

PERVAPORATION MEMBRANE PREPARED FROM POLYCONDENSATION-TYPE POLYMERS CONTAINING POLYDIMETHYLSILOXANE IN THE SIDE-CHAIN

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The two kinds of polysiloxane-grafted copolymers were prepared, one of which was aromatic polyamide/polydimethylsiloxane (PA/PDMS) graft copolymer and the other was polyester/polydimethylsiloxane (PE/PDMS) graft copolymer. PA/PDMS was obtained by a polycondensation using 3-(3,5-diaminobenzyloxy)propyl-terminated PDMS macromonomer, 2,4-diaminotoluene (DAT) and isophthaloyl dichloride (IPC) as monomers, and PE/PDMS was from 2,2-(dihydroxymethyl)butoxypropyl-terminated PDMS, 1,6-hexanediol and IPC. From the results of pervaporation experiments, the selective permeation of organic solvent was observed in the separation of aqueous organic solutions through these copolymer membranes, where the PDMS content was relatively high. In particular, PA/PDMS membrane could be used for the separation of aqueous mixtures of some alcohols, THF and acetone because of the durability of main-chain structure against several organic solvents, whereas PE/PDMS membrane was broken during the permeation of THF or acetone solution.

Key words: graft copolymer, polydimethylsiloxane, membrane, durability, pervaporation.

1. INTRODUCTION

In order to search durable membrane materials, which can be used for the separation of several organic solvents by using pervaporation technique, a series of polycondensation-type polymers with polydimethylsiloxane (PDMS) side-chain has been investigated. In our previous papers^{1,2}, we have presented the synthesis of polyimide/polydimethylsiloxane (PI/PDMS) graft copolymer by a macromonomer method. The obtained PI/PDMS copolymer membrane exhibited the stable and highly selective permeation toward the organic solvents, such as ethanol, 2-propanol, acetone, acetonitrile and THF in the pervaporation of their aqueous solutions. Moreover, this membrane can be applied to the separation of aqueous dichloromethane solution owing to its durability to organic solvents³. However, PI/PDMS copolymer membrane must be prepared by casting in the poly(amic acid) stage followed by thermal imidation, because the PI/PDMS copolymer is insoluble due to the property of its backbone component. Therefore, the purpose of this paper is the improvement of the process of preparing membrane to avoid such a thermal treatment by using soluble polymer materials. Then, the main chain of the PDMS-grafted copolymer was changed to aromatic polyamide to improve the solubility and to maintain the durability for the common organic solvents. Otherwise, the synthesis of PE/PDMS graft

copolymer was carried out to reveal the effect of main chain structure on the permselectivity in the pervaporation of aqueous organic solvents.

2. PREPARATION OF COPOLYMERS

2.1 PA/PDMS graft copolymer

At first, the synthesis of condensation-type PDMS macromonomer with diamino-terminal group was carried out as shown in *Scheme 1*. 3-(3,5-diaminobenzyloxy)propyl-terminated PDMS macromonomer (**4**, DAB-PDMS) was prepared by hydrosilylation of 3,5-dinitrobenzyl allyl ether, **1**, with hydrosilyl-terminated PDMS, **2**, followed by catalytic reduction of the two nitro groups of **3**. **2** having a narrow molecular weight distribution was prepared by anionic polymerization of hexamethylcyclotrisiloxane (D_3) initiated with lithium trimethylsilanolate, where the terminal hydrosilyl group was introduced by terminating the polymerization with chlorodimethylsilane. The average degree of polymerization, m , of **2** was controlled by changing the ratio of D_3 to the initiator, and the observed m agreed with the theoretical one. The hydrosilylation of **1** with **2** took place quantitatively, and the reduction of **3** gave DAB-PDMS also in high yield.

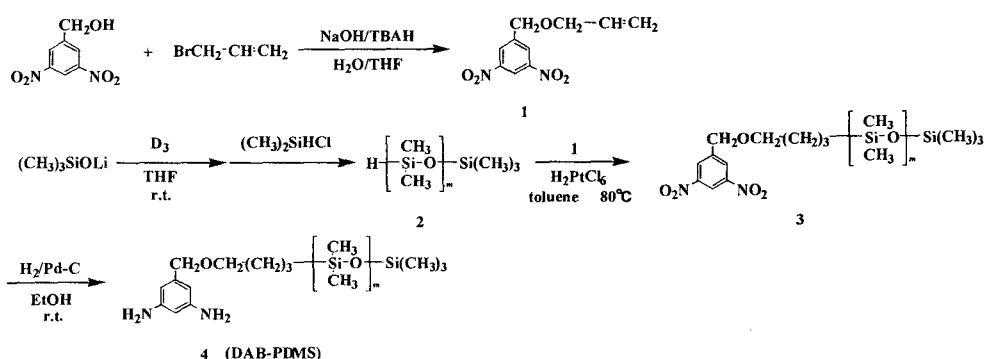
The synthetic diagram of PA/PDMS graft copolymer is shown in *Scheme 2*. PA/PDMS graft copolymer was prepared by polycondensation of DAB-PDMS and 2,4-diaminotoluene (DAT) with isophthaloyl chloride (IPC). The mole ratio, x/y ,

could be controlled by changing the ratio of DAB-PDMS and DAT. The composition (x/y), m of PDMS segment, and PDMS content of the obtained graft copolymers are summarized in *Table 1*. As shown in this table, the compositions of copolymers were in good agreement with the ratio of DAT/DAB-PDMS in feed, respectively.

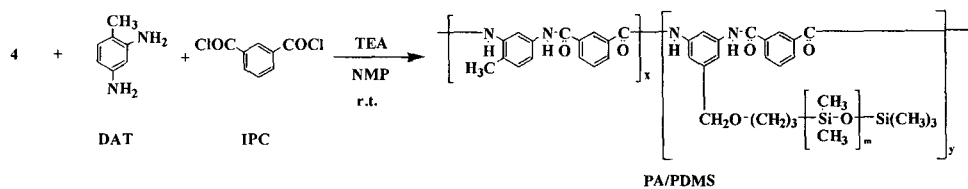
2.2 PE/PDMS graft copolymer

The synthesis of 2,2-di(hydroxymethyl)butoxy-propyl-terminated PDMS macromonomer was carried out to prepare polyester type copolymer. The macromonomer (7, DMBP-PDMS) was prepared by the similar procedure to DAB-PDMS by using

2,2-(benzyloxymethyl)butyl allyl ether, **5**, instead of **1**, as shown in *Scheme 3*. The hydrosilylation of **5** with polydimethylsiloxane, **2**, took place quantitatively, and the elimination of benzyl group of **6** by reduction with H_2/Pd gave the macromonomer, DMBP-PDMS, in high yield. PE/PDMS graft copolymer was prepared by polycondensation of DMBP-PDMS and 1,6-hexanediol with IPC as shown in *Scheme 4*. In this copolymerization, the mole ratio of DMBP-PDMS and 1,6-hexanediol was fixed at 80/20 to afford the graft copolymer, ES-5, quantitatively.



Scheme 1 Synthesis of 3-(3,5-Diaminobenzoyloxy) propyl-terminated PDMS macromonomer



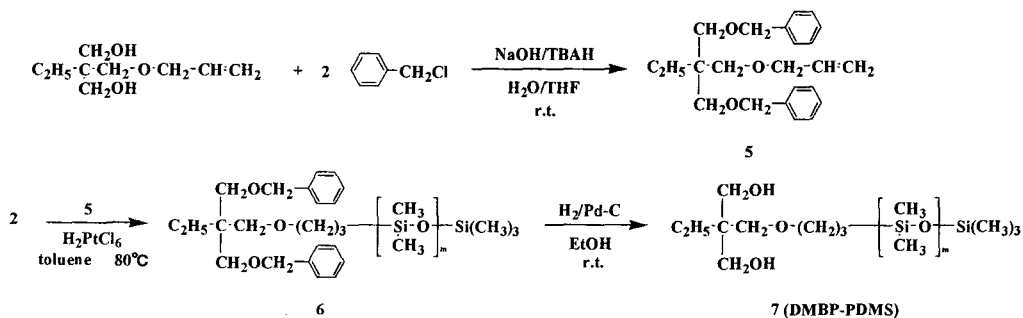
Scheme 2 Synthesis of polyamide/polydimethylsiloxane (PA/PDMS) graft copolymer

Table 1 Results of preparations of PA/PDMS graft copolymers.

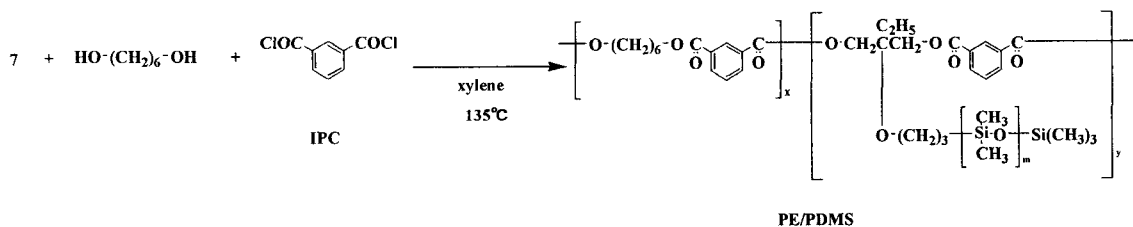
Code	DAT/DAB-PDMS in feed (mole ratio)	x/y in copolymer ^{a)} (mole ratio)	m ^{a)}	PDMS content ^{b)} (wt.%)
AS-1	86/14	85/15	17,6	13,2
AS-2	80/20	78/22	17,6	19,7
AS-3	75/25	72/28	17,6	32,7
AS-4	66/34	61/39	17,6	43,0

^{a)} determined by 1H -NMR spectra.

^{b)} determined by Fluorescent X-ray.



Scheme 3 Synthesis of 2,2-Di(hydroxymethyl)butoxypropyl-terminated PDMS macromonomer



Scheme 4 Synthesis of polyester/polydimethylsiloxane (PE/PDMS) graft copolymer

3. PERVAPORATION EXPERIMENTS

PA/PDMS membranes were prepared by casting the polymer solutions in NMP on micro-porous glassine papers and dried *in vacuo* at 150 °C. PE/PDMS membrane was prepared by the similar way using its THF solution and dried *in vacuo* at 60 °C. Sample membranes for the measurement of pervaporation were cut into circular pieces with a diameter of 47 mm. Pervaporation of aqueous organic liquid solutions through the membrane was carried out by the ordinary method using a stainless steel cell at 40 °C. The permeation area of the membrane was 9.6 cm². As the organic liquids, ethanol, 1-propanol, 2-propanol, acetone and THF were selected. The permeated vapor was trapped in a vessel cooled with liquid N₂, and the concentration was determined by the refractometric analysis.

4. RESULTS OF PERVAPORATION

We examined the permselectivity of a membrane consisted of aromatic homo-polyamide (PA), poly(6-methyl-1,3-phenylene isophthalamide), which was prepared by polycondensation of DAT with IPC, in order to compare its permselectivity in pervaporation with that of copolymer membranes. The permeation composition curves through the homopolymer membrane are shown in *Fig. 1*. As seen in this figure, the selective permeation of water was observed for all of the aqueous organic liquid solutions. On the contrary, for PA/PDMS copolymer membrane, the selective permeation of each organic solvent through AS-4 membrane was observed in the pervaporation of aqueous organic solutions, whereas AS-1 membrane exhibited a water-selectivity, as shown in *Fig. 2* and 3. Thus, the selectivity of pervaporation depended on the PDMS content of the copolymer membrane. On the other hand, as shown in *Fig. 4*, PE/PDMS copolymer, ES-5, membrane exhibited the selectivity toward organic solvents and the selectivities were higher than the cases of AS-4. The values of separation factor, α , and flux of 10 wt.% aqueous mixtures of organic solvents through PA, AS-4 and ES-5 membranes are listed in *Table 2*. It was found that the separation factors of these membranes for each mixture were quite different.

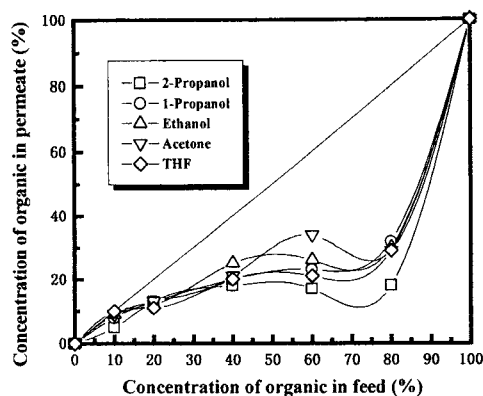


Fig.1 Permeation composition curves of aqueous solution of organic solvents through PA membrane

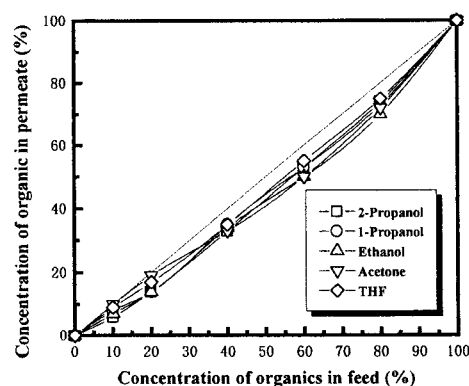


Fig.2 Permeation composition curves of aqueous solution of organic solvents through PA/PDMS graft copolymer membrane (AS-1)

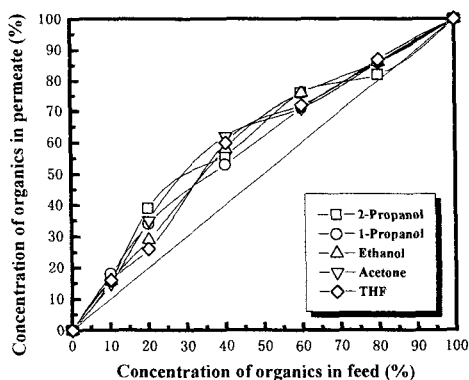


Fig. 3 Permeation composition curves of aqueous solution of organic solvents through PA/PDMS graft copolymer membrane (AS-4)

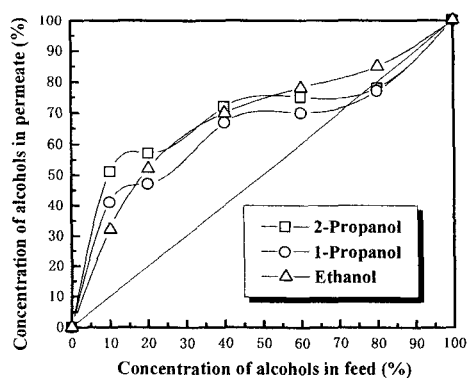


Fig. 4 Permeation composition curves of aqueous solution of alcohols through PE/PDMS graft copolymer membrane (ES-5)

Such a difference of selectivity of AS-4 and ES-5 would be due to the difference of main-chain structure of these copolymers. Polyamide is more hydrophilic than polyester, therefore, the phase separation would be easily induced in PA/PDMS system rather than PE/PDMS. However, ES-5 could not be used for the permeation of acetone and THF, because the ES-5 membrane was dissolved in these solvents. The solubilities of the two copolymers are summarized in Table 3. ES-5 was dissolved in many kinds of organic solvents, but AS-2 exhibited a low solubility against most of the organic solvents except NMP and DMF. Therefore, PA/PDMS system should be superior to PE/PDMS system in the point of durable membrane material for several organic solvents, although the selectivity was low in this stage.

The investigation for the effect of main-chain structure of polycondensation-type PDMS-grafted copolymers on the pervaporation property is now in progress to improve the selectivity toward several organic solvents with the durability of membrane to some extent.

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Table 2 The values of separation factor and flux of pervaporation of 10 wt.% aqueous mixtures of organic solvents through PA, AS-4 and ES-5 membranes at 40°C.

Code	2-Propanol		1-Propanol		Ethanol		Acetone		THF	
	α^a	Flux Kg/m ² ·h	α^a	Flux Kg/m ² ·h	α^a	Flux Kg/m ² ·h	α^a	Flux Kg/m ² ·h	α^a	Flux Kg/m ² ·h
PA	0.47	0.15	0.78	0.20	0.90	0.24	0.97	0.36	0.99	0.22
AS-4	1.76	10.34	1.98	2.99	1.71	4.19	1.59	7.79	1.74	4.62
ES-5	9.38	0.22	6.27	0.42	4.24	0.19	---	---	---	---

a) The separation factor, α , was calculated according to the following equation:

$\alpha = (X_{Org}/X_{water})/(Y_{Org}/Y_{water})$, where X_{Org} is the composition of organic liquid in permeate, X_{water} is the composition of water in permeate, Y_{Org} is the composition of organic liquid in feed, and Y_{water} is the composition of water in feed.

Table 3 Solubility of AS-2 and ES-5 in various solvents*.

Code	Acc.	THF	MeOH	EtOH	IPOH	2POH	H ₂ O	NMP	DMF	DMAc	Tol.	Hex.	CHCl ₃
AS-2	×	×	×	×	×	×	×	○	○	×	×	×	×
ES-5	○	○	×	×	×	×	×	○	×	○	○	○	○

* This evaluation was carried out by observing the solubility of 10 mg of each polymer in 1.0 ml of each solvent.
○: completely soluble, ×: insoluble.