

Sorption of propylene and propane in polyurethane membranes containing silver nanoparticles

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ABSTRACT: The preparation of a facilitated transport membrane of polyurethane (PU) containing silver nanoparticles is reported. The propylene and propane sorption was investigated aiming at the selective separation from C₃s mixtures. The silver particles were photogenerated *in situ* into the polyurethane matrix using UV light radiation and silver triflate (AgCF₃SO₃) as precursor. The morphological properties of these membranes (PUAg) revealed great dispersion of silver particles, which size was smaller than 110 nm. The propylene solubility in PUAg resulted more than four times superior to the one for the pure PU membrane, revealing the high affinity between silver and propylene. Flory–Huggins theory was more accurate to describe the propylene sorption behavior in PUAg than Henry's model. The ideal solubility selectivity of PUAg membrane resulted 24.4, indicating that there is a good potential for an industrial application aiming at the separation of propylene/propane. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42916.

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INTRODUCTION

The separation of propane and propylene mixtures using membranes has been studied for many years aiming to find alternatives to the current cost- and energy-intensive cryogenic distillation process.^{1,2} Polymeric membrane separations are in general based on difference in diffusion or solubility, but similar physical properties of these components allow little for an economically acceptable separation factor. One strategy to enhance the effectiveness of this separation has been to explore the inclusion carrier agents in the membrane matrix to simultaneously increase the olefin solubility and diffusivity by facilitated transport.

In the facilitated transport (FT) membranes, silver ions have been mostly used as olefin carriers since they can reversibly react with olefin molecules through the formation of complexes.^{3–6} Paraffins are unable to complex with silver ions and permeate only by a solution-diffusion mechanism. Therefore, there is a high potential to increase the selectivity and the permeability of the membrane.^{7–14}

However, there are two limiting factors in these FT membrane. First, the silver ion has a tendency of being reduced to Ag⁰ particles leading to a decrease of mechanical stability and selectivity of the membrane.^{15–19} To avoid this effect, many authors have used reduced silver particles as carrier agents and an electron acceptor such as *p*-benzoquinone to induce positive charge in

silver particles to enhance the carrier–olefin interaction.^{20–22} To avoid silver agglomeration, some authors have used PVP as surfactant in the preparation procedures.^{23–27}

The other limiting factor is related to plasticization effect, which is the partial solubilization of membrane caused by strong interaction with gas molecules. The plasticization effect is characterized by an increase in the polymer segmental mobility and in the free volume, leading to higher permeability for all components of the gas mixture. As a consequence, a drastic decrease in the diffusion selectivity occurs in permeation tests of multi-component mixtures.^{28–34}

Pollo *et al.*^{12,14} describe the preparation of FT polyurethane membrane by using silver salt (silver triflate) as carrier agent for propylene transport. In this paper, this methodology was adapted to obtain silver particles as carrier agent in a polyurethane matrix (PUAg), without using further additives. The silver particles were photogenerated *in situ* by using UV light radiation and silver triflate (AgCF₃SO₃) salt as precursor. A detailed sorption study was carried out to better understand the affinity between the C₃s gas molecules and PUAg, as well as the plasticizing effect.

EXPERIMENTAL

Materials

Polyurethane (ether based) was supplied by BASF and used as received. Silver triflate, and tetrahydrofuran (THF) solvent

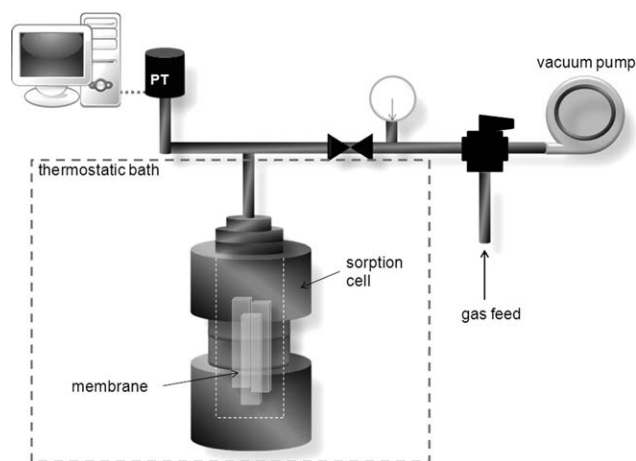


Figure 1. Schematic diagram of the sorption apparatus.

(synthesis grade) were purchased from Aldrich Chemical and used without further purification. The propylene and propane gases (>99.5% purity) were purchased from Linde and used as received.

Membrane Preparation

To prepare flat dense membranes of polyurethane (PU), the polymer was previously dried in an oven at 60°C for 24 h, dissolved in THF solvent and poured over a glass Petri dish. The solvent was allowed to evaporate for 24 h. The resulting PU films were approximately 0.13 mm. To include silver particles in the polyurethane matrix, appropriate amounts of silver triflate (AgCF_3SO_3) salt was added to the polymer solution in order to produce a final membrane containing 50 wt % of salt (dry base).^{12–14} The solution was stirred for approximately 15 min followed by sonication for 30 min and then immediately poured over a glass Petri dish. The solvent was allowed to evaporate while exposed to a UV–vis source (9 mW cm^{-2}) for 15 h to accelerate the silver reduction process. The resulting films were approximately 0.17 mm thick and silver content of 20% (dry base).

Membrane Characterization

Scanning Electron Microscopy. Scanning electron microscopy (SEM) was used to observe the membrane morphology. Surface, cross-section, and silver particles images in membrane were obtained using a Quanta 200 FEI Scanning Electron Microscope (SEM), operated in the secondary electrons detection mode with a 20 or 15 keV accelerating voltage. For the cross-section observation, the samples were fractured under nitrogen liquid. The samples were previously dried and then sputtered with $\sim 300 \text{ \AA}$ of Au (Coating system, Jeol, JFC 1500). Elemental analyses of the specific locus on the membranes were carried out using an energy dispersive spectroscope (EDS) equipped with SEM (SEM–EDS).

Dynamical Mechanical Thermal Analyses. Dynamical mechanical thermal analyses (DMA) were performed on a Perkin Elmer 8000 using tension mode at a frequency of 1 Hz and amplitude of $50 \mu\text{m}$. In this experiment, the heating rate of 3°C min^{-1} was used with a 100–120°C temperature range. The glass transition temperature (T_g) was determined as the peak of $\tan \delta$,

defined by the ration between the loss (E_∞) and storage modulus (E_0).

Solubility Measurement. The gas sorption of propylene and propane was determined by the pressure decay method with a

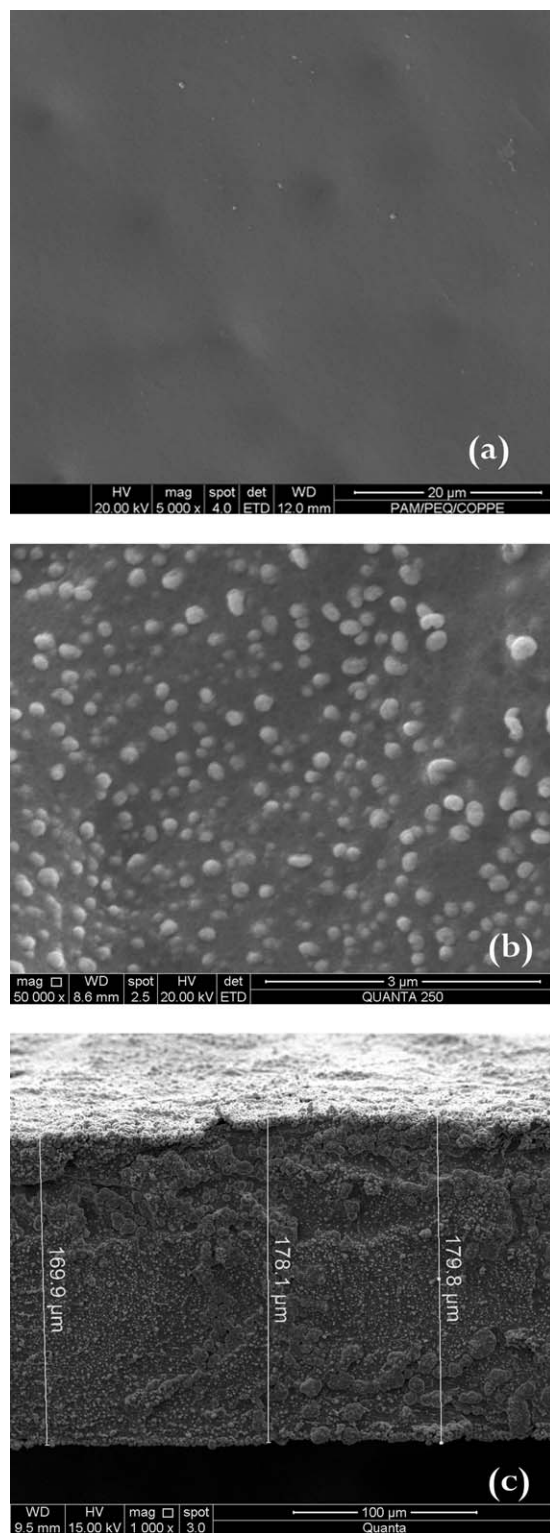


Figure 2. SEM photomicrographs: PU membrane (a), PUAg membrane surface (b), and cross-section of PUAg membrane (c).

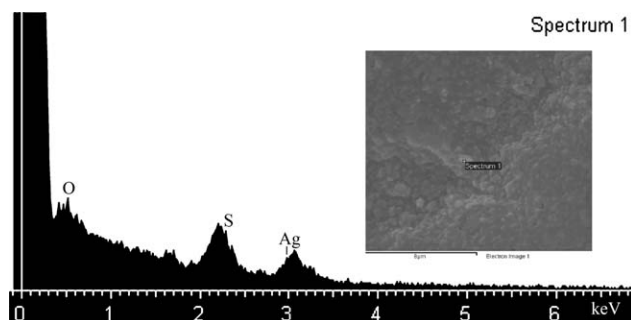


Figure 3. SEM-EDS micrograph of PUAg membrane.

single volume cell as shown in Figure 1.^{35,36} The sorption cell apparatus was maintained in a thermostatic bath. The sorption chamber volume was 58.75 mL. The pressure was monitored by a pressure transducer (Cole Parmer) with a full-scale of 500 psia and an accuracy of 0.04%

PU or PUAg membranes were placed into the cell, which was evacuated for at least 5 h to remove any dissolved gas molecules in the polymer matrix. Next, an appropriate amount of gas was fed into the cell at a desired initial pressure, initiating sorption into the polymer matrix. The pressure decay (ΔP) measurement starts immediately after the cell pressurization and it is related to the gas sorption by the membrane. The solubility coefficient was calculated when equilibrium pressure was reached, using eq. (1).

$$s = \frac{\Delta P V_{\text{sys}} M M_{\text{gas}}}{R T m_{\text{sample}}} \quad (1)$$

where s is gas mass concentration in the membrane (g gas/g pol), ΔP is the difference between initial and final pressures, V_{sys} is the chamber volume, $M M_{\text{gas}}$ is the gas molar mass, R is the gas constant, T is the bath temperature, m_{sample} is the membrane sample mass in the cell (ca. 4 g).

In this study, the solubility measurements were performed at 40 and 50°C and the initial pressure of C_3 ranged from approximately 3–7 bar.

RESULTS AND DISCUSSION

Morphological Characterization

The surface morphology of pure polyurethane membrane (PU) is homogeneous with slight roughness, as can be seen in Figure 2(a). In case of the membrane containing silver nanoparticles, these seem well defined and dispersed in the polyurethane matrix, as shown in Figure 2(b). The nanoparticles have sizes below 110 nm.

Figure 2(c) shows the cross section of the PUAg membrane with an average thickness of 175 μm . It can be observed that silver particles were also homogeneously distributed throughout the membrane cross section.

The energy dispersive spectroscopy (EDS) analysis of PUAg membrane surface reveals the presence of silver and elements oxygen and sulfur (coming from the triflate ion (SO_3CF_3^-)), as shown in Figure 3.

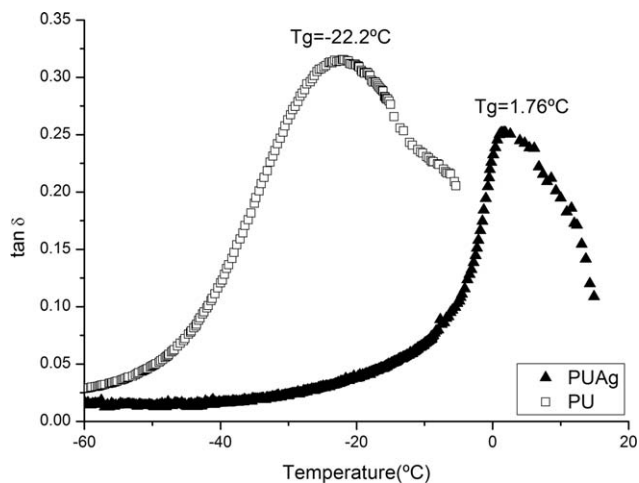


Figure 4. $\text{Tan } \delta$ ($= E_{\infty}/E_0$) of PU and PUAg membranes.

Dynamic Mechanical Analysis (DMA)

Figure 4 shows the loss tangent ($\text{tan } \delta$) curves of PU and PUAg membranes. The $\text{tan } \delta$ maximum values are related to the glass transition temperature (T_g) and it may be observed that addition of silver particles increases T_g from -22.2 to 1.76°C . Thus, it may be inferred that the presence of silver in the polymer matrix reduces the polymer chain mobility.

Sorption Measurement of C_3

The propylene (C_3) solubility was measured at 40°C for PU and PUAg membranes. As shown in Figure 5, the presence of silver particles increases dramatically the solubility of propylene in the PUAg membrane. For example, at approximately 4.5 bar, the PUAg sorbs almost five times more propylene than in pure PU. This provides evidence that the silver particles enhance the interaction between the membrane and propylene.

Table I presents the solubility coefficients (k_D), determined by Henry's law [eq. (2)] for propylene in PU and PUAg membranes. As expected, k_D obtained for PUAg is dramatically enhanced when compared with the pure polymer, increasing

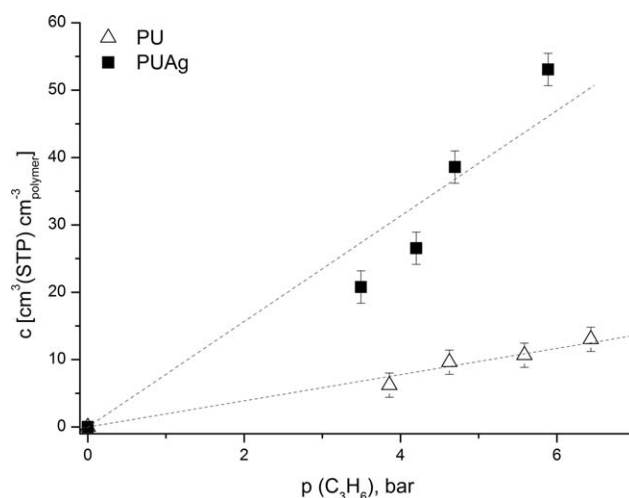


Figure 5. Propylene sorption isotherm for: PU (Δ) and PUAg (\blacksquare) at 40°C and Henry's model.

Table I. Henry's Solubility Constant for PUAg and PU membranes at 40°C

Membrane	k_D [$\text{cm}^3(\text{STP})$ $(\text{cm}^3)^{-1} (\text{bar})^{-1}$]	R^2 (Correlation coefficient)
PUAg	7.82	0.97
PU	1.94	0.99

more than four times. The Henry's model is used to describe the behavior of sorption isotherm for simple gases with low molar mass in elastomeric polymers and under relatively moderate pressures.³⁷

$$c = k_D p \quad (2)$$

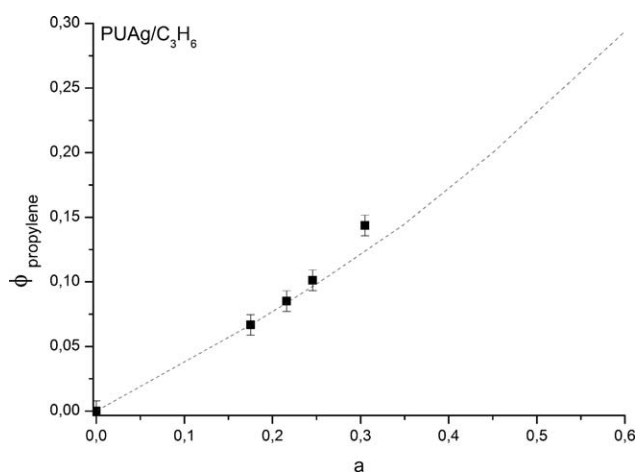
Deviations of Henry's model occur when the membrane swells due to the plasticizing effect by the sorbed molecules. In this case, the solubility coefficient is a function of gas concentration in the membrane matrix, $k_D(c)$

Due to the high affinity between propylene and the PUAg membrane, the sorption process can modify the conformational structure of the polymer, increasing the mobility of polymer segments.³⁷ Therefore, Henry's model seems not to be the better model to describe the experimental sorption data for PUAg-propylene system.

Flory-Huggins theory has already been used to describe the sorption behavior of numerous elastomeric polymers in organic solvents.^{38,39} Equation (3) is representative of this approach and may be applied to a gas/polymer system⁴⁰ such as the one being here investigated.

$$\ln\left(\frac{p}{p_o}\right) = \ln(1 - \Phi_{\text{pol}}) + \Phi_{\text{pol}} + \chi_{1\text{pol}} \Phi_{\text{pol}}^2 \quad (3)$$

where p is the applied propylene pressure, p_o is the saturation pressure, Φ_{pol} is the polymer volume fraction, and χ the Flory-Huggins interaction parameter.

**Figure 6.** Sorption isotherm of propylene in PUAg membranes at 40°C and Flory-Huggins model.**Table II.** Flory-Huggins Interaction Parameter for PUAg and PU at 40°C

Membrane	$\chi_{1\text{pol}}$	R^2 (Correlation coefficient)
PUAg	0.04	0.99
PU	1.3	0.98

As observed in Figure 6, the PUAg-propylene system shows a good agreement with eq. (3), better than that obtained with Henry's model. Table II presents the interaction parameter values for PUAg and PU polymer. The values of interaction parameters for PUAg indicate stronger interaction between propylene-membrane, which is related to the presence of silver particles in the polymer matrix.

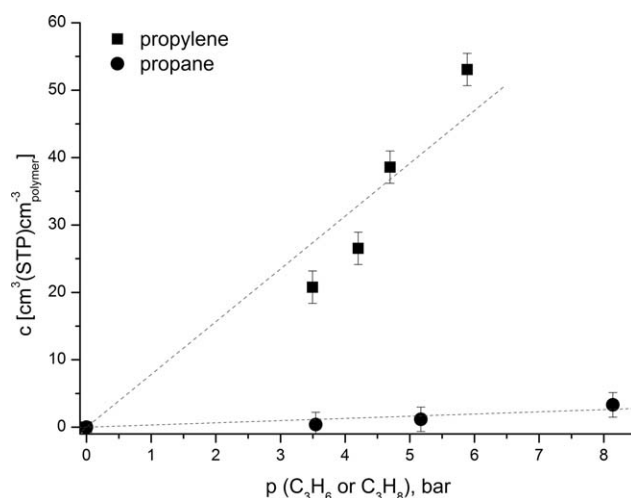
Figure 7 compares the sorption isotherms for propane and propylene in PUAg membrane at 40°C. It can be seen that the propylene concentration is higher than propane in the pressure range of 3–5 bar investigated. The saturated propane molecule does not interact with silver particles and, consequently, a low solubility is observed. The Henry's solubility constant (k_D) calculated for propane is $0.32 \text{ cm}^3 (\text{STP}) (\text{cm}^3)^{-1} (\text{bar})^{-1}$, much lower than $7.82 \text{ cm}^3 (\text{STP}) (\text{cm}^3)^{-1} (\text{bar})^{-1}$ for propylene.

The ideal solubility selectivity (α_s) for PUAg at 40°C was obtained as the ratio of Henry's solubility constants of propylene and propane as defined in eq. (4). It was estimated as being 24.4, and this value indicates that sorption has a strong contribution for the propylene-propane separation in PUAg membranes.

$$\alpha_s = \frac{k_{D\text{propylene}}}{k_{D\text{propane}}} \quad (4)$$

Effect of Temperature on Propylene Solubility Coefficient

The propylene sorption isotherms at 40 and 50°C are showed in Figure 8. As one may observe the propylene solubility decreases at a higher temperature, from 7.82 to $3.70 \text{ cm}^3 (\text{STP}) (\text{cm}^3)^{-1}$

**Figure 7.** Propylene (■) and Propane (●) sorption isotherms in PUAg at 40°C.

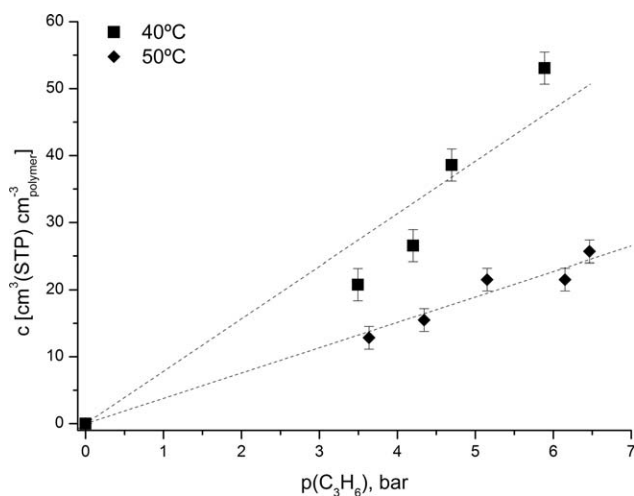


Figure 8. Propylene sorption isotherm for PUAg at: (■) 40°C and (◆) 50°C.

(bar)⁻¹. This is a typical behavior for vapor sorption in elastomeric polymers.³⁶

Barrer (1937) was the first one who showed that the permeation of small-size molecules in rubbery polymers is a thermally activated process. The apparent activation energy for permeation is equal to the sum of the apparent activation energy of the diffusion (E_D) and the heat of the solution (ΔH_S) [eq. (5)].

$$E_p = E_D + \Delta H_S \quad (5)$$

In spontaneous solution process, the Gibbs free energy is negative ($\Delta G < 0$). For dissolution of gases well above their critical temperature, such as H₂, N₂, O₂ at room temperature, the ΔH_S has low contribution, so that $E_p \sim E_D$ in eq. (5). In solution of vapors such as propylene, where the system temperature is below critical temperature, the enthalpic term has a stronger contribution, resulting an increase of the solubility with reduction of temperature. So a slight temperature reduction can lead to a plasticizing effect, as revealed in the deviation of Henry's model, and better described by Flory's model for PUAg membranes at 40°C.

CONCLUSIONS

Polyurethane membrane containing silver nanoparticle (PUAg) were successfully prepared *in situ* by UV reduction of silver triflate salt without any chemical stabilizing agent or charger inducer. Homogeneously dispersed silver particles were observed by SEM, with size below 110 nm. The silver nanoparticle reduced the segmental mobility of polyurethane as observed by thermal mechanical analysis.

It was observed that the PUAg membrane sorbed almost five times more propylene than pure PU, an is evidence that the silver nanoparticles enhance the interaction between the olefin such as propylene and the membrane. This higher propylene affinity of PUAg leads to the deviation of the Henry's model at 40°C. Flory–Huggins theory was more accurate to describe the propylene sorption, indicating a possible plasticizing effect.

The preferential interaction of silver and propylene than for propane was evident by ideal solubility selectivity value of 24.4, which indicates that sorption will probably have an essential contribution for the propylene–propane separation with PUAg membranes.

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REFERENCES

- Colling, C. W.; Huff, G. A, Jr.; Bartels, J. V. US Patent 0004040 A1 January 8, **2004**.
- Aitani, A. In *Encyclopedia of Chemical Processing, New Propylene production*; Lee, S., Eds.; Taylor & Francis: New York, **2006**, p 2461.
- Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697.
- Sakaki, S. *Theor. Chim. Acta (Berl.)* **1973**, *30*, 159.
- Hong, G. H.; Song, D.; Chae, S.; Oha, H.; Kang, S. W. *RSC Adv.* **2014**, *4*, 4905.
- Adachi, K.; Hu, W.; Matsumoto, H.; Ito, K.; Tanioka, A. *Polymer* **1998**, *39*, 2315.
- Pinnau, I.; Toy, L. G. *J. Membr. Sci.* **2001**, *184*, 39.
- Kim, J. H.; Kang, Y. S. *Macrom. Res.* **2004**, *12*, 145.
- Merkel, T. C.; He, Z.; Morisato, A.; Pinnau, I. *Chem. Commun.* **2003**, *13*, 1596.
- Kim, J. H.; Min, B. R.; Won, J.; Joo, S. H.; Kim, H. S.; Kang, Y. S. *Macromolecules* **2003**, *36*, 6183.
- Kang, Y. S.; Won, J.; Hong, S. US patent 6,468,331B2, October 22, **2002**.
- Pollo, L. D.; Duarte, L. T.; Anacleto, M.; Habert, A. C.; Borges, C. P. *Braz. J. Chem. Eng.* **2012**, *29*, 307.
- Duarte, L. T. *Desenvolvimento de Membranas Contendo Metais de Transição para o Transporte Facilitado de Propeno*. PhD Thesis, Universidade Federal do Rio de Janeiro, RJ, Brazil, **2004**.
- Habert, A. C.; Borges, C. P.; Toma, H. E.; Araki, K.; Pollo, L. D. (Petróleo Brasileiro S/A-PETROBRÁS, Universidade Federal do Rio de Janeiro-UFRJ). Brazilian Patent PI 1005594-0 A2, December 30, **2010**.
- Jose, B.; Ryu, J. H.; Lee, B. G.; Lee, H.; Kang, Y. S.; Kim, H. S. *Chem. Comm.* **2001**, *20*, 2046.
- Kim, J. H.; Kim, C. K.; Won, J.; Kang, Y. S. *J. Membr. Sci.* **2005**, *250*, 207.
- Shujahadeen, B. A.; Zul, H. Z. A.; Kadir, M. F. Z. *Phys. Scr.* **2015**, *90*, 1.
- Song, D.; Kang, Y. S.; Kang, S. W. *J. Membr. Sci.* **2015**, *474*, 273.
- Kang, Y. S.; Kang, S. W.; Kim, H.; Kim, J. H.; Won, J.; Kim, C. K.; Char, K. *Adv. Mater.* **2007**, *19*, 475.
- Kang, S. W.; Char, K.; Kang, Y. S. *Chem. Mater.* **2008**, *20*, 1308.

21. Chae, I. S.; Kang, S. W.; Park, J. Y.; Lee, Y.; Lee, J. H.; Won, J.; Kang, Y. S. *Angew. Chem. Int. Ed.* **2011**, *50*, 2982.
22. Kang, S. W. *Macromol. Res.* **2010**, *18*, 705.
23. Zhang, Z.; Zhao, B.; Hu, L. *J. Sol. State Chem.* **1996**, *121*, 105.
24. Kang, S. W.; Kang, Y. S. *J. Colloid Interface* **2011**, *353*, 83.
25. Zhang, J.; Chen, P.; Sun, C.; Hu, X. *Appl. Catal. A: Gen.* **2004**, *266*, 49.
26. Zhang, W.; Qiao, X.; Chen, J.; Wang, H. *J. Colloid Interface* **2006**, *302*, 370.
27. Chae, I. S.; Kang, S. W.; Kang, Y. S. *RSC Adv.* **2014**, *4*, 30156.
28. Wessling, M.; Schoeman, J.; van der Boomgaard, T.; Smolders, C. A. *Gas Sep. Purif.* **2001**, *5*, 222.
29. Visser, T.; Wessling, M. *J. Membr. Sci.* **2008**, *312*, 84.
30. Koros, W. J.; Fleming, G. K. *J. Membr. Sci.* **1993**, *83*, 1.
31. Staudt-Bickel, C.; Koros, W. J. *J. Membr. Sci.* **2000**, *170*, 205.
32. Ko, D.; Kim, J. H.; Kang, S. W.; Lee, D. H.; Wond, J.; Kang, Y. S. *J. Indus. Eng. Chem.* **2009**, *15*, 8.
33. Krol, J. J.; Boerrigter, M.; Koops, G. H. *J. Membr. Sci.* **2001**, *184*, 275.
34. Esmaeili, M.; Madaeni, S. S.; Barzin, J. *J. Appl. Polym. Sci.* **2013**, *129*, 1569.
35. Koros, W.; Paul, J. D. R. *J. Polym. Sci. Polym. Phys. Ed.* **1976**, *14*, 1903.
36. Stannett, V. Simple Gases, in *Diffusion in Polymers*; Crank, J., Park, G. S., Eds.; Academic Press: London and New York, **1968**, p 41.
37. Klopffer, M. H.; Flaconnèche, B. *Oil Gas Sci. Technol.* **2001**, *56*, 223.
38. Favre, E.; Nguyen, Q. T.; Schaetzel, P.; Clement, R.; Nee, J. *J. Chem. Soc. Farad. Trans.* **1993**, *89*, 4339.
39. Sadrzadeh, M.; Shahidi, K.; Mohammadi, T. *J. Appl. Polym. Sci.* **2010**, *117*, 33.
40. Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.