

Influence of Reactant Concentration on Formation of AgCl Particles in PEO–PPO–PEO Microemulsion and Morphology and Performance of AgCl–PMMA Membranes

Li-Guang Wu, Ting Wang, Wen Xiang, Chun-Hui Du

College of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

Received 27 May 2011; accepted 4 August 2011

DOI 10.1002/app.35421

Published online 21 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: AgCl/poly(methyl methacrylate) (PMMA) organic–inorganic hybrid membrane has been synthesized by reverse microemulsion polymerization using triblock copolymer polyoxyethylene–polyoxypropylene–polyoxyethylene as surfactant and MMA as oil phase. The results by ultraviolet–visible spectrum, transmission electron microscopy, and scanning electron microscopy showed that small AgCl nanoparticles distributed well in the F127 microemulsions and hybrid membranes at low reactant concentration. AgCl nanoparticles in the microemulsion became smaller with increasing reactant concentration. However, AgCl nano-

particles aggregated obviously in hybrid membranes, when reactant concentration was more than 0.15 mol L^{-1} . The performance of different hybrid membranes for separation of the benzene and cyclohexane was measured. The results indicated that the separation performance of membrane was promoted obviously due to presence of more well-dispersed AgCl particles in hybrid membranes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3463–3467, 2012

Key words: membranes; morphology; nanocomposites; microemulsion; benzene/cyclohexane mixtures

INTRODUCTION

With wide application of membrane separation in environment removal and chemical industry, researches on synthesis of membrane have paid more attention in enhancing the separation performance of membranes significantly. Because of excellent separation performance for some organic compounds, inorganic filled organic–inorganic hybrid membranes have attracted much interest.^{1–4} For instance, membranes filled with AgCl nanoparticles could separate several olefin/alkanes efficiently, due to π -complexation between Ag ion in membranes and unsaturated hydrocarbons.^{5,6}

Recently, many preparation methods of organic–inorganic hybrid membranes have been reported.^{7–11} In particular, in situ microemulsion polymerization was one of note-worthy preparation methods. By this method, nanoparticles were prepared first in microemulsion that consisted of surfactant, water, and polymerizable monomer, like methyl methacrylate (MMA). Then hybrid membranes filled with nanoparticles were synthesized after polymerization

of monomer.¹² Change in conditions could regulate the morphology of nanoparticles during preparation process of microemulsion. Then, hybrid membranes with different performances were prepared after polymerization of MMA. However, small-molecule surfactants like dioctyl sodium succinate (AOT) were usually used as emulsifiers in recent researches on microemulsion situ polymerization. These small-molecule surfactants were evaporated during polymerization to form membranes, which destroyed the structure of microemulsion and the protection of water pool on nanoparticles. So during polymerization, nanoparticles aggregated to form large particles due to absence of protection and even became big particles with several micrometers.¹² Both the continuous structure and the performance of hybrid membrane were damaged greatly due to the existence of big particles in membranes. Therefore, researches on preparation of hybrid membranes were focused on how to maintain the morphology and dispersion of nanoparticles in membranes during polymerization. However, detailed researches about this have not been reported.

In this article, polyoxyethylene–polyoxypropylene–polyoxyethylene (PEO–PPO–PEO, F127) triblock copolymer was used as surfactant to form microemulsion and prepare AgCl nanoparticles. As it could not be evaporated during polymerization to form membranes, the morphology and dispersion of AgCl nanoparticles could be maintained well in membranes. Then preparation experiments under different conditions were designed to explore the

Correspondence to: T. Wang (zjwwaiting@yahoo.com.cn).

Contract grant sponsor: National Science Foundation of China; contract grant numbers: 20876144, 21076190, 20806071.

TABLE I
Different Conditions in Preparation Experiments of AgCl Nanoparticles in F127 Microemulsions

Microemulsion number	Concentration of AgNO ₃ (mol L ⁻¹)	Concentration of NaCl (mol L ⁻¹)	Concentration of F127 (mol L ⁻¹)	ω ^a	Reaction time (min)
I	0.15	0.15	0.08	5	30
II	0.20	0.20	0.08	5	30
III	0.25	0.25	0.08	5	30

^a ω was H₂O to surfactant mole ratio in the microemulsion.

influence of conditions on the morphology of AgCl nanoparticles and its regulation on performance of organic–inorganic hybrid membranes.

EXPERIMENTAL

Materials

PEO–PPO–PEO triblock copolymer Pluronic F127 with a molecular weight of 12,600 and a PEO content of 70 wt % was purchased from Sigma-Aldrich (St Louis, USA). AgNO₃ was purchased from Shanghai Reagent Factory. NaCl was supplied by Shanghai Chemical Reagent Co. MMA, purchased from Chengdu Chemical Reagent Factory, was purified by vacuum distillation. 2-Azobisisobutyronitrile (AIBN) was obtained from Shanghai Chemical Reagent Co.

Preparation of AgCl nanoparticles and AgCl/PMMA hybrid membranes

Preparation of AgCl nanoparticles

A 1.5 g portion of Pluronic F127 (99% pure, Sigma-Aldrich) and 15 mL of MMA were placed in two flasks. AgNO₃ (or NaCl) solution (30 μL) with different concentrations (as listed in Table I) was added into the flasks in ultrasonic bath at room temperature. After 10 min, the homogeneous AgNO₃ and NaCl microemulsions were obtained, respectively. AgCl nanoparticles were generated by mixing the two kinds of microemulsions for 30 min.

Preparation of AgCl/PMMA hybrid membranes

The initiating agent AIBN was added into the MMA microemulsions (30 mL) that contained AgCl nanoparticles. The microemulsions were stirred to polymerize below 60–65°C. After polymerization for 2 h, the reaction solution was coated on a polysulfone film (cut-off molecular weight of 20,000). Then AgCl/PMMA hybrid membranes on the polysulfone film were obtained by continuing the reaction for 12 h below 60–65°C. The thickness of the top nanocomposite (casted film) layer was found to be approximately 25 μm using scanning electron microscopy (SEM).

Pervaporation experiments of benzene/cyclohexane mixtures

The membrane was positioned in the stainless-steel permeation cell, the membrane area in contact with the feed was 19.6 cm², the temperature of the cell was thermostatically controlled, and the vacuum at down streamside was maintained at about 160 Pa by a vacuum pump. The experiments were carried out in a continuous steady state, operated at constant temperature of 30°C for benzene/cyclohexane mixture. The pervaporation (PV) vapor was condensed by liquid nitrogen (N₂). After running the PV apparatus for 2 h, the composition of the permeation was analyzed by gas chromatography (GC-950, Shanghai Haixin Chromatography Instruments Co., China) equipped with a Thermal Conductivity Detector (TCD) detector.

Separation performance of a membrane is characterized by two parameters: flux and selectivity. Flux is defined as the rate of permeation of feed components through unit area of membrane at unit time. Two commonly used flux units in PV processes are kg m⁻² h⁻¹ and g cm⁻² s⁻¹. The permeation flux (*J*) and the separation factor (*α*) for all members were calculated according to the following equations:

$$J = \frac{\Delta m}{S \cdot \Delta t} \quad (1)$$

$$\alpha(A/B) = \frac{Y_A/Y_B}{X_A/X_B} \quad (2)$$

where Δm is permeated weight during operation time Δt , α is selectivity (separation factor), *X* and *Y* are molar concentrations of components in feed and permeate, respectively. A and B subscripts denote the two components to be separated.

Characterization

The ultraviolet (UV) absorption of AgCl nanoparticles in microemulsion was measured by UV-2450 spectrophotometer (Shimadzu Co., Japan). The wavelength was in the range from 280 to 650 nm. The morphology of AgCl nanoparticles was characterized by transmission electron microscopy (TEM; JEM-1230, JEOL, Japan). The surface of membranes

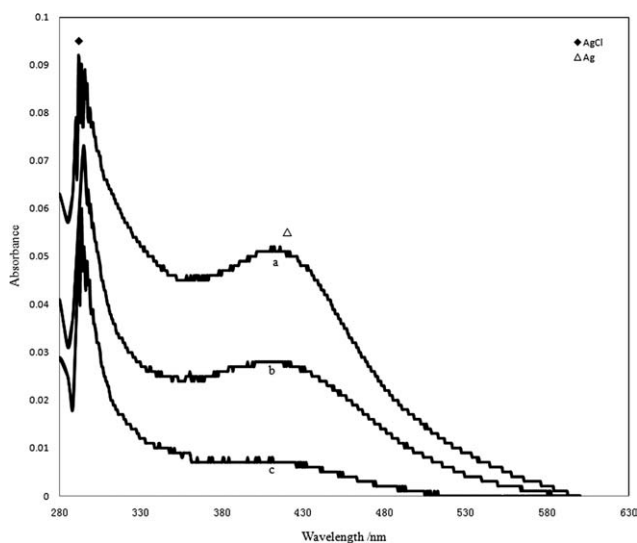


Figure 1 UV absorption spectra of AgCl nanoparticles under different reactant concentrations. Reaction time was 30 min, $\omega = 5$ (H_2O to surfactant mole ratio in the microemulsion), $C_{\text{F127}} = 0.008 \text{ mol L}^{-1}$, $C_{\text{NaCl}} = C_{\text{AgNO}_3}$: (a) 0.25 mol L^{-1} ; (b) 0.20 mol L^{-1} ; (c) 0.15 mol L^{-1} .

containing AgCl nanoparticles (casted film) were analyzed by SEM (S-4700, Hitachi, Japan).

RESULTS AND DISCUSSION

Influence of reactant concentration on formation of AgCl nanoparticles in water pool

Formation of AgCl nanoparticles under different reactant concentrations in microemulsion was characterized by UV absorption spectra, as shown in Figure 1.

Figure 1 shows the characteristic adsorption peaks at 292 nm that appeared in all UV spectra of microemulsion under different reactant concentrations. The results in literature¹³ indicated that AgCl nanoparticles were formed in the microemulsion. With increase of reactant concentration, the peaks at 292 nm became stronger which meant more AgCl nanoparticles were formed in the microemulsion. The size of AgCl particles decreased with increasing concentration, due to the wider characteristic peaks of AgCl in UV spectra.¹⁴ When reactant concentration was low, formation rate of AgCl particles became slow. Ag^+ and Cl^- were mainly consumed for the growth of nuclei. Whereas, large amount of AgCl particles were formed soon at high concentration of reactant and reactant was consumed completely for the formation of new nuclei. So, the size of AgCl particles gained at low reactant concentration was larger than those prepared at high concentration of reactant.¹⁵

In addition, it is also found in Figure 1 that a characteristic adsorption peak of Ag (at 420 nm)¹⁶ appeared obviously in UV spectra at high reactant

concentration (more than 0.15 mol L^{-1}). It meant that Ag particles were formed in the microemulsion when concentration of reactants was more than 0.15 mol L^{-1} . It might be due to the reduction of a few Ag ions during the ultrasonic process at high reactant concentration.

Morphology of nanoparticles formed in microemulsion by TEM analysis

Figure 2 shows the TEM photographs of nanoparticles formed in microemulsion and their particle size distribution under different reactant concentrations.

From TEM pictures, the average sizes of nanoparticles formed in microemulsion are all less than 10 nm under different reactant concentrations. Comparing with the morphology of AgCl particles in literature,¹² it was found that the average sizes of

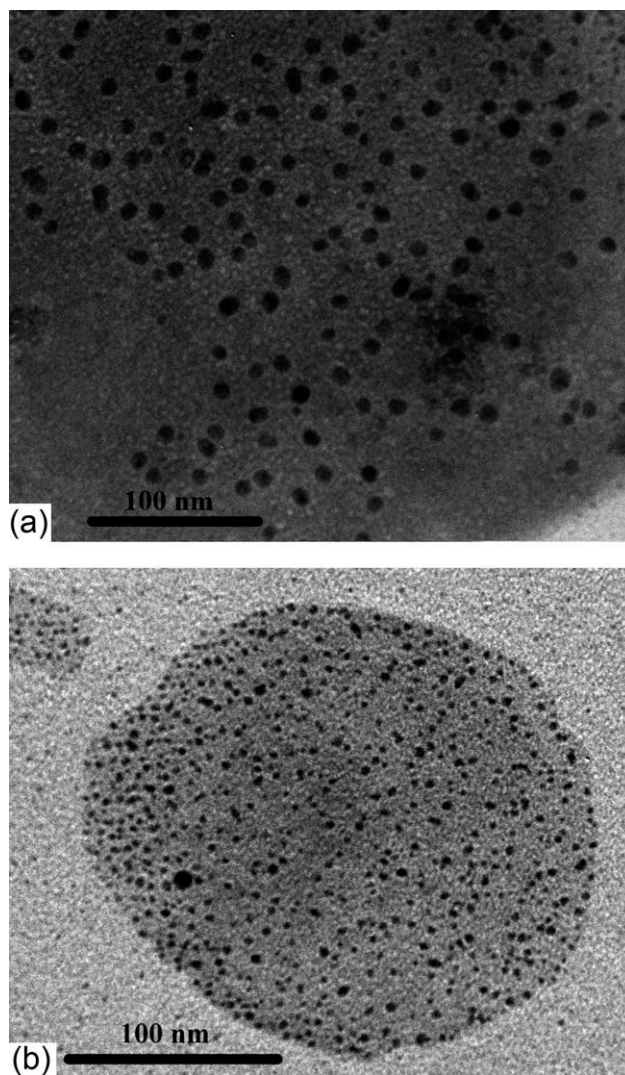


Figure 2 TEM photographs and the corresponding particle size distribution under different concentrations of reactant salt. Reaction time was 30 min, $\omega = 5$, $C_{\text{F127}} = 0.008 \text{ mol L}^{-1}$, $C_{\text{NaCl}} = C_{\text{AgNO}_3}$: (a) 0.15 mol L^{-1} ; (b) 0.25 mol L^{-1} .

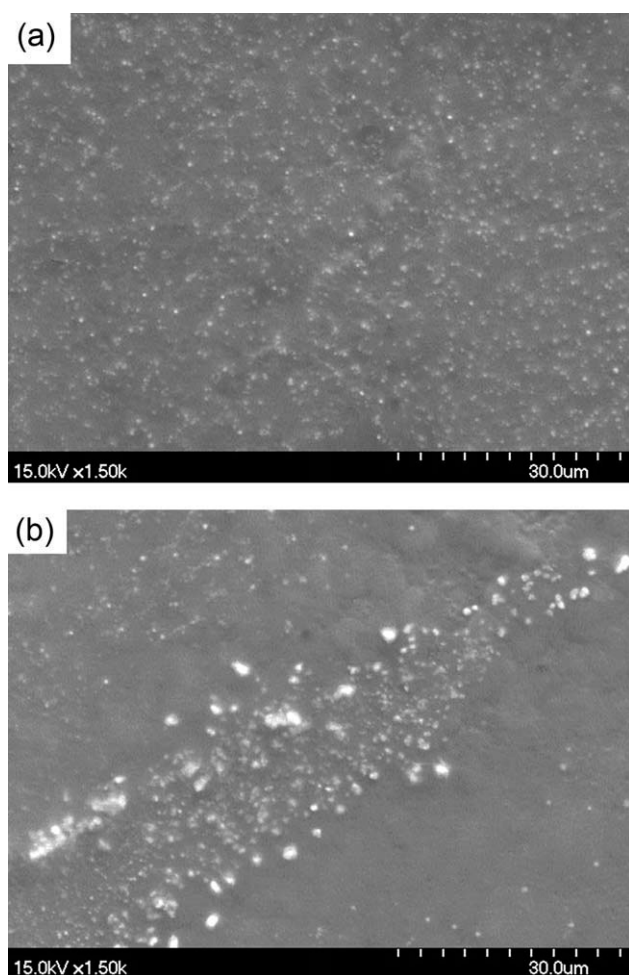


Figure 3 SEM photograph of AgCl/PMMA hybrid membrane under different concentrations of reactant salt. $\omega = 5$, $C_{F127} = 0.008 \text{ mol L}^{-1}$, $C_{NaCl} = C_{AgNO_3}$: (a) 0.15 mol L^{-1} ; (b) 0.25 mol L^{-1} .

nanoparticles generated in microemulsion using F127 as surfactant was close to those in microemulsion using AOT as surfactant. With increase in reactant concentration, the nanoparticles formed in the microemulsion become small. This result was consistent with conclusion by UV spectra analysis in Influence of Reactant Concentration on Formation of AgCl Nanoparticles in Water Pool section.

From the results of UV spectra analysis, it can be inferred that few particles that appeared in TEM pictures at high reactant concentration (0.25 mol L^{-1}) might be Ag nanoparticles, but it could not be distinguished obviously from the morphology of AgCl particles by TEM analysis.

Morphology of AgCl/PMMA hybrid membranes by SEM analysis

As shown in Figure 3, there are spherical AgCl nanoparticles distributed homogeneously in the hybrid membrane (white highlights), when concen-

tration of reactant salt was low. AgCl nanoparticles in F127/MMA membrane were much smaller than those in hybrid membranes gained using AOT as surfactant.¹² Comparing with the morphology of AgCl nanoparticles in TEM pictures, it was found that AgCl nanoparticles in hybrid membrane were a little bigger than those before polymerization. It might be ascribed to coating the AgCl nanoparticles by PMMA during polymerization process. Otherwise, the replacement of interface energy between monomer and surfactant was by that of polymer and surfactant before and after polymerization led to the changing of interface energy and AgCl particle agglutination.

However, it is also found that there are some nanoparticles aggregated to form large particles in membranes at high concentration of reactant salt. Combining with the results by UV spectra and TEM analysis, the obvious aggregation might be due to increase of nanoparticles at high reactant concentration. When more particles were formed in the emulsion, the distance between the small particles became short. So during the polymerization process, particles with short distance were easier to aggregate. In addition, generation of Ag nanoparticles at high reactant concentration might also lead to the aggregation.

Separation performance of hybrid membranes for benzene/cyclohexane mixtures

The performance of hybrid membranes was evaluated by separation of benzene/cyclohexane mixtures, as shown in Figure 4. It is found in Figure 4 that the separation performance of membranes is obviously enhanced due to fill with AgCl nanoparticles. With increasing concentration of reactant salt,

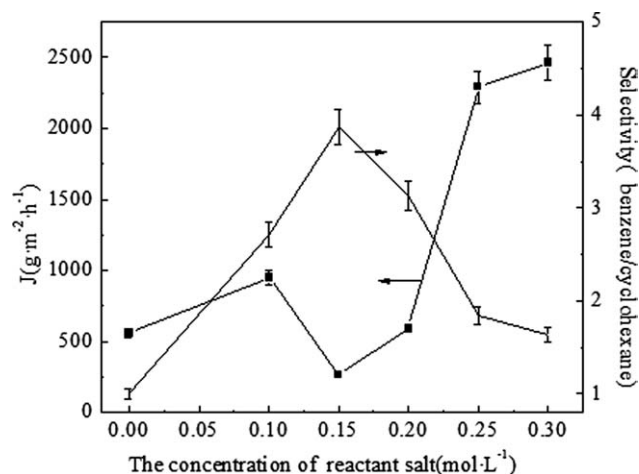


Figure 4 Effect of reactant salt concentration on permeation flux and separation factor of AgCl/PMMA hybrid membranes. Experimental temperature: 30°C , feed composition: $X_{\text{benzene}} = 50 \text{ wt } \%$.

selectivity of hybrid membranes for benzene/cyclohexane mixtures increased first and then decreased. When reactant salt concentration was 0.15 mol L^{-1} , separation performance of hybrid membrane reached the maximum. At low reactant concentration, AgCl nanoparticles became more with concentration of reactant salt increasing and more AgCl particles filled in the hybrid membranes, which resulted in significant enhancement of separation performance of membrane. However, it was found by SEM analysis that small AgCl particles aggregated to form large particles in membrane after polymerization, when concentration of reactant salt was high (more than 0.15 mol L^{-1}). The appearance of big inorganic particles reduced obviously the separation performance of membranes. In addition, the performance of membranes also decreased due to generation of Ag nanoparticles at high concentration of reactant salt.

CONCLUSIONS

Small AgCl nanoparticles (less than 10 nm of size) could be generated in the microemulsion using F127 as surfactant. With increasing reactant concentration, the number of smaller AgCl particles also increased. However, many Ag particles would appear in the microemulsion when reactant concentration was high than $0.15 \text{ mol}\cdot\text{L}^{-1}$. The performance of hybrid membranes filled with AgCl nanoparticles was higher than that of PMMA membranes without

nanoparticles. With increasing of reactant salt concentration, the separation performance of hybrid membranes reached maximum. Both formation of more AgCl particles and appearance of Ag led to the aggregation of nanoparticles in AgCl/PMMA hybrid membranes, which depressed the separation performance of hybrid membranes for benzene/cyclohexane mixtures.

References

1. Ye, L.; Liu, Q.; Zhang, Q.; Zhu, A.; Zhou, G. *J Appl Polym Sci* 2007, 105, 3640.
2. Liu, J.; Ma, Y.; Hu, K.; He, H.; Shao, G. *J Appl Polym Sci* 2010, 117, 2464.
3. Koh, J. H.; Kang, S. W.; Park, J. T.; Seo, J. A.; Kima, J. H.; Kang, Y. S. *J Membr Sci* 2009, 339, 49.
4. Kulkarni, S. S.; Kittur, A. A.; Kariduraganavar, M. Y.; Davis, F. J. *J Appl Polym Sci* 2008, 109, 2043.
5. Teramoto, M.; Takeuchi, N.; Maki, T.; Matsuyama, H. *Sep Purif Technol* 2002, 28, 117.
6. Kima, J. H.; Won, J.; Kanga, Y. S. *J Membr Sci* 2004, 237, 199.
7. Wu, Y.; Wu, C.; Gong, M.; Xu, T. *J Appl Polym Sci* 2006, 102, 3580.
8. Wu, C.; Wu, Y.; Xu, T.; Fu, Y. *J Appl Polym Sci* 2008, 107, 1865.
9. Kumar, R.; Pandey, A. K.; Dhara, S.; Misra, N. L.; Ramagiri, S. V.; Bellare, J. R.; Goswami, A. *J Membr Sci* 2010, 352, 247.
10. Wu, C.-S. *J Appl Polym Sci* 2004, 92, 1749.
11. Kang, S. W.; Lee, D. H.; Park, J. H.; Char, K.; Kim, J. H.; Won, J.; Kang, Y. S. *J Membr Sci* 2008, 322, 281.
12. Shen, J. N.; Zheng, X. C.; Ruan, H. M.; Wu, L. G.; Qiu, J. H.; Gao, C. J. *J Membr Sci* 2007, 304, 118.
13. Bagwe, R. P.; Khilar, K. C. *Langmuir* 2000, 16, 905.
14. Zhang, W. Z.; Qiao, X. L.; Chen, J. G. *Chem Phys* 2006, 330, 495.
15. Husein, M. M.; Eva, R.; Vera, J. H. *J Nanopart Res* 2007, 9, 787.
16. Singh, N.; Khanna, P. K. *Mater Chem Phys* 2007, 104, 367.