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Photoblock Copolymerization of Styrene with Acrylic Acid and Utilization for Reverse Osmosis Membrane

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ABSTRACT

It was reported previously that carbon monoxide-styrene copolymer in benzene is photodegraded by irradiation from high pressure mercury lamp, and is block copolymerized in the presence of methyl methacrylate. In the present paper, by using macroradical produced by photolysis with main chain scission of carbon monoxide-styrene copolymer, a styrene-acrylic acid block copolymer was prepared. The block copolymer could be utilized as a reverse osmosis membrane, if the thin layer was formed on a support membrane (Tyvek or Celgard).

INTRODUCTION

The present author has reported previously on preparation and photodegradation of carbon monoxide-styrene and carbon monoxide-vinyl chloride copolymers [1, 2]. It was found that carbon monoxide-styrene copolymer photodegraded with main-chain scission and macroradical production by photolysis could be used in preparation of block copolymers [3]. In the present paper, preparation of block copolymer of styrene with acrylic acid (hydrophilic monomer) in

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the same manner, and its utilization to prepare reverse osmosis membranes of the block copolymers are described.

Reverse osmosis membranes from block or graft copolymers or polymers involving poly(acrylic acid) as a composite were prepared and utilized by many authors [4-13]. Some successful examples for composite membranes have been cited by Hwang and Kammermeyer [14].

In the present report, block copolymers of styrene and acrylic acid were used for composite reverse osmosis membranes supported on polyethylene paper (Tyvek) or polypropylene membrane (Celgard).

EXPERIMENTAL

Preparation of Poly(styrene-b-Acrylic Acid)

Carbon monoxide-styrene copolymer containing 2.05 mole % of carbon monoxide units was dissolved in benzene in a quartz cell, and then an appropriate quantity of acrylic acid was added. A stream of nitrogen was bubbled through the contents of the cell, and then the cell was sealed by a stopcock, was set in metal block controlled by thermoregulator, and photoirradiated with a 250-W high-pressure mercury lamp, with or without filter, at a distance of 30 cm from the light source. After photoirradiation for a given period, the polymer solution was poured into n-hexane, and the precipitate was collected by filtering and dried in vacuum oven.

In order to limit the photoirradiation to a particular wavelength range, different kinds of optical glasses (Hoya Glass Works) were used as filters. The obtained polymer was extracted with methanol at reflux temperature, and separated into soluble and insoluble fractions. The insoluble fraction was considered to be block copolymer of styrene with acrylic acid, which was soluble in pyridine and N,N-dimethylacetamide.

The results of photoblock copolymerizations are tabulated in Table 1, and the infrared spectrum of the block copolymer is shown in Fig. 1.

Reverse Osmotic Membranes from Poly(styrene-b-Acrylic Acid)

Dope of poly(styrene-b-acrylic acid) dissolved in N,N-dimethylacetamide (2% solution) was cast on Tyvek 1422R (supplied by DuPont Far East Co.) or Celgard 2400 (porous hydrophobic polypropylene

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TABLE 1. Results of Photoblock Copolymerization of Styrene (St) with Acrylic Acid at 30°C for 3 hr

No.	Polymer (g) Type	Polymer (g) Wt (g)	Acrylic acid (ml)	Benzene (ml)	Residue after extraction with methanol (g)	Weight increase (g)	Degree of block (%)	Efficiency of block (%)[b]	Wavelength in Hg lamp, nm
1	CO-St	0.51	2.0	8.0	0.962	0.447	86.9	54.0	Whole range
2		0.50	1.0	9.0	0.635	0.133	26.4	29.9	Whole range
3		0.52	1.5	8.5	0.800	0.285	56.4	54.2	Whole range
4		0.52	1.5	10.5	0.803	0.280	53.6	40.0	Whole range
5		0.52	1.5	13.5	0.854	0.338	65.5	43.5	Whole range
6		0.52	1.52	10.5	0.940	0.423	81.9	40.2	> 280
7		0.51	1.5	10.5	0.933	0.423	83.5	39.8	> 300
8		0.52	1.5	10.5	0.493	0	0	0	> 340
9	St	0	1.5	10.5	0	0.070			Whole range
10		0.53	1.5	10.5	0.615	0.088			Whole range
11		0	1.5	10.5	0	0.095			> 280
12		0.51	1.5	10.5	0.601	0.095			> 280

[a] Degree of block was estimated by weight increase (g)/polymer used (g) × 100.

[b] Efficiency of block was estimated by blocked acrylic acid/consumed acrylic acid × 100.

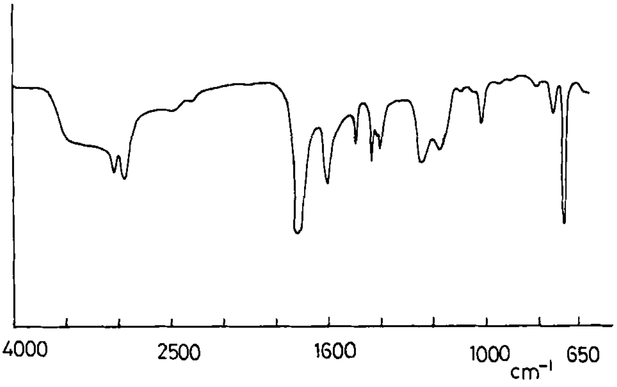

FIG. 1. Infrared spectrum of poly(styrene-b-acrylic acid. Sample No. 6 in Table 1.

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membrane manufactured by Celanese Corp. and supplied by Polyplastics Co., Japan; maximum hole diameter, 0.2 × 0.02 μm; degree of void, 38%; thickness, 25 μm) and dried in a vacuum oven at 60°C for 1/2 hr. Successively, heat treatment was carried out at 90°C or 110°C for about 2 hr.

Film cast on Celgard contracted considerably in a uniaxial direction with heat treatment. Generally, the polymer layer formed adhered tightly on Tyvek or Celgard and did not peel.

Because the composite membrane without heat treatment led to low rejection with rapid flow, as shown in Fig. 2, the cast film was treated by heating at 90°C or 110°C on a membrane supported with Tyvek or Celgard in all subsequent experiments.

Reverse Osmosis

Measurement of reverse osmosis was carried out by using an Abcor RO-3 type (180 ml) reverse osmometer. The 0.3% sodium chloride aqueous solution (3000 ppm) was fed in at 40 or 70 kg/cm^2 at room temperature. Concentration of the permeated solution was determined by electric conductmeter. Degree of salt rejection was estimated by the equation:

$$\text{Degree of salt rejection} = 1 - (C_2/C_1)$$

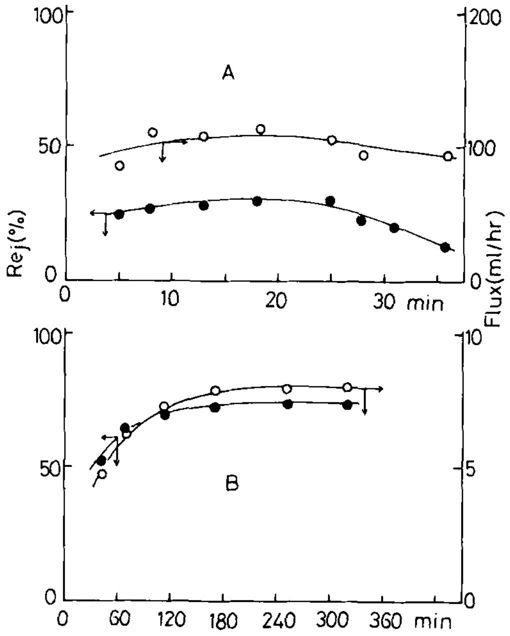

FIG. 2. Rejection and flux of composite membrane of poly(styrene-b-acrylic acid on Celgard: (A) membrane dried in vacuo at 60°C; (B) membrane dried in vacuo at 60°C, then treated at 110°C for 2 hr. Feed, 0.3% NaCl aqueous solution.

where C_1, C_2 are concentration of sodium chloride in the feed solution and in the permeated solution, respectively. The effective surface area of a composite layer membrane in the reverse osmosis was 30.2 cm^2. The thickness of the polymer layer coated on the support could not be determined exactly but was approximated from weight of coated polymer and effective surface area.

RESULTS AND DISCUSSION

In photoblock copolymerization of styrene with acrylic acid by photolysis of carbon monoxide-styrene copolymer in benzene, the degree of blocking affected by the acrylic acid concentration, as shown in Fig. 3. Moreover, it was also affected by the wavelength

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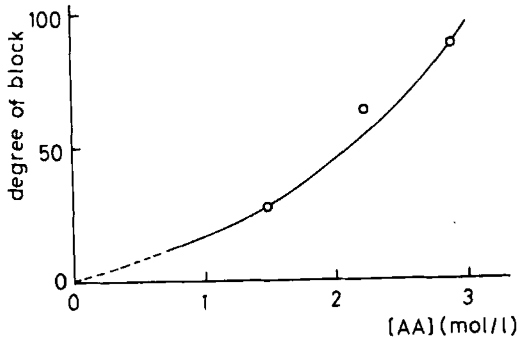

FIG. 3. Relation of degree of blocking to concentration of acrylic acid in feed mixture.

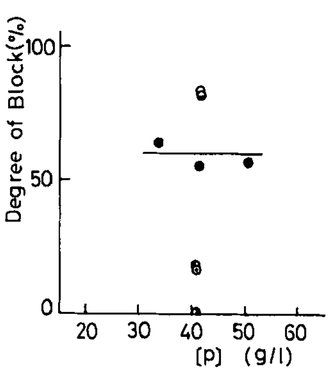

FIG. 4. Effect of wavelength on degree of blocking in photopolymerization of acrylic acid in the presence of styrene-carbon monoxide copolymer (CO-St) or polystyrene (St): (●) CO-St, whole: (◓) CO-St, > 280 nm: (○) CO-St, > 300 nm; (◑) CO-St, > 340 nm; (◐) St, > 280 nm: (◎) St, whole.

of the light source (Fig. 4). Wavelengths between 300 nm and 340 nm were most effective for photoblock copolymerization, while wavelengths over 340 nm showed no effect.

In the presence of polystyrene, the residue after extraction with methanol showed an increase of weight at about 18%. This phenomenon is attributable to photograft formation rather than to block copolymerization, and the weight increase showed no enhancement on filtering

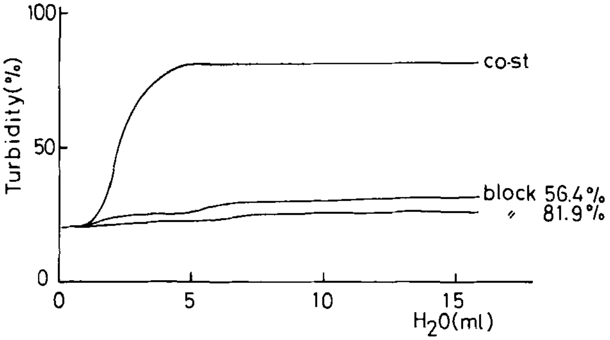

FIG. 5. Turbidities of styrene-carbon monoxide copolymer and poly(styrene-b-acrylic acid) in 1% N,N-dimethylacetamide solution (precipitant: water).

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the light from the high-pressure mercury lamp, unlike the case of photopolymerization of acrylic acid in the presence of carbon - monoxide-styrene copolymer (Fig. 4).

These facts proved that photoblock polymerization of acrylic acid occurred in addition to some graft polymerization in the presence of carbon monoxide-styrene copolymer. Infrared spectra of poly(styrene-b-acrylic acid) showed the absorptions of carboxylic acid at 1720 cm^{-1} and of monosubstituted phenyl group at 700 cm^{-1}, as shown in Fig. 1.

Results of turbidmetry of poly(styrene-b-acrylic acid) in N,N-dimethylacetamide with water as precipitant are shown in Fig. 5. No remarkable increase of turbidity was evident in block copolymer, which was made up to a large extent of hydrophilic groups (acrylic acid unit), but in the original polymer (carbon monoxide-styrene copolymer), an abrupt increase of turbidity was observed on addition of a small amount of precipitant.

Reverse osmosis of a composite membrane of poly(styrene-b-acrylic acid) with Tyvek support paper was carried out at 40 kg/cm^2 three times successively, and the results are shown in Fig. 6. In all cases, salt rejection remained at 50-55%.

Increase of pressure from 40 kg/cm^2 to 70 kg/cm^2 scarcely improved this of salt rejection figure, although the flux became higher (Fig. 7).

Reverse osmosis of a composite membrane of poly(styrene-b-acrylic acid) with a Celgard support membrane was also carried out, and results are shown in Fig. 8. Multiplication of the block copolymer

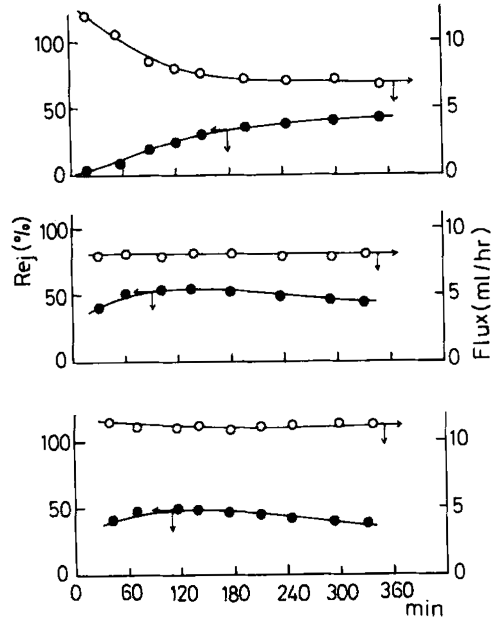

FIG. 6. Rejections and fluxes of composite poly(styrene-b-acrylic acid) (No. 6 in Table 1) membrane on Tyvek in three successive experiments. Heat treatment, 90°C for 1 hr; thickness, about 10 μm; feed, 0.3% NaCl aqueous solution; pressure, 40 kg/cm^2.

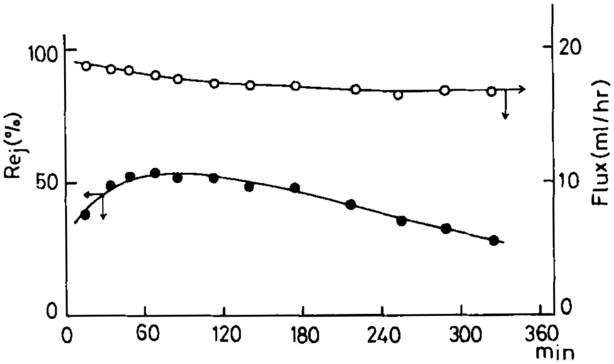

FIG. 7. Rejection and flux of composite poly(styrene-b-acrylic acid) (No. 6 in Table 1) membrane on Tyvek. Heat treatment, 90°C for 1 hr; thickness, about 20 μm; feed, 0.3% NaCl aqueous solution; pressure, 70 kg/cm^2.

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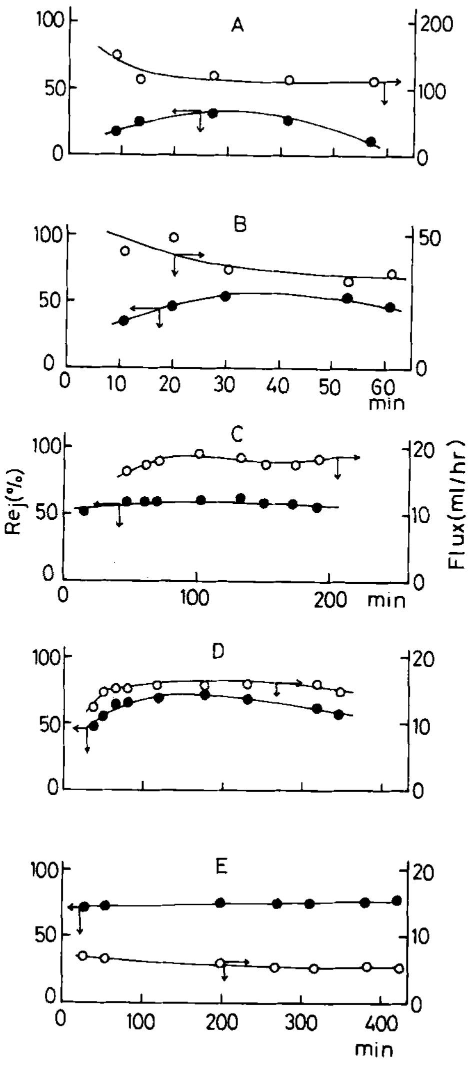

FIG. 8. Effect of multiplication by coating repeatedly on rejection and flux in composite poly(styrene-b-acrylic acid) (No. 6 in Table 1) membrane on Celgard of various thicknesses: (A) 0.4 μm; (B) 0.7 μm; (C) 2.0 μm; (D) 3.0 μm; (E) 4.0 μm. Heat treatment, 110° C for 2 hr after vacuum drying at 60° C; feed, 0.3% aqueous solution; pressure, 70 kg/cm^2.

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TABLE 2. Effects of Thickness of Block Copolymer Layer Cast on Celgard Membrane in Reverse Osmosis[a]

Sample	Thickness (μm)	Flux (ml/hr)	Flux (gal/ft^2-day)	Rejection (%)[b]
1	ca. 0.4	110	20.5	31
2	ca. 0.7	35	6.5	54
3	ca. 2.0	18	3.4	62
4	ca. 3.0	16	3.0	71
5	ca. 4.0	5	0.9	77

[a] Block copolymer used is No. 6 in Table 1.

[b] These values were accepted at maximum degree of rejection, because in batch type experiment, gradual decreases of rejection due to concentration polarization were observed.

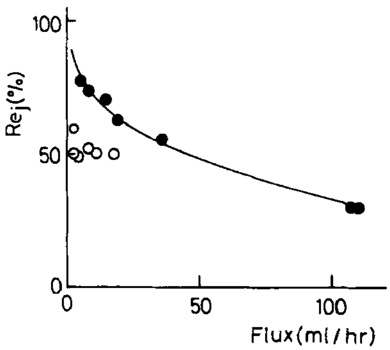

FIG. 9. Relation of rejection with flux in composite poly(styrene-b-acrylic acid) (No. 6 in Table 1) membranes on Tyvek and Celgard: (○) Tyvek; (●) Celgard.

layer by repeated casting on the supported membrane improved the salt rejection from 30% to 77% (Table 2). An increase in thickness of the block copolymer layer contributed to improvement of salt rejection, but unfortunately flux decreased gradually (Fig. 9).

It is noteworthy that the composite membrane on Celgard membrane

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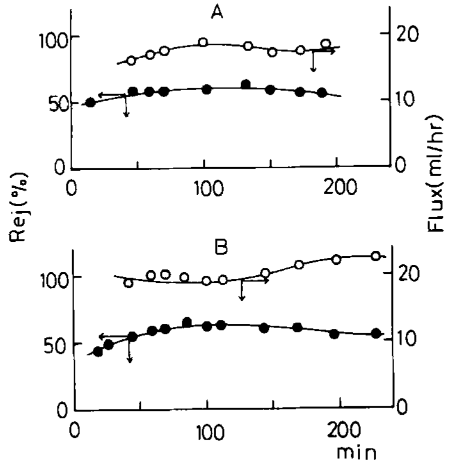

FIG. 10. Influence of degree of blocking on rejection and flux in composite poly(styrene-b-acrylic acid) membrane on Celgard at 70 kg/cm^2: (A) degree of blocking = 81.9%; (B) degree of blocking = 53.6%. Heat treatment, 110°C for 2 hr after vacuum drying at 60°C; thickness, about 2 μm, feed, 0.3% aqueous solution.

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afforded better rejection than on the membrane Tyvek paper. This fact implies that in a composite reverse membrane, the combination of coated polymer layer with support material is one of important factor. Sachs and Lonsdale [10] had already reported that poly(acrylic acid)-cellulose nitrate-cellulose acetate composite membrane showed good rejection with high flux for 3000 ppm sodium chloride aqueous solution. Milstead and Tagami [12] also reported that polyacrylic acid-polysulfone composite membrane brought good results at such levels as in the case of poly(acrylic acid)-cellulose nitrate-cellulose acetate composite membrane.

Although poly(styrene-b-acrylic acid) is insoluble in water, in which it is different from poly(acrylic acid), and it has an advantage that the polymer does not contaminate in a draining solution on reverse osmosis, the composite membrane composed of polymer with the support (Celgard) affords a rather lower flux than in the cases of poly(acrylic acid)-cellulose nitrate-cellulose acetate of poly(acrylic acid)-polysulfone composite membranes, in spite of similar good rejection.

Reverse osmosis by use of composite membranes of the same thickness from poly(styrene-b-acrylic acid) involving different degrees of blocking of 81.9% and 53.6% were compared; salt rejection was 60% and 63% and flux was 18 and 20 ml/hr, respectively, as shown in Fig. 10. A difference in degree of blocking of the acrylic acid unit produced no remarkable improvement of salt rejection and flux.

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