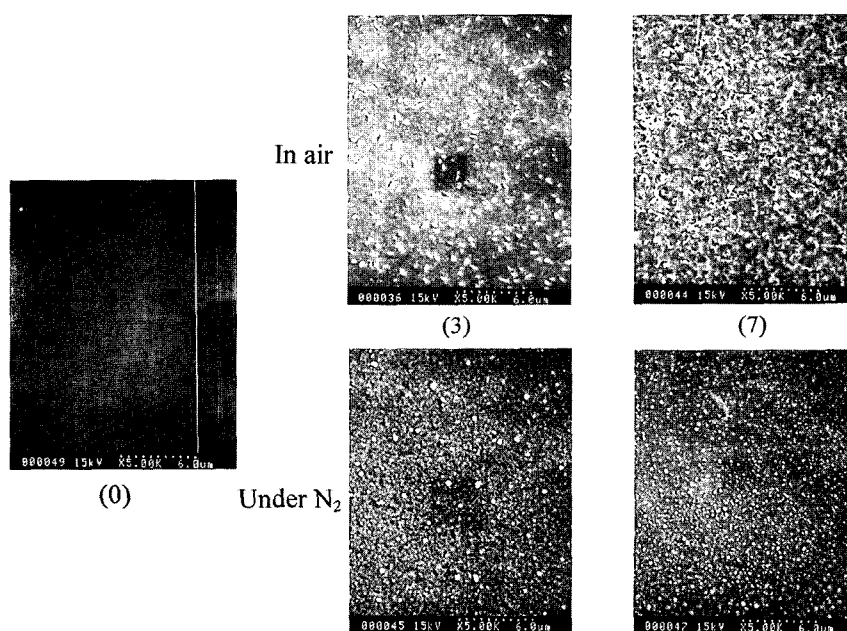
Figure 2. SEM micrograph of the surface of films irradiated with different irradiation time in air and under N_2. The number in parentheses represents the irradiation time.
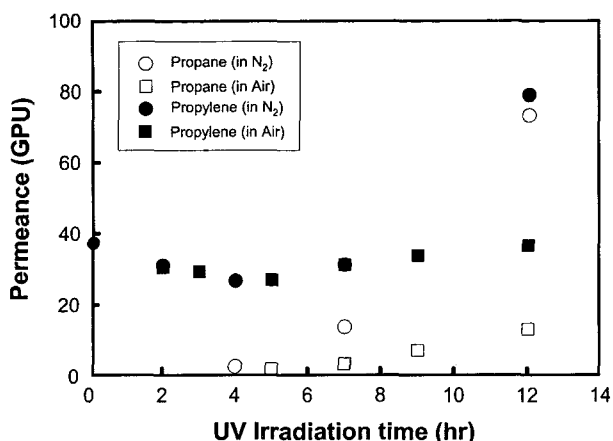
Figure 3. Propane and propylene permeances through silver/POZ composite films with varying UV irradiation time (Δp = 413.5 kPa, T = 23 °C, 1 GPU = 10^{-6} cm^3(STP)/(cm^2 s cmHg)).

Figure 4. Separation coefficient through silver/POZ composite films with UV irradiation time (Δp = 275.6 kPa, T = 23 °C, θ< 0.02).

oxygen at 1, implying that silver polymer electrolytes could be successfully used as a facilitated transport material for the separation of olefin/paraffin mixtures.[5]

Figure 3 shows the pure gas permeance through the silver/POZ membranes with varying irradiation time. At the early stage of the irradiation time for less than 4 hrs in air, the propylene permeance slightly decreased but the propane permeance was remained low not to be detected, therefore a high selectivity of propylene over propane was maintained. The propane permeance start to be detected after 4 hrs of the irradiation under N$_2$ (or 5 hrs in air), implying that the possibility of the formation of defects in the membrane. The defect would be formed first at the interface between the matrix and silver nanoparticle due to their incompatibility[12] and might become bigger with agglomeration. In general, the existence of defects in membranes leads high permeance but no selectivity in gas transport, which is clearly shown for the membrane irradiated under N$_2$ for 12 hrs. This is because the permeances of propylene and propane through defects would be comparable with each other. It is also notable that the propane permeance increases more rapidly for the membrane irradiated under N$_2$ than that in air.

The mixed-gas separation properties of the silver/POZ membrane with varying UV irradiation time were measured in order to evaluate the separation performance. The separation coefficients were determined by the ratio of the mole fraction of the gas components in permeate to that in feed streams, and the results are shown in Figure 4. Note that the ideal separation factor obtained from the pure gas permeance of Figure 3 is at least 350, which is much higher than the mixed gas selectivity from Figure 4. The degree of swelling of the membrane was much higher in the mixed gas experiment than that in pure gas owing to the presence of the highly soluble propylene in the mixed gas. Therefore, the propane permeance may be much high through the highly
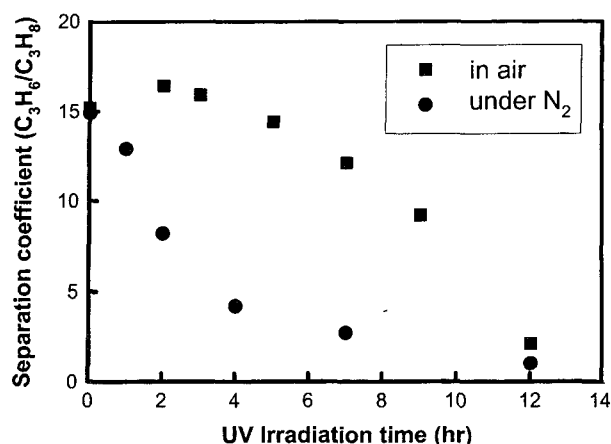
swollen membrane by the mixed gas, compared to that through the far less swollen membrane by pure propane. The difference between them may be associated with the difference in the degree of swelling of the polymer electrolyte membrane for mixed gas and pure propane as well as the concentration polarization. Both of the membranes treated in different environment showed a large difference in the separation coefficient; the separation coefficient of propylene over propane decreased sharply with irradiation for the membrane treated under N$_2$ whereas the significant decrease in the separation coefficient was not observed until the radiation time of 5 hrs in air.

The amount of silver ions left in the silver polymer electrolyte measured by ion conducting electrodes was ca. 60% after 5 hrs of UV irradiation under N$_2$, which is comparable with the one irradiated for 5 hrs in air. Although there are silver species other than silver ion, the separation coefficient remained almost unchanged up to the 2 hrs irradiation. The sustenance of the olefin/paraffin separation coefficient means that there are comparable amount of active species other than Ag$^+$ to form a reversible complex with olefin for a facilitated transport, which could be silver metal particle, some kinds of excited state of silver or highly oxidized silvers[13] created during the UV irradiation. In general, it has been known that the photoreduction results in unstable colloids[14] to be partially oxidized due to the sensitivity of the colloidal silver nanoparticles towards oxidation.[15] Therefore, it would be suggested that silver species other than Ag$^+$ were formed during UV irradiation procedure, which may also act as an olefin carrier to form reversible complexes with olefin for facilitated transport.

Conclusions

When polymer electrolytes containing silver salts are irra-

diated by UV, their UV-VIS spectra, surface morphologies and transport properties strongly depend on their irradiation environment. This result suggests that silver ions in POZ may go through a different photoreduction mechanism depending on the environment, which seems to be associated with the presence of water and oxygen from air. Upon UV irradiation, silver species other than silver ion are formed, but the separation coefficient remained almost unchanged at the early stage of the UV irradiation time. This implies the possible presence of an active olefin carrier other than the silver ion, which makes reversible silver-olefin complexes. The details of silver species formed by UV irradiation and their effect on transport properties are under investigation in this lab.

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