

PERVAPORATION FOR SEPARATING BENZENE/CYCLOHEXANE MIXTURE BY P(AA-MA) COPOLYMER MEMBRANES*

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Abstract P(AA-MA) copolymers composed of acrylic acid and methyl acrylate with different molecular weights and sequence structures were synthesized by combination of ATRP and selective hydrolysis. These copolymers were used as membrane materials to separate benzene/cyclohexane mixture by pervaporation. The effects of molecular weight and sequence structure of the copolymers on the pervaporation performance were investigated in detail. For the random copolymers, the permeate flux decreased rapidly with the increasing of molecular weight. The separation factor was also influenced by the molecular weight, which was changed from no selectivity to cyclohexane selectivity with increasing the molecular weight. Contrarily, the block copolymer membrane showed good benzene selectivity with separation factor of 4.3 and permeate flux of 157 g/(m²h) to 50 wt% benzene/cyclohexane mixture.

Keywords: Pervaporation; ATRP; Copolymer; Molecular weight; Sequence structure; Benzene/cyclohexane mixture.

INTRODUCTION

Separating benzene/cyclohexane mixture is industrially significant^[1–3]. But this mixture separation has posed a challenge^[4] because of the close boiling point and approximately equal molecular volume. Conventional technologies such as extractive distillation need both high energy and capital investment, yet still reach to low efficiency^[5].

Pervaporation is regarded as a prospective industrial separation process for a variety of liquid mixtures, especially where the traditional separation technologies are not efficient, such as the separation of azeotropes, close boiling mixtures, isomers and temperature sensitive products^[6–14]. Since early 1960's^[15], the separation of benzene/cyclohexane mixture by pervaporation has been studied, numerous kinds of membrane materials had been explored to assess their separation properties through pervaporation. Among these membrane materials, methyl acrylate containing copolymers showed good benzene selectivity to benzene/cyclohexane mixture^[16, 17].

However, as far as we know, only a few researchers had thrown their insights into the effects of polymer's microstructure on separation properties during pervaporation. Uragami^[18, 19] *et al.* investigated the differences between block and graft copolymer membranes on the separation of aqueous ethanol solutions and aqueous benzene solutions. Inui^[20] *et al.* reported random and graft copolymer membranes for separating benzene/cyclohexane mixture. Yet studies on the relationship between polymer microstructure and pervaporation performance were far inadequate because of the difficult synthesis of various copolymers with well controlled composition, sequence structure and molecular weight.

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In this study, by combining ATRP with selective hydrolysis, random and block poly(acrylic acid-co-methyl acrylate) (P(AA-MA)) copolymers with well controlled composition and molecular weight were synthesized. The pervaporation characteristics through both random and block copolymer membranes for separating benzene/cyclohexane mixture were investigated.

EXPERIMENTAL

Materials

Methyl acrylate (MA, Aladdin) and *tert*-butyl acrylate (*t*BA, Aladdin) were purified by passing through a basic alumina column to remove the inhibitor. CuBr (Aladdin) was purified by stirring with glacial acetic acid, followed by filtration and washing the solids with ethanol (three times) and diethyl ether (two times). *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich), methyl-2-bromopropionate (Aldrich), trifluoroacetic acid (TFA, Aladdin) and other chemicals were used as received.

Synthesis of P(AA-MA) Copolymers

Synthesis of P(*t*BA-*r*-MA) random copolymer via ATRP

Certain amount of MA, *t*BA, PMDETA and methyl-2-bromopropionate were dissolved in acetone and added to a 25 mL Schlenk flask with a magnetic stirring bar, and oxygen was removed by subjecting the contents of the flask to three freeze-pump-thaw cycles. Then, CuBr was added under nitrogen flow. The stirred flask was placed in an oil bath thermostated at 50°C and the polymerization was quenched by opening the flask and exposing the contents to air at scheduled time.

Synthesis of P(*t*BA-*b*-MA) block copolymer via ATRP

P(*t*BA-*b*-MA) block copolymer was prepared using PMA-Br as macroinitiator. Both PMA-Br macroinitiator and P(*t*BA-*b*-MA) block copolymer were synthesized through standard ATRP procedure similar as above mentioned.

Synthesis of P(AA-MA) copolymers by selective hydrolysis

The P(*t*BA-MA) copolymer was dissolved in dichloromethane and stirred at room temperature for 48 h with 5 mol equiv. of trifluoroacetic acid to *t*BA units in the copolymer. After distilling off the solvent and the extra trifluoroacetic acid, the crude product was collected and purified through an ethanol-water dissolution-precipitation process. The final product was recovered by drying under vacuum for 24 h.

Membrane Preparation

The casting solutions of P(AA-MA) copolymer with a concentration of 130 g/L were prepared by dissolving the copolymer in ethanol at room temperature for 24 h. Then the membrane for pervaporation was prepared by cast-dry process on a polyacrylonitrile ultra-filtration membrane. The solvent evaporating process was kept at 40°C for 48 h.

Pervaporation

The pervaporation process through P(AA-MA) copolymer membrane was operated on the similar apparatus reported previously^[21]. Experiments were carried out in a continuous steady state with a downstream vacuum maintained at about 60 Pa and a constant feed temperature at 50°C. The permeate components were condensed by cold trap and determined by gas chromatograph. Separation factor (α) and permeation flux (J) were calculated according to the following equations:

$$\alpha = \frac{P_{\text{benzene}} / P_{\text{cyclohexane}}}{F_{\text{benzene}} / F_{\text{cyclohexane}}} \quad (1)$$

$$J = \frac{\Delta g}{S \times \Delta t} \quad (2)$$

where F_{benzene} and $F_{\text{cyclohexane}}$ are the weight fractions of benzene and cyclohexane in the feed mixture, P_{benzene} and $P_{\text{cyclohexane}}$ are those in the permeate mixture. Δg is the permeate weight collected during the operation time (Δt) and S is the effective membrane area (18.09 cm^2).

Swelling Measurements

The degree of swelling (DS) of the membrane is defined through the following equation:

$$\text{DS} = \frac{m_s - m_o}{m_o} \times 100\% \quad (3)$$

where m_o and m_s are the weight of dry and solvent swollen membranes. The swelling experiments were operated at a constant temperature of 25°C . Before weighing, the free liquid on the surface of the swollen membrane were scraped quickly by a filter paper.

The sorption selectivity (α_s) and diffusion selectivity (α_d) were defined as follows:

$$\alpha_s = \frac{S_{\text{benzene}} / S_{\text{cyclohexane}}}{O_{\text{benzene}} / O_{\text{cyclohexane}}} \quad (4)$$

$$\alpha_d = \frac{\alpha}{\alpha_s} \quad (5)$$

where S_{benzene} , $S_{\text{cyclohexane}}$ are the concentration of benzene and cyclohexane in the swollen membrane at equilibrium. O_{benzene} , $O_{\text{cyclohexane}}$ are the concentration of benzene and cyclohexane in the original solution. α is the separation factor of pervaporation process.

Characterization

^1H -NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in CDCl_3 or DMSO corresponding to P(*t*BA-MA) and P(AA-MA) copolymers, respectively with tetramethylsilane as internal standard. The molecular weight and molecular weight distribution were determined by size-exclusion chromatography (SEC) performed on a Waters 150°C apparatus in THF (1.0 mL/min) at 25°C . The differential scanning calorimetry (DSC) curves of P(AA-MA) copolymers were obtained through a TA Q200 under nitrogen (N_2) atmosphere at a heating rate of 10 K/min from -40°C to 140°C after eliminating the influence of thermal history. The composition of benzene/cyclohexane mixtures was analyzed by a 6890N gas chromatograph equipped with a flame ionization detector (Column: DB-608, Backinlet: 230°C , Frontdetector: 250°C , Flow: 1.0 mL/min).

RESULTS AND DISCUSSION

Synthesis and Characterization of P(AA-MA) Copolymers

Random and block P(*t*BA-MA) copolymers were synthesized by ATRP of *t*BA and MA at 50°C in acetone as summarized in Table 1. P(*t*BA-MA) copolymers were characterized by ^1H -NMR as shown in Fig. 1. The spectra of random and block copolymer are similar. However, the slight difference of the chemical shifts of the protons on the backbone indicates the different sequence structures of random and block copolymers. The ratio of MA to *t*BA units in the copolymers was determined by the integral intensities of corresponding protons:

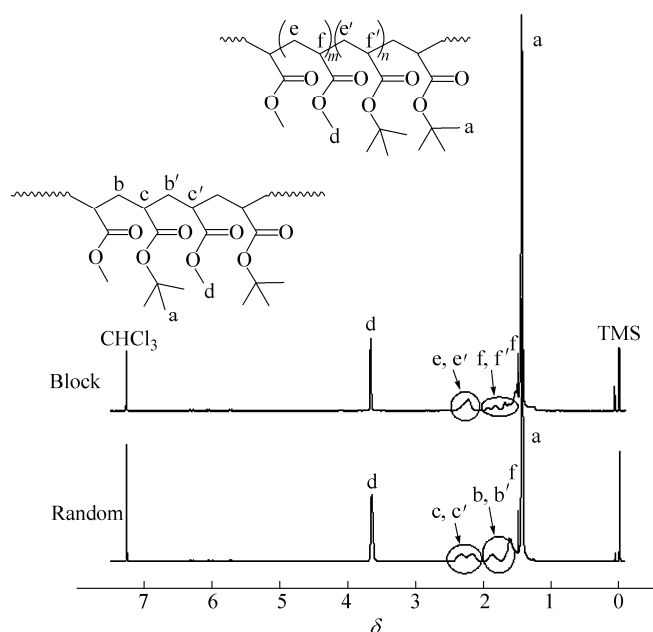
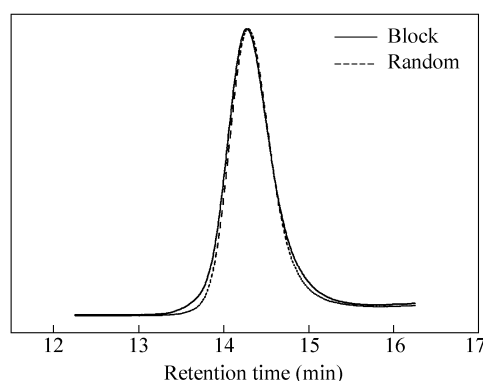
$$\text{MA} : t\text{BA} = I^d : I^a / 3 \quad (6)$$

where I^d and I^a were the integral area of H^d and H^a respectively. The SEC curves of the random and block copolymers are displayed in Fig. 2, indicating that the copolymerization was a controlled/living process and the P(*t*BA-MA) copolymers with controlled molecular weight and narrow molecular weight distribution have been prepared successfully.

Table 1. Synthesis of random and block P(*t*BA-MA) copolymers via ATRP ^a

Sample	M/I/C/L ^b	Reaction time (h)	Conversion (%)	MA/ <i>t</i> BA (mole ratio)		M_n	PDI
				Feeding	In polymer (NMR)		
P(<i>t</i> BA- <i>r</i> -MA)-1	1000/10/5/5	4	40	1:1	1:1.12	5800	1.13
P(<i>t</i> BA- <i>r</i> -MA)-2		24	73		—	8400	1.12
P(<i>t</i> BA- <i>r</i> -MA)-3	1000/5/2.5/2.5	8	45		1:1.11	10400	1.12
P(<i>t</i> BA- <i>r</i> -MA)-4		24	57		—	14300	1.07
P(<i>t</i> BA- <i>r</i> -MA)-5	1000/2.5/1.25/1.25	12	43		1:1.14	32000	1.10
P(<i>t</i> BA- <i>r</i> -MA)-6		24	60		—	51100	1.11
PMA-Br	1000/2.8/1.4/1.4	1.5	33	—	—	4900	1.09
P(<i>t</i> BA- <i>b</i> -MA) ^c	1000/5/2.5/2.5	24	85	1.86:1	1.94:1	8500	1.14
P(<i>t</i> BA- <i>r</i> -MA)-7	1000/10/5/5	24	81		1.80:1	8400	1.13

^a Reaction conditions: 50°C, in acetone solution (40 vol%); ^b M: monomer, I: initiator (methyl-2-bromopropionate), C: CuBr, L: ligand (PMDETA); ^c PMA-Br as macroinitiator

**Fig. 1** ¹H-NMR spectra of P(*t*BA-MA) random and block copolymers
Block: P(*t*BA-*b*-MA); Random: P(*t*BA-*r*-MA)-7**Fig. 2** SEC curves of P(*t*BA-MA) random and block copolymers
Block: P(*t*BA-*b*-MA); Random: P(*t*BA-*r*-MA)-7

Then, the selective hydrolysis of *t*BA unit in the P(*t*BA-MA) copolymer was carried out to prepare P(AA-MA) copolymers. In the $^1\text{H-NMR}$ spectrum (Fig. 3), the characteristic peak of *tert*-butyl group in *t*BA units at $\delta = 1.44$ could not be detected any more after hydrolysis reaction. Nevertheless, the methyl group in MA unit was still reserved showing signals at $\delta = 3.6$ in the spectrum. This indicates that the selective elimination of isobutylene from P(*t*BA-MA) copolymer was successful. Meantime, the characteristic peak of carboxyl proton is also detected at $\delta = 12.3$, which further confirms that the hydrolysis of *tert*-butyl group has been achieved.

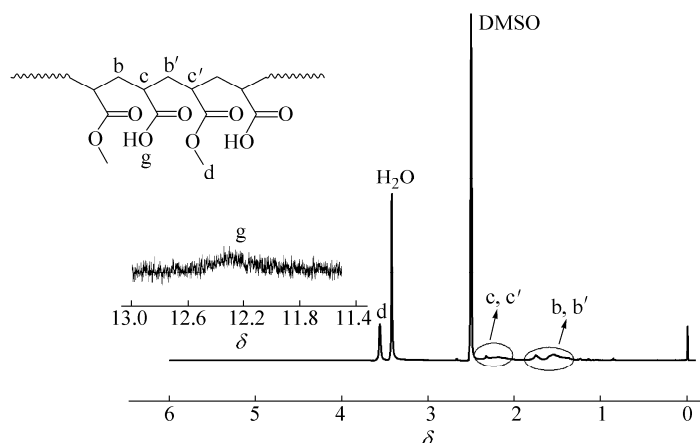


Fig. 3 $^1\text{H-NMR}$ spectrum of P(AA-MA) copolymer (from P(*t*BA-*r*-MA)-7)

The DSC curves of P(AA-MA) copolymers are shown in Fig. 4. For random copolymer, only one T_g was detected around 45°C between the T_g of PMA and PAA homopolymers, indicating the random sequence structure of the copolymer. However, for the block copolymer, two T_g s at 20°C and 90°C corresponding to PMA and PAA blocks were detected respectively. The DSC results further demonstrated the successful synthesis of random and block P(AA-MA) copolymers.

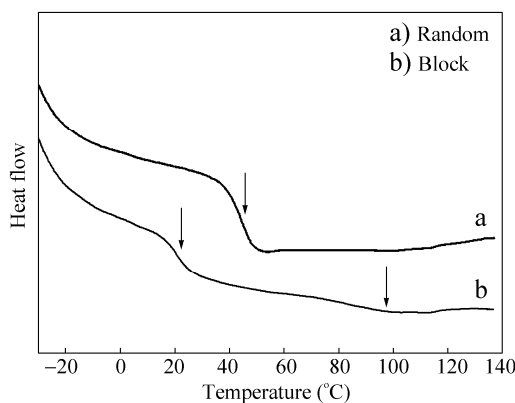


Fig. 4 DSC curves of the P(AA-MA) random and block copolymers
Block: from P(*t*BA-*b*-MA); Random: from P(*t*BA-*r*-MA)-7

Pervaporation Performance

A series of P(AA-*r*-MA) random copolymers with similar composition (MA/AA $\approx$ 1:1, mol/mol) but different molecular weights have been synthesized and used as membrane materials for the separation of 50 wt% benzene/cyclohexane mixture *via* pervaporation. As Fig. 5 shows, with the increasing of copolymer molecular weight, the permeate flux decreased rapidly. On the other hand, the P(AA-*r*-MA) random copolymer membranes showed no selectivity for both benzene and cyclohexane at low molecular weight, and cyclohexane selectivity at high molecular weight.

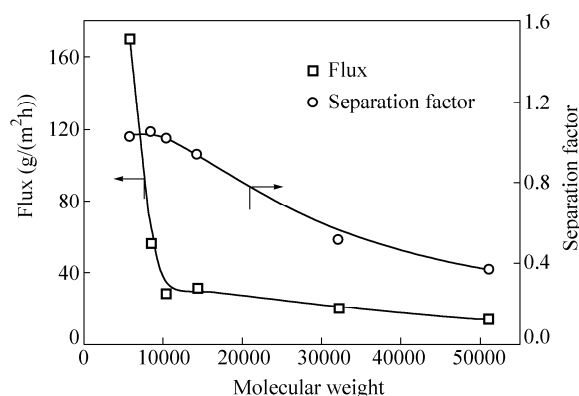


Fig. 5 Effect of molecular weight of random copolymers on separation factor and permeate flux to 50 wt% benzene/cyclohexane mixture

P(AA-*r*-MA) random copolymer and P(AA-*b*-MA) block copolymer with similar molecular weight (8500 Dalton) and composition (MA/AA $\approx$ 1.86:1, mol/mol) were also synthesized and used for separation of benzene/cyclohexane mixture by pervaporation. As shown in Fig. 6, for random copolymer, although the benzene-affable component MA in copolymer was raised to 64 mol%, the membrane still shows no selectivity on benzene when the benzene concentration was ranged from 10 wt% to 90 wt%. Nevertheless, the P(AA-*b*-MA) block copolymer showed good benzene selectivity under the same conditions, and the separation factor generally decreased with the increasing of benzene concentration. At low benzene concentration (10 wt%), the separation factor was also low, which might be attributed to the fact that the membrane couldn't be properly swollen and the relative equilibrium was hard to be built at low benzene concentration^[22, 23]. Comparing the pervaporation performances of block and random copolymer membranes, a conclusion could be drawn that the membrane selectivity is affected by the sequence structure rather than the composition of copolymers. Figure 7 describes the relationship between permeate flux and benzene concentration using random and block P(AA-MA) copolymer membranes. The permeate flux of block copolymer membrane raised rapidly when benzene concentration increased. For the random copolymer, the permeate flux didn't change significantly with different benzene concentrations.

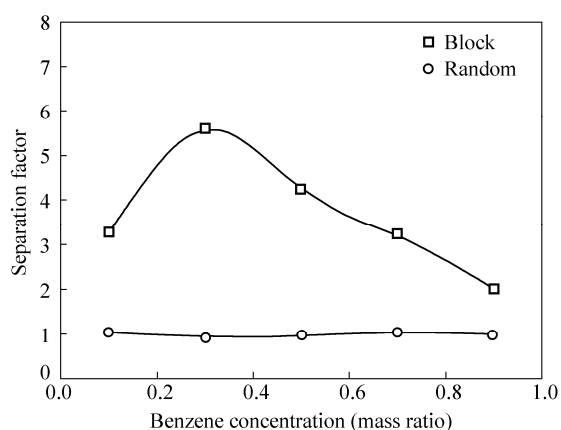


Fig. 6 Effect of sequence structure on separation factor to benzene/cyclohexane mixture
Block: from P(*t*BA-*b*-MA); Random: from P(*t*BA-*r*-MA)-7

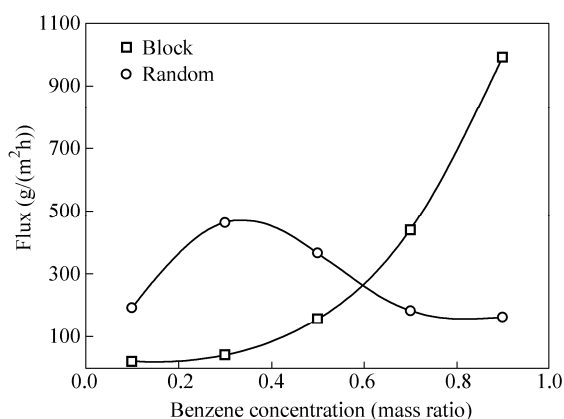


Fig. 7 Effect of sequence structure on permeate flux at different benzene concentrations
Block: from P(*t*BA-*b*-MA); Random: from P(*t*BA-*r*-MA)-7

Swelling Behavior and Permselectivity Analysis of *P(AA-MA)* Copolymer Membranes

To further investigate the mechanism of selectivity, the swelling behavior of copolymer membranes with different sequence structures was studied in benzene/cyclohexane mixture at 30 wt% (low) and 70 wt% (high) benzene concentration respectively. As shown in Fig. 8, the swelling degree of block copolymer membrane increases with the increasing of benzene concentration, which suggests that the copolymer with block sequence structure is more affable to benzene than cyclohexane. However, for random copolymer, the trend is opposite.

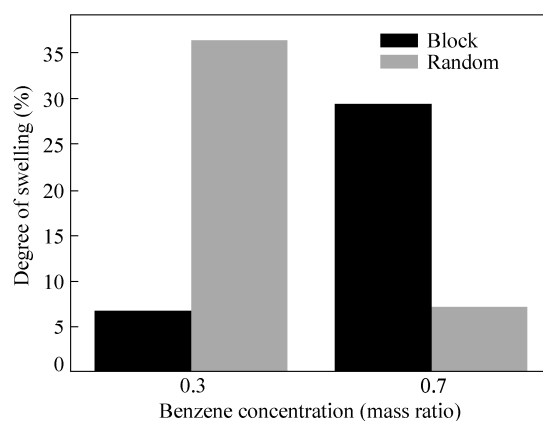


Fig. 8 Effect of sequence structure on swelling degree at different benzene concentrations
Block: from *P(tBA-*b*-MA)*; Random: from *P(tBA-*r*-MA)*-7

Figure 9 shows the membrane selectivity in different separation processes respectively. For block copolymer membranes, both the sorption and diffusion process preferred benzene selectivity. But both the diffusion and total selectivity decreased when benzene concentration increased, which indicated that the sorption selectivity was more essential than diffusion selectivity. For random copolymer, the sorption, diffusion and total selectivity didn't change much with different benzene concentrations. This fact demonstrates that the random sequence structure in copolymer not only destroys the diffusion channel in membrane, but also changes the essential property of membrane material.

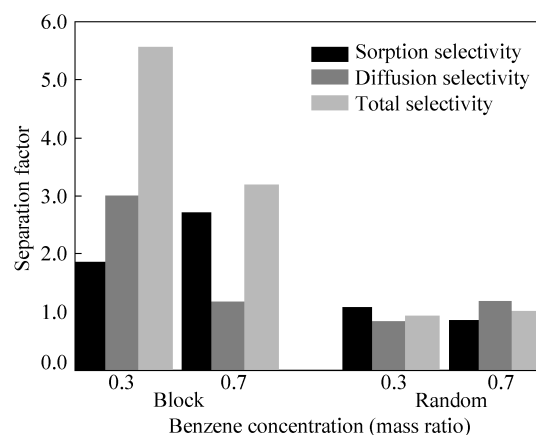


Fig. 9 Effect of sequence structure on selectivity at different benzene concentrations
Block: from *P(tBA-*b*-MA)*; Random: from *P(tBA-*r*-MA)*-7

CONCLUSIONS

Combining ATRP with selective hydrolysis, P(AA-MA) copolymers with different molecular weights and sequence structures were prepared. These copolymers were used as membrane materials to separate benzene/cyclohexane mixture by pervaporation. Random copolymer membranes showed no selectivity or cyclohexane selectivity to benzene/cyclohexane mixture, yet block copolymer ones showed good benzene selectivity with a separation factor of 4.3 and a permeate flux of 157 g/(m²h) to 50 wt% benzene/cyclohexane mixture.

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