Study on Swelling Behavior and Pervaporation Properties of AA–MMA–BA Copolymers for Separation of Methanol/MTBE/C_5 Mixtures

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ABSTRACT: In this study, the copolymers with different ratios of AA(acrylic acid)–MMA(methyl methacrylate)–BA (butyl acrylate) are synthesized to prepare pervaporation membrane for the separation of methanol/MTBE (methyl *tert*-butyl ether)/C_5 mixtures. Swelling experiment of these copolymers in pure methanol, MTBE, C_5, and methanol/MTBE mixtures are carried out, respectively. The results show that there is a strong interaction between MTBE and copolymer with high content of BA. The pervaporation characteristics of the membranes prepared with different copolymer are measured in the separation of methanol/MTBE mixture. The experimental results show that the pervaporation ability changes with swelling degree in the same direction. The copolymers are characterized by FTIR. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2267–2271, 2003

INTRODUCTION

Currently, petrochemical mixtures are separated by physical or chemical adsorption process, low-temperature distillation at high pressure, azeotropic and extractive distillation. The high investments and energy consumption of these technologies provide the incentive for continuous efforts to develop more economic separation processes. The pervaporation separation is considered as one of the most promising processes for energy-saving and efficient separation technology. It is the potential method to separate azeotropic mixtures, mixtures having nearly the same boiling points, heat-sensitive compounds, and structural isomers. Then, there has been increased use of the pervaporation membrane technique in recent years, for the selective separation of organic liquid mixtures. In general, pervaporation membranes have to be either fully dense nonporous membranes or composite-type membranes because petrochemical mixtures of small organic molecules cannot be separated through porous membranes.

Now, the number of research on pervaporation has been carried out and reported; however, these studies have not been applied in large-scale for the organic–organic mixtures separation in the petrochemical industry. This is mainly due to the lack of appropriate membranes for these specific applications. Many studies have been concentrated on the development of tailor-made membrane materials for these applications, such as the synthesis of new (co)polymers,[1–4] the modification of the existing polymers,[5–8] and the blending of polymers.[9–12] The synthesis of new (co)-polymers is the feasible way to obtain special membrane materials; these new (co)polymers showed an improved permselectivity for they contained specific groups that could preferentially interact with one component of the mixture.

As is well known, AA (acrylic acid) is a highly hydrophilic reagent, BA (butyl acrylate) is a hydrophobic reagent, and the hydrophilia of MMA(methyl methacrylate) is between that of AA and BA. The hydrophilia of the homopolymers prepared from the three monomers are consistent to their monomers. It could be presumed that the copolymers with different ratios of AA–MMA–BA have different hydrophilia, and the hydrophilia could be changed by adjusting the copolymer composition. In the present article, the copolymers with different ratios of AA–MMA–BA are synthesized to prepare pervaporation membrane for the separation of methanol/MTBE/C_5 mixtures.

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EXPERIMENTAL

Materials and copolymerization of AA–MMA–BA

MTBE from Zhejiang Refining Company, and C_5 from Qilu Petrochemical Corporation, both were of indus-

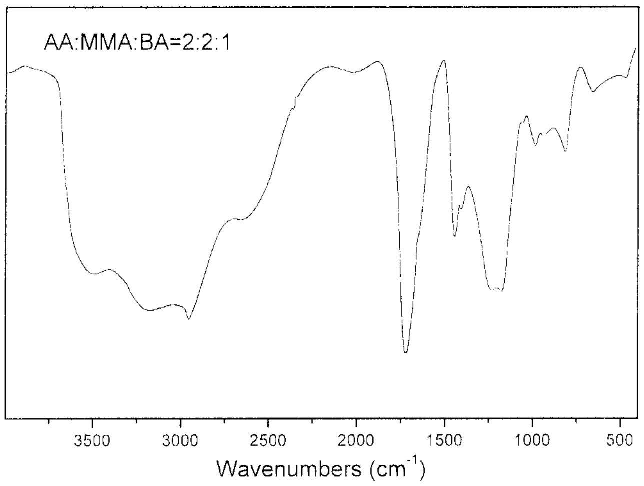

Figure 1 Diagram of FTIR spectra analysis for membrane from the AA–MMA–BA(2 : 2 : 1) copolymer.

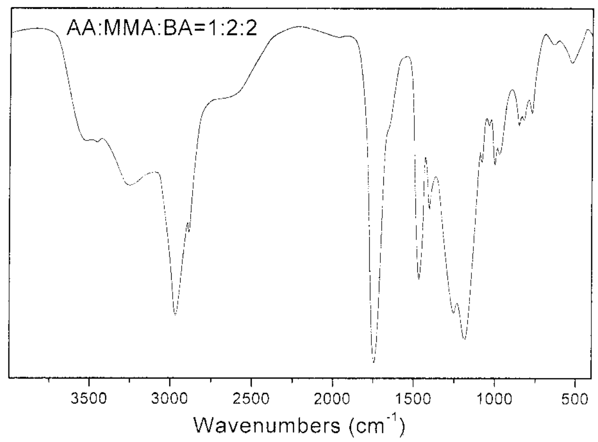

Figure 3 Diagram of FTIR spectra analysis for membrane from the AA–MMA–BA (1 : 2 : 2) copolymer.

trial grade. Other reagents in the experiment were of chemical grade, from Hangzhou Chemical Reagent Supply Station. The comonomers, AA, MMA, and BA in different ratios (such as 1 : 1 : 1, 2 : 2 : 1, 1 : 2 : 1) were mixed in a glass reactor. The copolymerizations were carried out at 30°C for 5 h in the presence of azodiisobutyronitrile as an initiator. Then the reaction mixture is slowly heated up to 55°C, and the reaction proceeds at the temperature for 5 h. After that, the temperature is raised to 65°C for continuing copolymerization until the monomers vanishes. The random copolymers with viscosity-average molecular weight of about 220,000 are gained.

Experiments of swelling

The swelling experiment is carried out in the following steps. At first, immerse the dry specimens of the copolymer in pure methanol, MTBE, C_5, or the mixtures of methanol and MTBE, respectively, at room temperature for a sufficient time until a constant weight is obtained. Then removed from these liquids, and clean the free liquid on the surface of the swollen copolymer carefully by using filter paper. The degree of swelling (S) of the copolymer at a given time is defined by the following equation:

$$S = \frac{m_t - m_0}{m_0}$$

where m_0 and m_t are the weights of dry copolymer and swollen copolymer at a definite time, respectively.

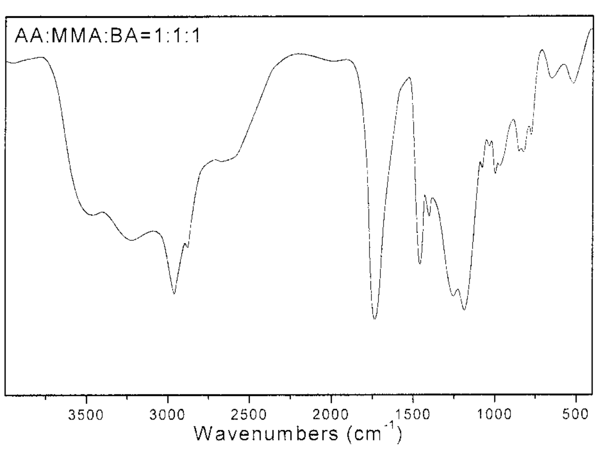

Figure 2 Diagram of FTIR spectra analysis for membrane from the AA–MMA–BA (1 : 1 : 1) copolymer.

Preparation of membrane

The preparative procedure of the membranes is as follows: dissolve the copolymers in THF (tetrahydrofuran) to keep the concentration of the casting solution of 8 g/100 mL, then allow the casting solution to stand at room temperature for 72 h. The pervaporation membranes are obtained by casting the solution on PAN ultrafiltration asymmetric membrane as a support layer. All the membranes with about 23 μm in thickness have been prepared by the dry phase transform method. The evaporating temperature of solvent is maintained at about 30°C.

Pervaporation experiments

The pervaporation experiments were conducted in an equipment as reported previously.[13] The vacuum system in the downstream side was maintained under about 150 ± 30 Pa. The experiments were carried out in a continuous steady state, operated at constant temperature for methanol/MTBE mixture. The permeate was condensed by liquid nitrogen. The separation factor, α, and the permeate flux, J, for all membranes were calculated according to the following equations.

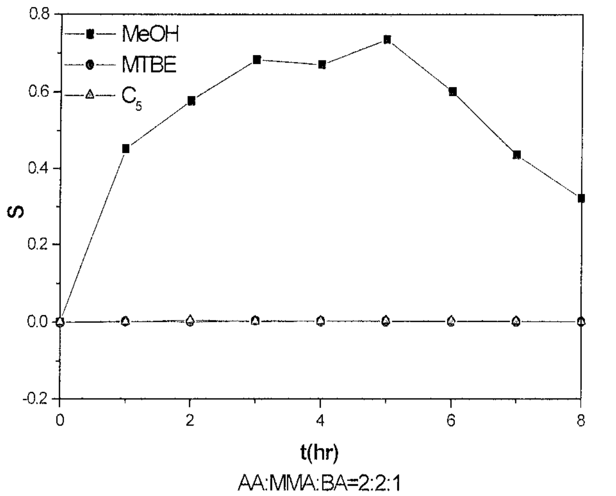

Figure 4 Swelling behaviors of copolymers with 2 : 2 : 1 for pure methanol, MTBE, and C_5.

$$J = \frac{\Delta g}{A \times \Delta t} \qquad \alpha = \frac{y_1/y_2}{x_1/x_2}$$

where Δg, A, and Δt is the weight of permeate, the membrane area, and the time of experiment, respectively, and x and y represent the weight fractions in the feed and in the permeate respectively. Indices 1 and 2 refer to methanol and MTBE, respectively.

RESULTS AND DISCUSSION

Properties of the copolymers

From Figures 1, to 3 it can be seen that the —CH_3 and —CH_2 absorbance peaks for these copolymers are different from 2800–3000 cm^{-1}, and that the peaks became narrower with an increase of BA content in the copolymer. At the same time, the absorption bands at

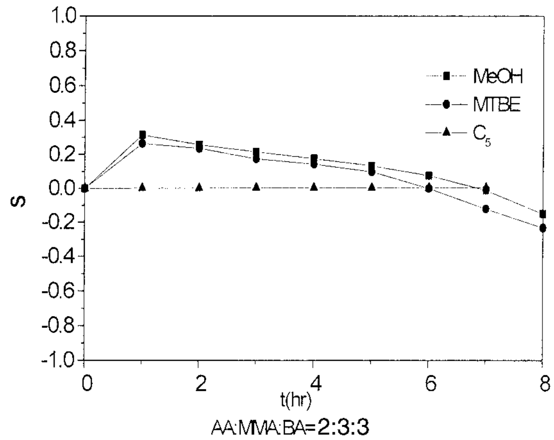

Figure 6 Swelling behaviors of copolymers with 2 : 3 : 3 for pure methanol, MTBE, and C_5.

3570–3100 cm^{-1} in these copolymers are weakened, which are characteristic bands of poly(acrylic acid).[14] Compared with the FTIR spectra of three homopolymers,[14] the FTIR spectra of copolymers are the superimposition of those of three homopolymers with different ratios. The FTIR spectrograms of membranes show that copolymers with high content of BA are more hydrophobic.

Swelling behavior of copolymers

The swelling experiments are carried out by immersing the copolymer specimens with different compositions in pure methanol, MTBE, and C_5, respectively. It is found that the copolymers with 2 : 2 : 1 (AA : MMA : BA) ratios do not swell in pure C_5 and MTBE, and has a strong swelling in methanol (as Fig. 4). Figure 5 shows that there is no interaction between the copolymer with a 1 : 1 : 1 ratio and pure C_5, and this copolymer is swollen in pure MTBE, and also re-

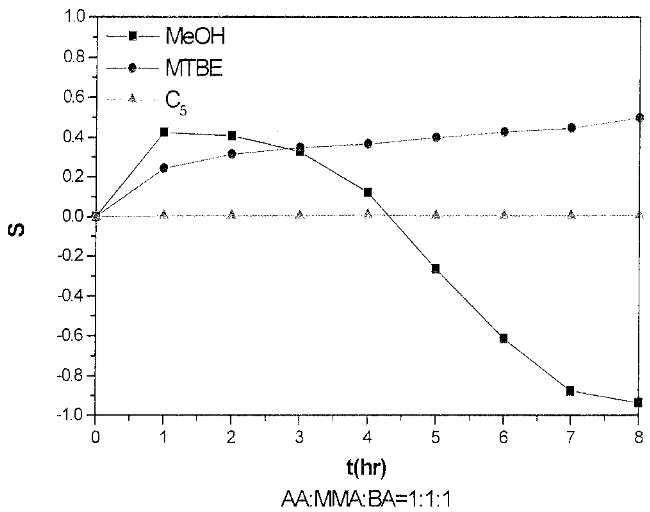

Figure 5 Swelling behaviors of copolymers with 1 : 1 : 1 for pure methanol, MTBE, and C_5.

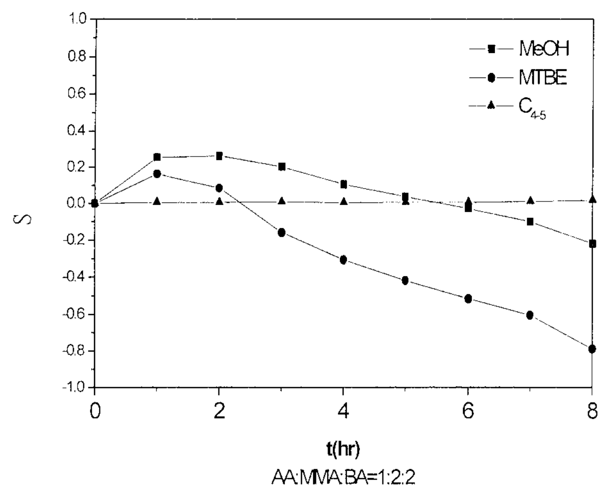

Figure 7 Swelling behaviors of copolymers with 1 : 2 : 2 for pure methanol, MTBE, and C_5.

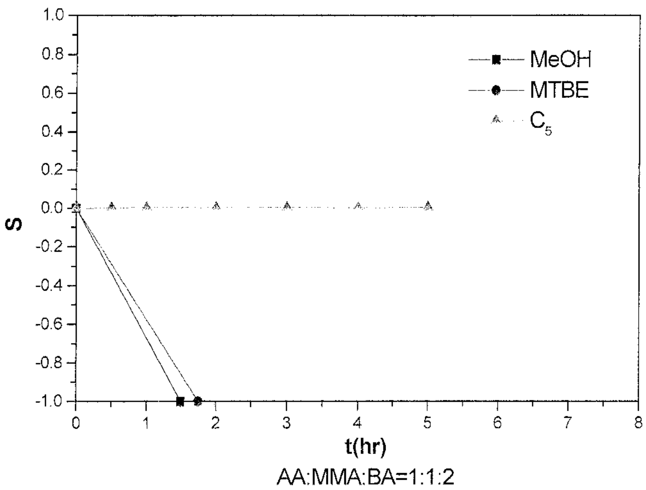

Figure 8 Swelling behaviors of copolymers with 1 : 1 : 2 for pure methanol, MTBE, and C_5.

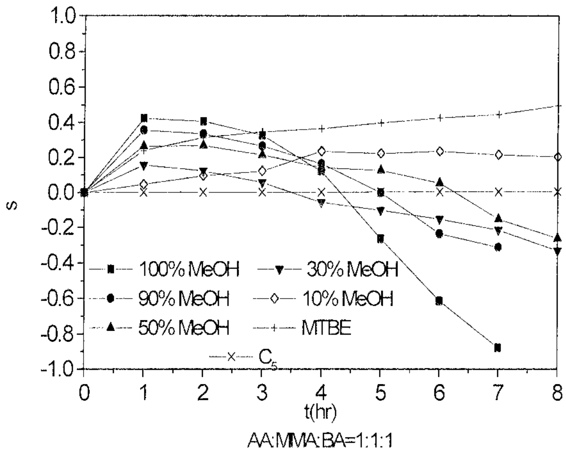

Figure 10 Swelling behaviors of copolymers with 1 : 1 : 1 for MeOH/MTBE mixtures with different concentrations.

laxedly dissolved in pure methanol in 8 h. From Figures 6 and 7, the copolymers with 2 : 3 : 3 and 1 : 2 : 2 ratios will partly dissolute in pure MTBE and methanol; in other words, there is more intensive interaction between them. The weights of those two copolymers are unchanged in pure C_5 solvent. Figures 8 and 9 show that the copolymer with 1 : 1 : 2 will be fully dissolved in pure methanol and pure MTBE, and the copolymer with 1 : 2 : 1 cannot be swollen in these three pure solvents.

It is well known that the solubility parameters may be used to interpret the molecular interactions between two components, and a good solvent for a certain polymer has a solubility parameter value close to that of the polymer. The solubility parameter value of MTBE is 18.49MPa$^{1/2}$, and that of BA is 17.7MPa$^{1/2}$. From these results of swelling experiments, the interactions between copolymers and MTBE will enhance with increasing of the content of BA in copolymers. The solubility parameter value of methanol is 29.7 MPa$^{1/2}$, and that of MMA is 18.9MPa$^{1/2}$. Then, it is found that the interaction between copolymer and methanol will increase with a decrease of the content of MMA in copolymers.

In addition, Figure 10 gives the swelling behaviors of polymers with a 1 : 1 : 1 ratio in methanol/MTBE mixtures with different concentrations. As the weight fraction of methanol in mixtures is higher than 10 wt %, the copolymer is partly dissolved. Therefore, the membrane prepared with this copolymer can be used for the pervaporation of mixtures with the weight fraction of methanol less than 10 wt %. From Figure 11, it can be seen that the copolymer with a 2 : 2 : 1 ratio will be dissolved in part, when the weight fraction of methanol is higher than 30 wt % in mixtures. With an increase of the weight fraction of methanol in mixtures, the interactions between the two abovementioned copolymers and mixtures will increase.

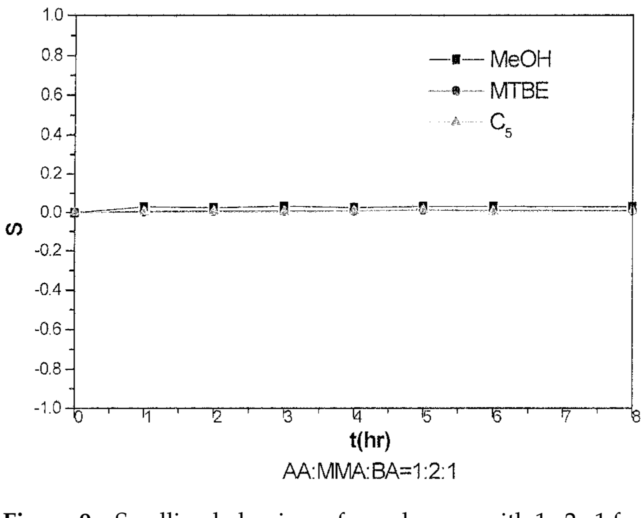

Figure 9 Swelling behaviors of copolymers with 1 : 2 : 1 for pure methanol, MTBE, and C_5.

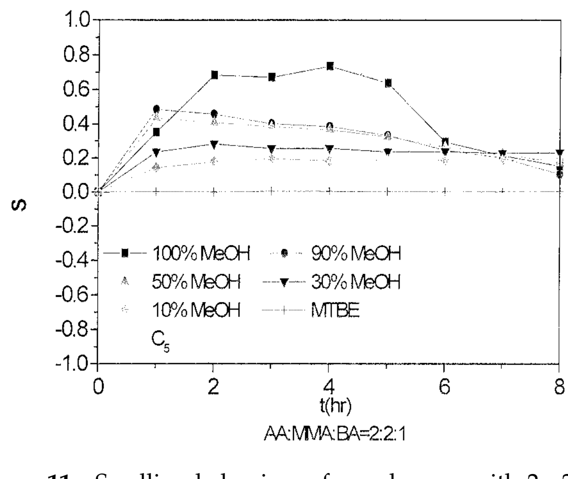

Figure 11 Swelling behaviors of copolymers with 2 : 2 : 1 for MeOH/MTBE mixtures with different concentrations.

TABLE I
Separation Properties of the Membranes with Different Ratios of (AA–MMA–BA) Copolymers

Ratios of copolymer	J_1	J_{MeOBB}	$\alpha_{MeOH/MTBE}$
2:2:1	13.0	12.5	764.0
1:1:1	896.5	318.1	15.3
1:1:2	1163.4	279.3	8.8

Feed concentration: 3wt%; downstream pressure: 267Pa; operating temperature: 30°C, J(g/m^2 · h)

Pervaporation properties

The composite membranes are made of the copolymers with three copolymer ratios (2 : 2 : 1, 1 : 1 : 1, and 1 : 1 : 2), respectively, and the pervaporation properties of these membranes are measured for separation of methanol/MTBE mixture, and the results are listed in Table I.

The membrane with a 2 : 2 : 1 ratio has a higher separation factor, $\alpha = 764$, and a lower methanol flux, $J_{MeOH} = 12.5\ g \cdot m^{-2} \cdot h^{-1}$. However, for the membrane with a 1 : 1 : 1 ratio, there are a lower separation factors, $\alpha = 15.3$, and a higher methanol flux $J_{MeOH} = 318.1\ g \cdot m^{-2} \cdot h^{-1}$. For the copolymer with a 1 : 1 : 2 ratio that can be dissolved in methanol and MTBE after one and a half hours, the pervaporation experiment of the membrane with this copolymer will be carried out for a half hour, and the separation factor of this membrane is lower than that of membrane with a 1 : 1 : 1 ratio, and the total flux is higher. The experiments show that the pervaporation ability changes with swelling degree in the same direction. Thus, the swelling degree may be used to predict the pervaporation ability qualitatively.

CONCLUSIONS

1. From the FTIR spectrograms of membranes with copolymers, the copolymers with high content of BA are highly hydrophobic.
2. The swelling of membrane in MTBE will enhance with increasing the content of BA in copolymers.
3. With increasing the content of MMA in copolymers, the membrane will be less swollen in methanol.
4. As the weight fraction of methanol in solution is higher than 10wt%, the copolymer with 1:1:1 was dissolved in part.
5. The membrane from AA–MMA–BA copolymers with a 2 : 2 : 1 ratio has a higher separation factor with a lower methanol flux. However, there is a lower separation factor with a higher methanol flux for the membrane with a 1 : 1 : 1 ratio.

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