

SYNTHESIS OF POLYDIMETHYLSILOXANE-GRAFTED POLY(AMIDE-IMIDE) AND ITS APPLICATION FOR PERVAPORATION MEMBRANE

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Polydimethylsiloxane-grafted aromatic poly(amide-imide) copolymer was prepared to investigate the durable membrane material for the separation of several organic solvents by using pervaporation technique. Poly(amide-imide) reacted with NaH in DMSO to produce polyanion at the N-position of the amide group, followed by the reaction with chloromethylphenyl-terminated polydimethylsiloxane to obtain the desired graft copolymer. By this polymer reaction, polydimethylsiloxane chains with the average degree of polymerization of 13 were substituted on about 30 mol% of the amide group, where the degree of substitution was depended on the main chain structure. The obtained copolymer was soluble in aprotic polar solvents such as DMSO, DMF and NMP, and insoluble in the ordinary organic solvents such as acetone, THF, benzene and chloroform. Therefore, the copolymer membrane, which exhibited the selective permeation of organic solvents from their aqueous mixture solutions, was easily prepared by the solvent-casting method.
Key words: poly(amide-imide), polydimethylsiloxane, graft copolymer, membrane, pervaporation.

1. INTRODUCTION

Recently, the pervaporation (PV) technique with a polymer membrane has been focused in much attention for the separations of mixtures of several organic liquids and water. It is possible to separate organic solvents from, for example, waste fluid by using PV technique. For this purpose, it is an important factor that the membrane exhibits the organic-permselectivity, not the water-permselectivity, and the durability against several organic solvents. A cross-linked polydimethylsiloxane (PDMS) membrane has been known to show a selective permeation of organic liquids and a high permeability in the pervaporation of aqueous organic solutions. We have investigated the syntheses of siloxane-grafted copolymers, the main chain of which consisted of several aromatic polymers¹⁻⁴⁾, for the PV material in order to improve the mechanical strength and the durability. Then, it was found that the membrane of polyimide/polydimethylsiloxane (PI/PDMS) graft copolymer²⁾ exhibited the high permselectivity and the excellent durability for the separations of aqueous solutions of organics. However, PI/PDMS copolymer must be prepared by casting in poly(amic acid) stage, followed by thermal imidation. In other words, this membrane contains the high separation property and durability but the less processability due to the chemical structure of the backbone component.

In this study, a novel membrane material, which possesses the practical properties of permselectivity, durability and processability, has been investigated. Then, the preparation of PDMS-grafted poly(amide-imide) (PAI) was carried out. The backbone, PAI, is soluble in some solvents such as aprotic polar solvents, to be easily prepared the membrane, and insoluble in the other organic solvents to be durable to separating organic components. In this paper, we will describe the synthesis

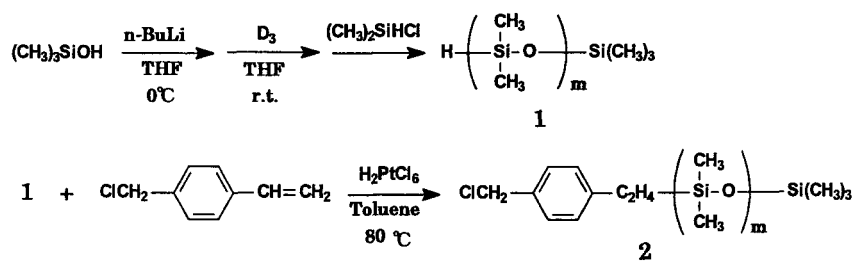
of poly(amide-imide) substituted with polydimethylsiloxane chains on the N-position of amide groups, which is derived from polymer reaction, and the separation characteristics of the obtained membrane, evaluated by PV experiments.

2. RESULTS AND DISCUSSION

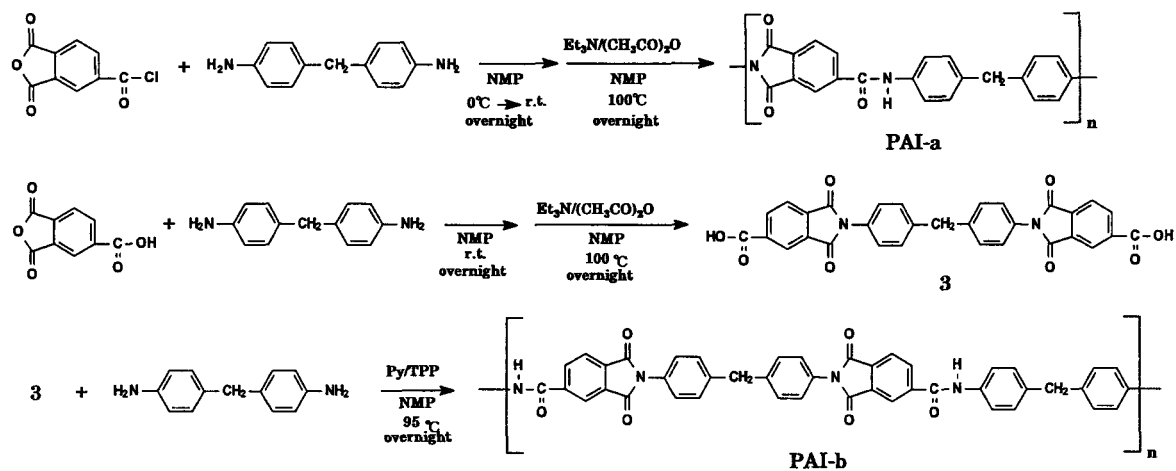
2.1 Preparation of PAI/PDMS graft copolymer

For the reactive PDMS compound used in the polymer reaction, chloromethylphenyl-terminated PDMS (2) was prepared at first as shown in Scheme 1. The starting PDMS, 1, was prepared by anionic ring-opening polymerization of hexamethylcyclotrisiloxane (D₃) initiated with trimethylsilylanolate anion, followed by terminating the reaction with dimethylchlorosilane. The average degree of polymerization of 1, *m*, could be controlled by changing the ratio of D₃ and trimethylsilanol in the polymerization. Then, the desired PDMS, 2, was prepared by hydrosilylation of 1 with 4-chloromethylstyrene in the presence of chloroplatinic acid as catalyst. In the polymer reaction described later, the PDMS 2 with *m* of 13 was employed.

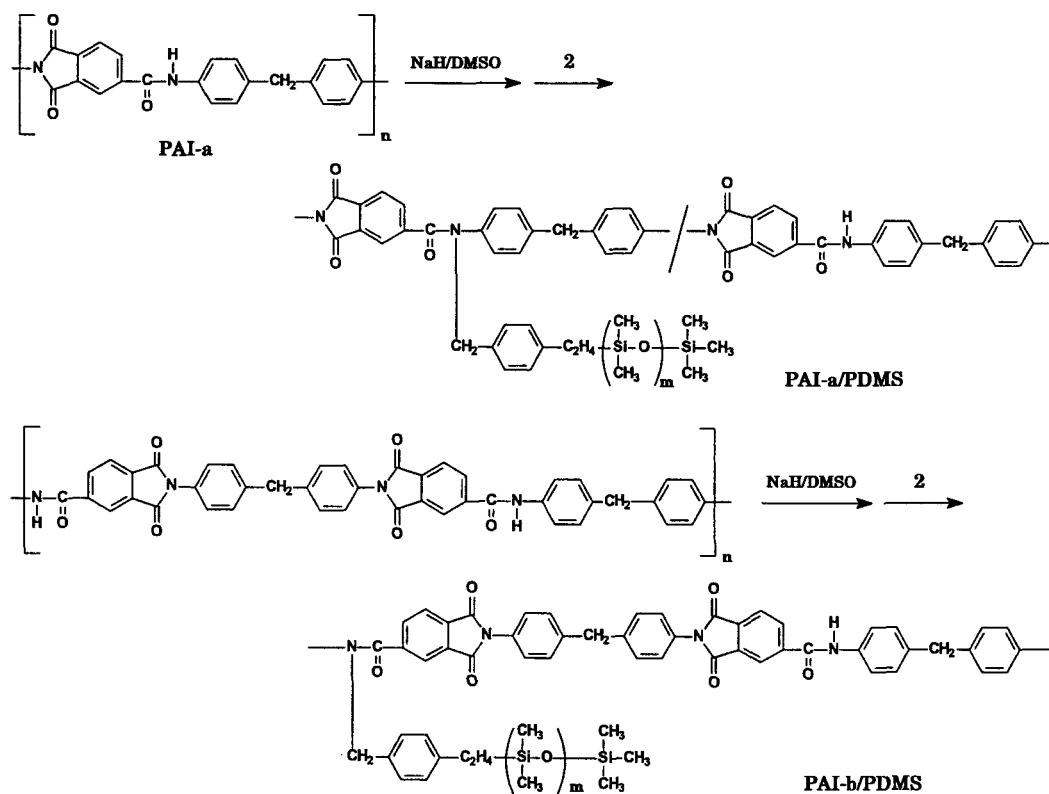
As the backbone polymers, two kinds of aromatic poly(amide-imide)s were prepared as shown in Scheme 2. One of them was PAI-a obtained by polycondensation of 4,4'-diaminodiphenylmethane (DADM) with trimellitic anhydride chloride (TMAC), and the other was PAI-b obtained from MDA and the diacid compound 3. The compound 3 was synthesized by the condensation reaction of DADM with the twice molar amount of TMAC. These two polymers, PAI-a and PAI-b, had the similar repeating unit, but the different repeating order. In addition, both of them were soluble in aprotic polar solvents such as DMSO, DMF and NMP, and insoluble in the ordinary organic solvents such as acetone, THF, benzene and chloroform.



Scheme 1 Preparation of chloromethylphenyl-terminated PDMS (2).



Scheme 2 Preparations of poly(amide-imide)s.



Scheme 3 Preparations of PAI/PDMS graft copolymers.

PAI/PDMS graft copolymer was prepared by substitution reaction between **2** and polyanion of PAI-a or PAI-b derived from the reaction of these PAIs with sodium hydride (NaH) in DMSO. The synthetic procedure is shown in Scheme 3. According to this polymer reaction, the PDMS chain was substituted on the N-position of amide group. In this case, a half equivalent amount of NaH was used as a base against the amide unit of PAI-a or PAI-b, where the maximum degree of substitution of PDMS chain was 50 mol% of the total amide groups. However, as shown in Table 1, the degrees of substitution of the obtained graft polymers were very low, and less than 10 mol%. Probably, this result would be due to the different solubility of PDMS **2** and polyanion of PAI in the reaction mixture. Therefore, in order to improve the substitution rate, another solvent was added in the reaction mixture with aim to change the co-solubility. As a result, the addition of pyridine was effective to improve the degree of substitution of PAI-b as shown in Table 1, although that of PAI-a was almost same as the case without pyridine. All of the obtained copolymers showed the similar solubility to the PAI homopolymers, PAI-a and PAI-b.

2.2 Results of pervaporation experiments

The membranes were prepared by the solvent-casting method from the NMP solution of PAI/PDMS graft copolymer with the highest siloxane

content (Run 4 in Table 1), and the separation properties of organic liquids from their aqueous solutions were evaluated by PV experiments. Table 2 shows typical results of the permeation of dilute aqueous solutions of organic liquids through the PAI/PDMS graft copolymer membrane. Ethanol, acetone and tetrahydrofuran (THF), were used as organic liquids. In all the cases, the selective permeation of organic liquid was observed. These results suggested that the continuous PDMS domain was formed in the copolymer membrane similar to PI/PDMS graft copolymer membrane²⁾. As seen from Table 2, acetone and THF were efficiently concentrated from their 10 wt.% dilute aqueous solution with high permeability coefficients, although the selectivity of ethanol was not so high. Furthermore, the stable permeation was observed even in the separations of acetone and THF. Therefore, it would be possible that this membrane material can be used for the removal of organic components from wastewater, since this graft copolymer membrane exhibits the high organic-permeability and the durability to separating organic components.

The separation of other organic solvents, for example, benzene or dichloromethane, from their dilute aqueous solutions and the effect of the degree of substitution of PDMS side chain on the separation characteristics are now in progress, and the results will be presented in the near future.

Table 1 Results of polymer reactions of PAIs with chloromethylphenyl-terminated PDMS (2).

| Run | Polymer | Solvent | m of 2 ^{a)} | Mole ratio of [NaH]/[amide] (%) ^{b)} | Degree of Substitution (%) ^{c)} | Mn × 10 ⁻⁴ ^{d)} | Mw/ Mn ^{d)} |
|-----|---------|-----------------------|-----------------------------|---|--|-------------------------------------|----------------------|
| 1 | PAI-a | DMSO | 13 | 50 | 5 | 28.8 | 1.10 |
| 2 | | DMSO/Py ^{e)} | 13 | 50 | 13 | 22.1 | 1.23 |
| 3 | PAI-b | DMSO | 13 | 50 | 8 | 9.34 | 1.93 |
| 4 | | DMSO/Py ^{e)} | 13 | 50 | 28 | 32.9 | 1.56 |

a) The average degree of polymerization (m) of **2**, determined on the basis of ¹H-NMR spectra.

b) The mole ratio of NaH against the total amide units of PAI in the preparation of polyanion.

c) The degree of substitution of PDMS chain on the amide group (see Scheme 2), determined by ¹H-NMR spectra.

d) Number-average molecular weight (Mn) and weight-average molecular weight (Mw) were determined by gel-permeation chromatography with DMF as eluent.

e) Py (pyridine) was added to the reaction mixture with chloromethylphenyl-terminated PDMS.

Table 2 Results of PV experiments of aqueous organic liquid solutions through PAI-b/PDMS graft copolymer membrane prepared from the product of Run 4 in Table 1.

| Organic liquid | Composition in wt.-% | | α ^{a)} | J ^{b)} Kg m ⁻² h ⁻¹ | P ^{c)} × 10 ⁻⁵ Kg m m ⁻² h ⁻¹ |
|-----------------|----------------------|----------|------------------------|---|--|
| | Feed | Permeate | | | |
| Ethanol | 10.8 | 13.6 | 1.3 | 0.65 | 3.50 |
| Acetone | 9.86 | 84.5 | 50.0 | 0.47 | 2.51 |
| Tetrahydrofuran | 9.56 | 89.3 | 78.8 | 0.88 | 4.73 |

a) Calculated according to the equation: $\alpha = (X_{\text{Org.}}/X_{\text{Water}}) / (Y_{\text{Org.}}/Y_{\text{Water}})$, where $X_{\text{Org.}}$ is the mass fraction of organic liquid in permeate, X_{Water} is the mass fraction of water in permeate, $Y_{\text{Org.}}$ is the mass fraction of organic liquid in feed, and Y_{Water} is mass fraction of water in feed.

b) Total flux of permeates.

c) Permeability coefficient.

3. EXPERIMENTAL

3.1 Synthesis of hydrosilyl-terminated PDMS (1)

A solution of trimethylsilanol (4.06 g, 45.0 mmol) in 100 ml of dry THF was prepared under an argon atmosphere, and 28.1 ml of 1.6 M hexane solution of butyllithium was added to this solution. After stirring for 30 min, hexamethylcyclotrisiloxane (D₃, 50.0 g, 225 mmol) dissolved in 150 ml of dry THF was added, and the reaction mixture was stirred at room temperature for 4 h. Then, dimethylchlorosilane (8.51 g, 90 mmol) was added in order to terminate the polymerization. The low-molecular-weight substances were removed by heating at 120°C *in vacuo* for 2 h to afford 49.3 g of **1**. Yield: 87.1 %.

3.2 Synthesis of 4-chloromethylphenyl-terminated PDMS (2)

1 (15 g, 11.1 mmol) and 4-chloromethylstyrene (2.55 g, 16.7 mmol) were mixed under an argon atmosphere. To this solution, 0.02 ml of 1.0 M isopropyl alcohol solution of chloroplatinic acid was added, and the mixture was stirred at 80°C for overnight. After heating at 120°C *in vacuo* for 2h, the product was purified by column chromatography on silica gel with hexane to afford 6.44 g of **2**. Yield : 43.8 %.

3.3 Synthesis of 4,4'-bis(4-carboxylphthalimide)-diphenylmethane (3)

Under an argon atmosphere, trimellitic anhydride (7.25 g, 37.6 mmol) and 4,4'-diaminodiphenylmethane (3.00 g, 15.1 mmol) was dissolved in 100 ml of NMP, and the solution was stirred at room temperature for overnight. Then, 14.4 ml of triethylamine and 9.2 ml of acetic anhydride were added to this solution, and the temperature was raised to 100°C with continuous stirring for overnight. After this solution was poured into an excess amount of water, the crude product was obtained. The product was washed with hot ethanol to obtain 6.13 g of **3**. Yield: 74.3 %.

3.4 Synthesis of PAI-b

The compound **3** (13.0 g, 23.8 mmol) and 4,4'-diaminodiphenylmethane (4.72 g, 23.8 mmol) were dissolved in 86 ml of NMP, and the mixture was stirred for 5 min under argon atmosphere. Then, 52 ml of triphenylphosphine and 32 ml of pyridine were added to this solution, and it was stirred at 100°C for overnight. After this solution was poured into an excess amount of methanol, the precipitate was filtered and dried, to obtain 13.1 g of PAI-b. Yield: 77.9 %.

3.5 Synthesis of PAI/PDMS graft copolymer

NaH (60 % in oil, 56.4 mg, 1.41 mmol) was dispersed in 4 ml of dry DMSO, and the mixture was stirred at 70°C for 2h. To this solution, 1.0 g of PAI-b and 2.0 ml of dry DMSO was added, and the mixture was stirred at 100°C for another overnight. Then, after 2 (1.69 g, 1.41 mmol) and 5 ml of pyridine were added, it was stirred at 100°C for overnight. Finally, the reaction mixture was poured into an excess amount of methanol to precipitate the polymer. By this polymer reaction, 1.54 g of PAI/PDMS graft copolymer was obtained.

3.6 Pervaporation experiment

The sample membrane for the measurement of pervaporation was cut into circular pieces with a diameter of 47 mm and a thickness of 100 μm. Pervaporation of aqueous organic liquid solutions through the membrane was carried out by the ordinary method using a stainless steel cell, which was dipped in a feed solution kept at 30°C. The permeation area of the membrane was 9.6 cm². Ethanol, acetone and THF were selected as the organic liquids. The permeated vapor was trapped in a vessel cooled with liquid N₂, and the concentration of permeate was determined by gas chromatography. The flux (J) and the permeability coefficient (P) were calculated from the weight of permeate (w) in the vessel, the permeation time (t), the membrane area (A) and the membrane thickness (L), according to the equations shown below;

$$J = w/At, \quad P = wL/At.$$

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