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SPECIALTY POLYMERIC MEMBRANES. 11. PERVAPORATION OF BENZENE/CYCLOHEXANE MIXTURES THROUGH POLY(VINYL ALCOHOL)-GRAFT-POLY(ACRYLIC ACID) MEMBRANES

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NOTE

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Key Words: Graft Polymerization, Pervaporation, Membrane, Poly(vinyl alcohol), Poly(acrylic acid), Benzene, Cyclohexane

ABSTRACT

Poly(viny alcohol)-graft-poly(acrylic acid) was prepared by graft polymerization of acrylic acid onto poly(vinyl alcohol) initiated by ceric ammonium nitrate. Membranes prepared from grafted poly(vinyl alcohol) permeated benzene from benzene/cyclohexane mixtures by pervaporation. Permselectivity toward benzene increased with the increase in poly(acrylic acid) content in the membrane, and the separation factor reached around 10.

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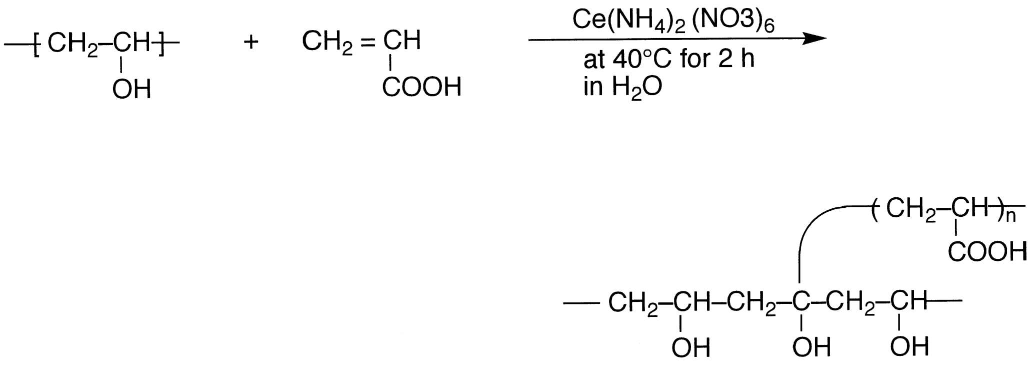
INTRODUCTION

In the petroleum refinery process, aromatics are separated from aromatics/ aliphatics mixtures by applying azeotropic distillation, extractive distillation, adsorption, solvent extraction, crystallization, etc. Those separation techniques are energy-intensive ones. Pervaporation and vapor permation are alternatives because membrane separation techniques are recognized as potentially more economical and energy-saving processes. Separation of aromatics/aliphatics mixtures by using a membrane is one of the interesting subjects in petroleum industries. Removal of benzene, (one of the typical aromatics) is one of the interesting and important subjects in connection with environmental issues [1]. Based on this, the authors' research group has been developing novel membrane materials [2-4].

There are a couple of ways to develop novel polymeric materials for membranes; one is polymerization of functional monomers. The other is to modify existing polymeric materials. The first might be time consuming and may not give a desired molecular weight, which is enough to form a self-stand membrane. On the contrary, the latter is of convenience. So far, polyamide nylon 6 has been adopted as a starting material, modifications of nylon 6 have been carried out and their pervaporation performance of benzene/cyclohexane mixtures has been investigated [2-4]. Poly(vinyl alcohol), **PVA**, is one of the promising polymeric materials for pervaporation separation of aromatics/aliphatics mixtures, because **PVA** shows good stability to gasoline and other oil derivatives [5]. In addition to the nature of **PVA** mentioned above, **PVA** is susceptible to a simple chemical modification of graft polymerization initiated by ceric ions [6-9].



Scheme 1. Synthetic scheme of PVA-graft-PAA.

In the present article, we desribe preparation of poly(vinyl alcohol)-graft-poly(acrylic acid), **PVA-graft-PAA**, and pervaporation performance of benzene/cyclohexane mixtures through modified **PVA** membranes.

EXPERIMENTAL

Materials

Poly(vinyl alcohol), **PVA**, with the degree of polymerization being ca. 2,000 and degree of saponification being 99.3%, was purchased from Nacalai Tesque, Inc., and used without further purification. Acrylic acid (**AA**) was purified by the usual method [10]. Ceric ammonium nitrate (**CAN**) was dried in a vacuum oven at 80°C for 4 hours. Other reagents, such as nitric acid, dimethyl sulfoxide (**DMSO**), and ethanol (**EtOH**), were used as received. Water was deionized.

Graft Polymerization

Graft polymerization of **AA** onto **PVA** was carried out as follows [6-9]: a 2.0 g (4.54×10^{-2} unit mol) of **PVA** and prescribed amount of **AA** were dissolved in 30 cm^3 of water in an ampule. To this ampule was added a 5 cm^3 of 1.7 mol dm^{-3} nitric acid aqueous solution containing a 0.498 g (9.08×10^{-4} mol) of **CAN**. And then, an additional 10 cm^3 of water was added. After N_2 was bubbled into the reaction mixture for 5 minutes, the graft polymerization was carried out at 40°C for 2 hours. The reaction mixtures were poured into water (Method 1) or into **DMSO** (Method 2) to be dissolved and then the solutions were poured into **EtOH**. The precipitates obtained were centrifuged by methods summarized in Figure 1.

Spectroscopic Measurement

IR spectra were taken on a JASCO FT/IR-5300 Fourier Transform Infrared Spectrometer.

^{1}H NMR spectra were obtained with a BRUCKER ARX-500. The spectra were measured at ambient temperature, using a 20 g dm^{-3} DMSO-d_6 solution with tetramethylsilane (**TMS**) as an internal standard.

Preparation of Membrane

Membranes were prepared from an aqueous solution (100 g dm^{-3}). The

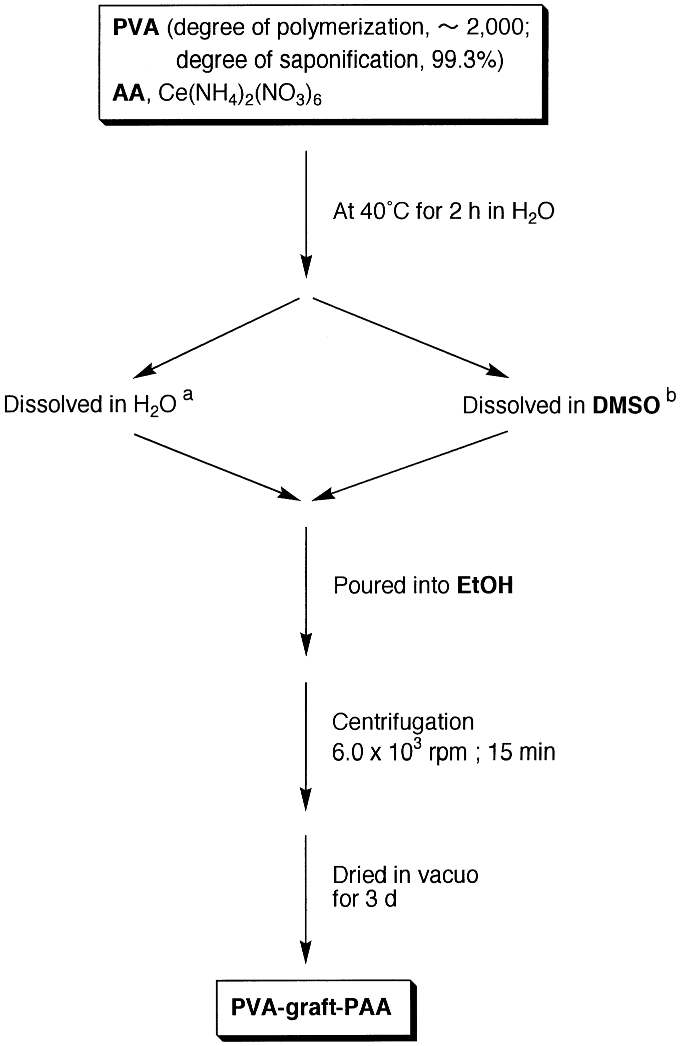


Figure 1. Synthetic schemes of poly(vinyl alcohol)-graft-poly(acrylic acid) (PVA-graft-PAA). (a, Method 1; b, Method 2).

solution was poured onto a POREFLON FP022 with the casting thickness of 0.268 mm and dried at 50°C for 24 hours.

Pervaporation

Permeation of benzene/cyclohexane mixture was performed by an ordinary pervaporation technique [11]. The membrane area in contact with the liquid feed was 17.3 cm^2. The downstream pressure applied was kept at around 267

Pa (2.0 mmHg). Pervaporation experiments were carried out at the constant temperature of 50°C.

Separation analysis was carried out on a Shimadzu GC-8APT gas chromatograph equipped with a 3.0 m long column packed with polyethyleneglycol 6000 (Shimalite TPA).

The separation factor, α, is defined as

$$\alpha = (Y_{benzene} / Y_{cyclohexane}) / (X_{benzene} / X_{cyclohexane})$$

where Y_is are weight fractions in the permeate and X_is are those in the feed, respectively.

RESULTS AND DISCUSSION

Graft Polymerization

The introduction of **PAA** onto **PVA** was confirmed by IR and ^{1}H NMR spectra of graft polymers. An example of IR and ^{1}H NMR spectra are shown in Figure 2. In the IR spectrum, a new absorption band at 1720 cm^{-1}, which is assigned to C=O stretching band of **PAA**, can be detected. The existence of **PAA** in **PVA** was also confirmed by ^{1}H NMR measurement. ^{1}H NMR spectrum of grafted polymer is also shown in Figure 2. The signal assigned to carboxyl proton was newly observed at around 12.2 ppm. By using the area of carboxyl proton and that of hydroxyl proton at around 3.8 ppm, (**PAA**)/(**PVA**) ratio, which is the ratio for unit mole of **PAA** to that of **PVA**, was determined to be 1.05. The results of graft polymerization are summarized in Table 1. As for **PVAPAA-235**, a part of the grafted polymers was gelated. **PVAPAA**, of which the (**AA**)/(**PVA**) ratio being 5.0, the whole of obtained polymer was found to be gelated. From Table 1, it can be said that the (**AA**)/(**PVA**) feed ratio should be kept below around 3 in the present graft polymerization in order to obtain soluble grafted polymers. The effect of graft polymerization conditions on the composition of the grafted polymer is given in Figure 3. In Figure 3, the datum of **PVAPAA-235**, which was partially gelated polymer, is omitted.

Pervaporation

Pervaporation performance of benzene/cyclohexane separation through grafted polymeric membranes were studied at the weight fraction of benzene in

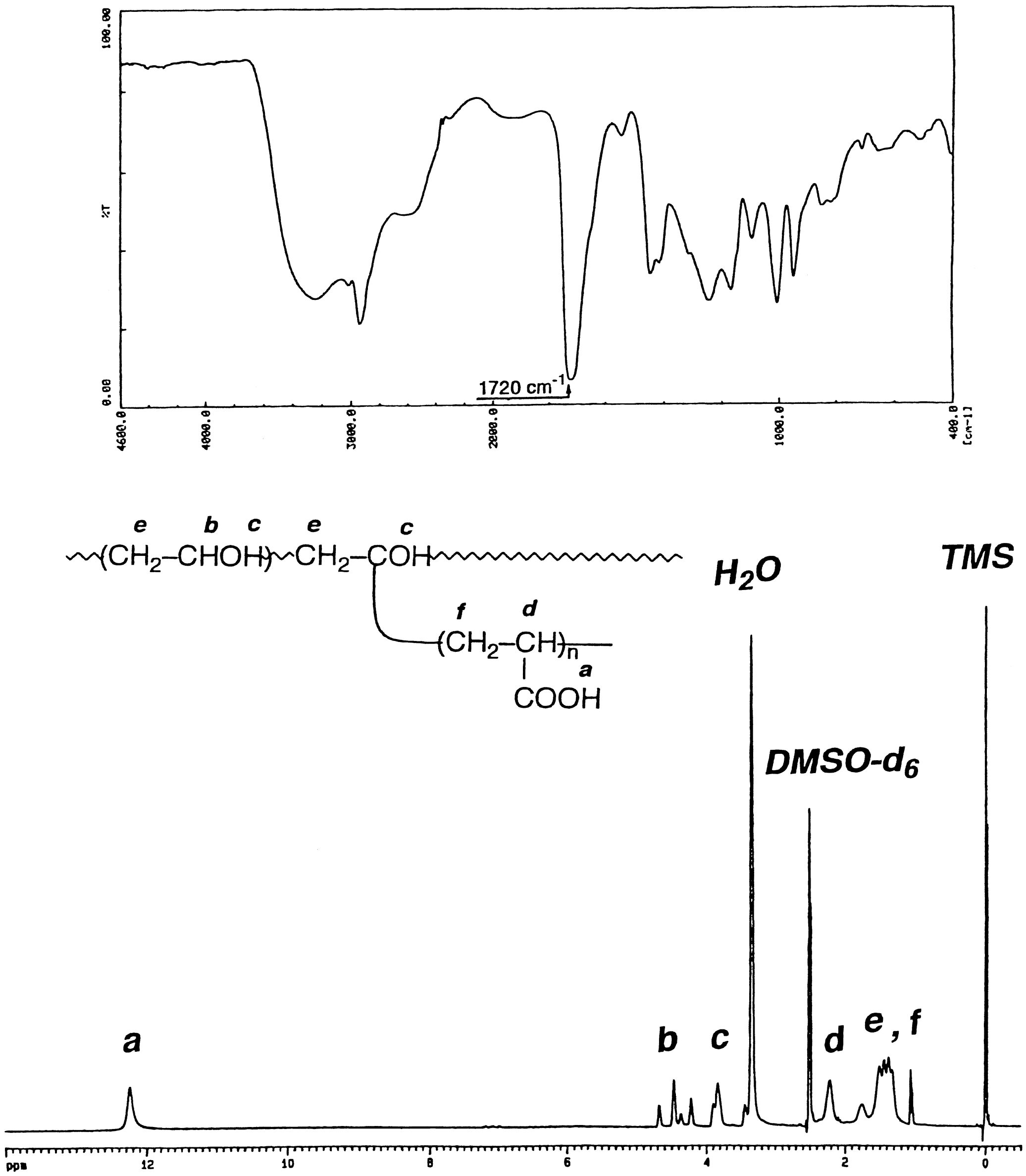


Figure 2. IR and ^{1}H NMR spectra of PVAPAA-105. ((PAA)/(PVA) = 1.05).

a feed of 0.5. The results are given in Figures 4-6; the effect of polymer composition on weight fraction of benzene in permeate (Figure 4), that on separation factor (Figure 5), and that on total flux (Figure 6). The membrane performance of unmodified **PVA** membrane [12] is given in Figures 4 and 5. Modified **PVA** membranes permeated benzene in preference to cyclohexane as well as unmod-

TABLE 1. Preparation and Characterization of PVA-Graft-PAA[a]

Sample	Charged amounts				PVA-graft-PAA		PAA fraction	
	PVA/g	**AA**/g	**CAN**/g	(**AA**)/(**PVA**)[b]	Yield/g	(**PAA**)/(**PVA**)[c]	wt.	mol
PVAPAA-021[d]	2.00	1.64	0.50	0.5	2.68	0.21	0.258	0.176
PVAPAA-066[e]	2.00	3.28	0.50	1.0	4.31	0.66	0.522	0.400
PVAPAA-078[d]	2.00	4.91	0.50	1.5	4.94	0.78	0.562	0.439
PVAPAA-105[d]	2.00	6.55	0.50	2.0	3.80	1.05	0.633	0.513
PVAPAA-121[d]	2.00	8.19	0.50	2.5	5.10	1.21	0.665	0.548
PVAPAA-306[e]	2.00	9.82	0.50	3.0	8.08	3.06	0.834	0.754
PVAPAA-235[d,f]	2.00	13.08	0.50	4.0	7.00	2.35	0.794	0.702
PVAPAA[g]	2.00	16.37	0.50	5.0	-	-	-	-

[a] Graft polymerization was carried out at 40˚C for 2 h in 40 cm^3 of H_2O.
[b] Ratio for mole of charged **AA** to unit mole of charged **PVA**.
[c] Ratio for unit mole of **PAA** to that of **PVA**.
[d] Grafted polymers were purified by Method 1.
[e] Grafted polymers were purified by Method 2.
[f] Grafted polymer was partially gelated.
[g] Grafted polymer was gelated.

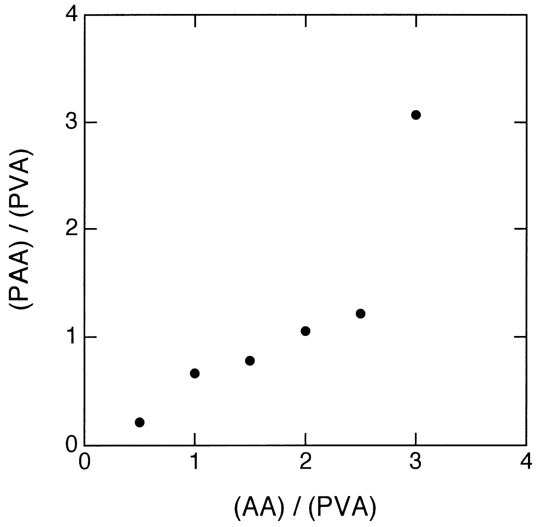


Figure 3. Relationship between composition of PVA-graft-PAA and graft polymerization conditins. (Graft polymerization was carried out at 40EC for 2 hours in water).

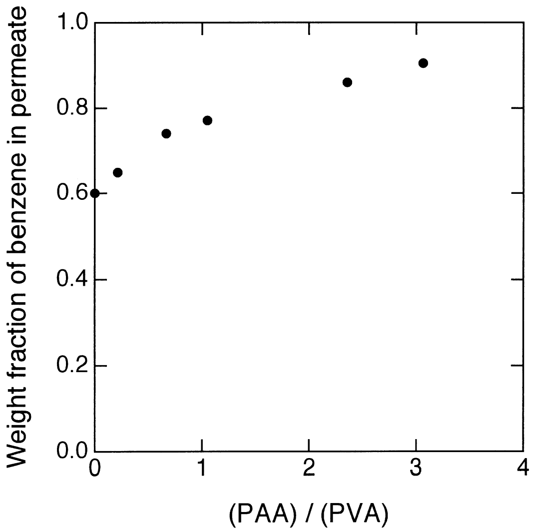


Figure 4. Effect of composition of PVA-graft-PAA on the prevaporation of benzene/cyclohexane mixture. (Weight fraction of benzene in feed, ca. 0.5; operating temperature, 50EC, down-stream pressure, ca. 267Pa (2.0mmHg)).

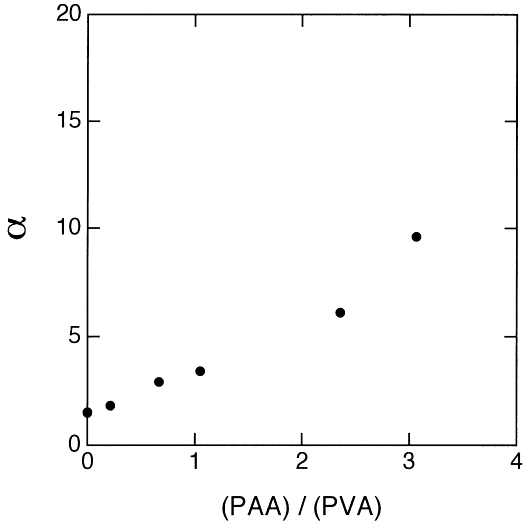


Figure 5. Effect of composition of PVA-graft-PAA on separation factor (α) of benzene/cyclohexane mixture. (Weight fraction of benzene in feed, ca. 0.5; operating temperature, 50EC; downstream pressure, ca. 267Pa (2.0mmHg)).

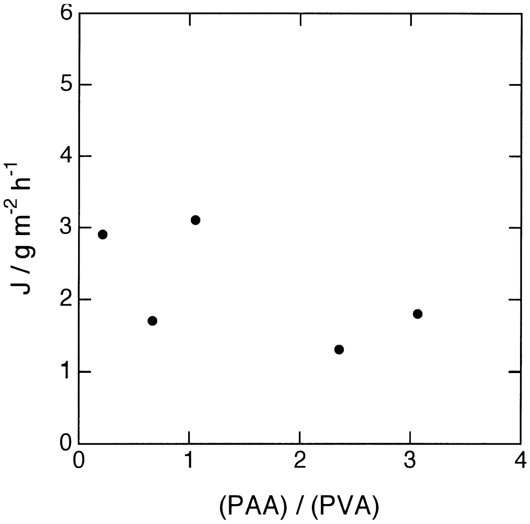


Figure 6. Effect of composition of PVA-graft-PAA on flux (J) of benzene/cyclohexane mixture. (Weight fraction of benzene in feed, ca. 0.5; operating temperature, 50EC; downstream pressure, ca. 267Pa (2.0mmHg)).

ified **PVA** membrane. The introduction of **PAA** onto **PVA** led the enhancement of permselectivity toward benzene. Permselectivity toward benzene increased with the increase in **PAA** content in the membrane. This might be due to the interaction between carboxyl group in **PAA** and benzene, which might be more polar than cyclohexane [13]. Against all expectations, flux values were not enhanced by the introduction of **PAA** onto **PVA**.

CONCLUSION

Poly(viny alcohol)-graft-poly(acrylic acid) was prepared by graft polymerization of acrylic acid onto poly(vinyl alcohol) initiated by ceric ammonium nitrate. Membranes prepared from grafted poly(vinyl alcohol) permeated benzene from benzene/cyclohexane mixtures by pervaporation.

ACKNOWLEDGEMENT

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