Polyacrylonitrile Ultrafiltration Membranes Containing Negatively Charged Groups for Permeation and Separation of Dextran and Dextransulfate

TAKAOMI KOBAYASHI,* TAKURO MIYAMOTO, TOSHIHIKO NAGAI, and NOBUYUKI FUJII

Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata, 940-21 Japan

SYNOPSIS

Ultrafiltration membranes of poly(acrylonitrile-co-sodium styrenesulfonate) [P(AN-co-SSS)] were prepared by casting the copolymer solution into water. The ultrafiltration rate of P(AN-co-SSS) membranes was controlled by adding poly(ethylene glycol) (PEG) of various molecular weights to the casting solution. The effect of the PEG addition on the membrane properties was examined. By using the P(AN-co-SSS) membranes, which possess various molecular weight cutoff (MWCO) properties, the permeation behaviors of dextran (D) and dextransulfate (DS) were compared. The P(AN-co-SSS) membranes markedly restricted the permeation of DS, owing to electrostatic barrier of the negatively charged groups in the membrane. The electrostatic sieve separation of DS and D, each having similar molecular size, with the membranes was also investigated. The membrane having negatively charged groups effectively rejected to DS with a high permselectivity. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the past decade, many high-performance membranes have been developed.[1,2] Among them, charged ultrafiltration membranes[3-8] have been paid much attention for the separation and concentration of macromolecular solute because of the electrostatic repulsion to ionic solute having same sign as that of the membrane.[3,4]

With a typical ultrafiltration membrane having only a mechanical sieve, it is impossible to separate the solute components having similar molecular size. However, ultrafiltration membranes having charges separate the components, because the membrane markedly restricts the transport of ionic solute having same sign of the charges as that of the membrane. Therefore, it is a challenging subject to evaluate the electrostatic sieve effect of the ultrafiltration membranes having charges on the permeation and separation of the solute mixtures.

For charged ultrafiltration membranes, polymers having ionic moieties such as sulfonic acid or the quaternary ammonium group were synthesized by some chemical modifications on polysulfone,[9] poly(vinylidene fluoride),[10] poly(phenylene oxide),[11] and poly(ether ether ketone).[12]

In our previous works,[4,5,7,8] charged ultrafiltration membranes were prepared from copolymers of polyacrylonitrile with some ionic monomers by photochemical method. Recently, we prepared a random copolymer,[13] poly(acrylonitrile-co-sodium styrene sulfonate) [P(AN-co-SSS)], by a conventional technique utilizing azobisisobutyronitrile (AIBN). It was reported that the ultrafiltration membranes of P(AN-co-SSS) have an effective permselective barrier with a high separation yield of dextran/dextransulfate (D/DS) components, having similar molecular size. In the present report, the preparation and properties of the ultrafiltration membranes of P(AN-co-SSS) were examined in detail. The effect

of the electrostatic barrier to the permeation of the anionic solute was also discussed.

EXPERIMENTAL

Materials

All reagents used in the experiment were of reagent grade, unless otherwise described. Acrylonitrile (AN), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were distilled before use. Sodium styrene sulfonate (SSS) was a product of Tokyo Kasei and used without further purification.

Dextran (D) (Pharmacia) and dextransulfate (DS) having 1.6 mol % content of sodium sulfonate groups (Tokyo Kasei) were employed without further purification. Various molecular weight (M_w) dextrans in the range of 1×10^4 to 2×10^6 were employed as a probe for measuring molecular weight cutoff (MWCO) of the ultrafiltration membranes. Various M_w's of poly(ethylene glycol) (PEG) (Nakarai) having 7.5×10^3, 2×10^4, and 5×10^4 were used as additives in order to obtain various ultrafiltration rates for the membrane.

Polymerization

Copolymerization of AN and SSS was carried out in DMSO solution at 60°C as follows: In a reaction vessel of 500 mL capacity, 50 g (0.94 mol) of purified AN, 5.84 g (0.028 mol) of SSS, 170 mL of DMSO, and 1.38 g (9.7 mmol) of AIBN were introduced. Polymerization was carried out at 60°C for 4 h in a nitrogen flow. The mixture was poured into a large quantity of aqueous methanol to precipitate the copolymer, P(AN-co-SSS) (62.2% conversion). The content of SSS groups in the copolymer was determined from acid–base titration[4] for 0.51 mmol/g. The copolymer having a low content of SSS groups (0.03 mmol/g) was prepared analogously from a mixture of 40 g (0.75 mol) of AN, 0.156 g (0.7 mmol) of SSS, and 10.74 g (4.5 mmol) of AIBN in 132 mL of DMSO (49.4% conversion). The preparation of other copolymers having SSS contents for 0.11 and 0.058 mmol/g was reported previously.[13] Acrylonitrile homopolymer (PAN) was prepared by photopolymerization in the presence of carbon tetrabromide according to literature.[14]

Polymer Characterization

Properties of P(AN-co-SSS) obtained by copolymerization of AN and SSS are summarized in Table

I. To check the SSS content in the copolymer, ^{1}H-NMR spectra for the copolymer were measured in d_6-DMSO at 60°C using a JNM-GX 270 FT-NMR spectrometer. The SSS content was calculated from the integrals of the total aromatic and aliphatic proton region. The values obtained are all in good agreement with those of acid–base titration as shown in Table I.

Viscosity of the copolymer in DMF solution containing $0.5M$ LiCl was measured at 30°C using an Ubbelohde viscometer. In the range of the polymer concentration (C) from 0.5 (g/100 mL) to 0.15, the values of intrinsic viscosity, $[\eta]$, were estimated by extrapolating the linear η_{sp}/C vs. C plot.

Membrane Preparation and Permeation Experiments

Preparation of the ultrafiltration membranes containing negatively charged groups was followed by the phase-inversion method as reported previously;[5] DMSO solution containing 9 wt % of the base copolymer and 1 wt % of PEG was used. The membranes were made by spreading the mixture solution on a glass plate (120×25 mm²) using a pair of 100 μm-thick spacers, coagulating it in water at 30°C for overnight, and washing it with water to remove DMSO and PEG. P(AN-co-SSS) membranes having about 70–80 μm thickness and 43 mm diameter were used for permeation experiments.

The apparatus for ultrafiltration is similar to that previously used.[4,8] The experiment was carried out under hydraulic pressure of 760 mmH₂O, corresponding to 7.5 kPa. The experimentally obtained rejection, R, is defined as $R = (C_b - C_p)/C_b$, where C_b and C_p denote the concentration of bulk and permeated solutes, respectively. The feed solution and the eluents were analyzed by GPC (type CCPD UV8000 of Toyo Soda Co., with a 30 cm column of

Table I Properties of Copolymers Obtained by Copolymerization of AN and SSS

| Run | SSS Contents (mmol/g) | | $[\eta]$ |
	Titration	NMR	$(cm^3/g)^a$
A-1	0.51	0.55	1.22
A-2	0.11	0.12	1.88
A-3	0.058	0.054	1.89
A-4	0.03	0.02	1.58
N-1	0	0	2.00

^{a} $[\eta]$ is intrinsic viscosity of the polymer DMF solutions containing $0.5M$ LiCl.

a)   b)   c)
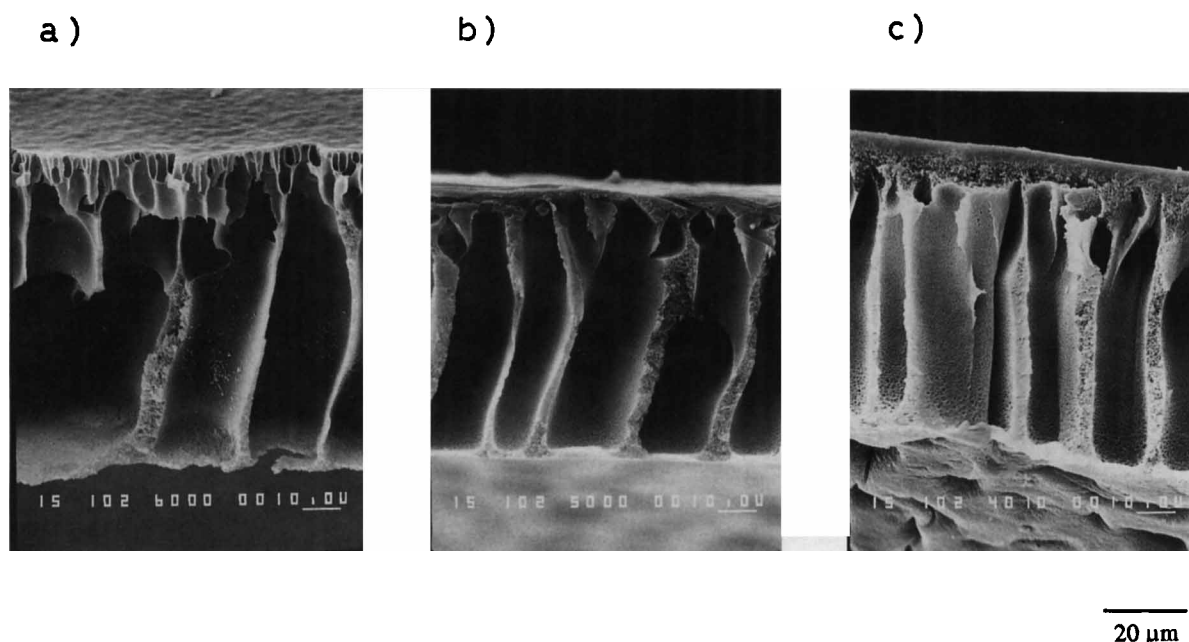

20 μm

Figure 1 Scanning electron micrographs of cross section of (a) PAN and P(AN-*co*-SSS) membranes for the SSS content of (b) 0.03 and (c) 0.51 mmol/g. The membranes were prepared from 9 wt % of DMSO polymer solution in the absence of PEG additive.

TSK$_{gel}$ G5000PW$_{XL}$) equipped with refractometer (RI8000).

Morphology of the cross section of the membrane was observed by a scanning electron micrograph (SEM), JXA-733 (JEOL). The wet sample of the membrane was lyophilized. The cross section was obtained by fracturing the membrane at liquid nitrogen temperature and coating with gold by use of spatter SPM-112 (Anelva).

RESULTS AND DISCUSSION

Characteristics of Ultrafiltration Membranes Containing Negatively Charged Groups

Figure 1 shows SEM photographs of a cross section of (a) PAN and P(AN-*co*-SSS) membranes having SSS contents of (b) 0.03 and (c) 0.51 mmol/g. These membranes were prepared from 9 wt % of DMSO polymer solution in the absence of PEG. It is obvious from the photographs of the cross section that the membranes have asymmetric structure; these membranes consist of a dense top layer supported by a porous sublayer having a fingerlike structure. It is well known[1] that the top layer determines the transport rate of the solute and the porous layer acts only as a support. The size of the macropores in the support becomes large with a decrease in the

SSS content. Also, it is noted that the dense layer on the top surface for a high SSS content, 0.51 mmol/g, is about 6–10 μm thickness. In contrast with the cross section, the dense layer of the membrane having a low SSS content, 0.03 mmol/g, is about 0.6–1.2 μm thickness. Further, the thickness of PAN having no charges is very thin (about 0.1 μm). The thickness of the dense layer decreased with the SSS content in the copolymer.

Table II shows the properties of the ultrafiltration membranes prepared from the casting solution without addition of PEG. The water content of the P(AN-*co*-SSS) membrane decreased in the range

Table II   Properties of P(AN-*co*-SSS) Membranes Prepared from the Copolymer Solutions Without Addition of PEG

Run	SSS Content[a] (mmol/g)	Water Contents (%)	Volume Flux of Water/10^{-6} (m^3/m^2 s)
A-1	0.51	92.6	0.87
A-2	0.11	84.5	1.23
A-3	0.058	87.5	2.57
A-4	0.03	90.4	2.64
N-1	0	93.5	5.61

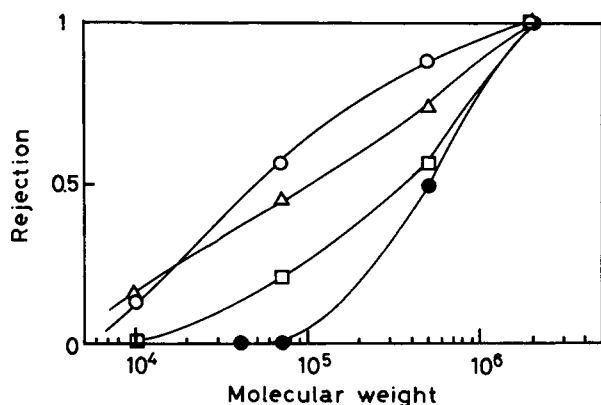[a] Measured by acid–base titration.

Figure 2 Molecular weight cutoff curves of P(AN-co-SSS) membranes having various amounts of the SSS content: (O) 0.51; (△) 0.11; (□) 0.058, (●) 0.03 mmol/g. The membranes were prepared from the casting solution of P(AN-co-SSS) without addition of PEG.

of the SSS contents from 0.03 to 0.11 mmol/g. But the value of the water content inversely increased at 0.51 mmol/g of the SSS content. This may be due to high hydrophilic nature of the copolymer for the 0.51 mmol/g; the copolymer itself highly absorbs water.

For the ultrafiltration rate of the membranes, the rate decreases with an increase in the charge contents between 0.058 and 0.11 mmol/g. The permeation rate of water for the asymmetric membranes having a thin top layer and a large macropores in the support is fast.

To estimate the permeation behavior of P(AN-co-SSS) membranes having a molecular sieve effect, various molecular weight dextrans (D) in the range of 1×10^4 to 2×10^6 were used. Figure 2 shows molecular weight cutoff (MWCO) curves of P(AN-co-SSS) membranes for different charge contents. The MWCO curves of the membranes markedly shift toward a high molecular weight side of D, when the amounts of the charge content in the membrane decreased. As mentioned above, the increase of the charge contents in the membranes decreased the permeation rate of water. In the same manner, the permeability of the D for $M_w = 7 \times 10^4$ and 5×10^5 decreases with the increase of the charge content. The cutoff of the D by the membrane takes place, owing to molecular sieve effect. This suggests that the pore size in the top layer of the membrane reduces, as the charge content increases.

As compared by the SEM photographs of the cross section, it seems that the P(AN-co-SSS) membrane for 0.51 mmol/g has a spongy structure. But there is almost no spongy layer for PAN membrane. In the P(AN-co-SSS) copolymer consisting

of hydrophobic parts of the AN group and the hydrophilic SSS group, the aggregation of the hydrophobic parts in water is responsible for the formation of the membrane having asymmetric structure. But the aggregation in water may be inhibited by the SSS segments of the copolymer because of the hydrophilic nature. As indicated, the membrane structure and the ultrafiltration properties strongly depended on the components of the copolymer; the increase of charge content in the copolymer results in the decrease of the pore size in the top layer of the membrane. This may be due to a loose aggregation of the hydrophobic parts for P(AN-co-SSS) having a high SSS content. In addition, the electrostatic repulsion between the charged neighboring groups contributes to the pore size of the top surface in the membrane. As a result of the expanded coil conformation of the SSS group surrounding the aggregated hydrophobic segment, the pore size of the P(AN-co-SSS) membrane decreases.
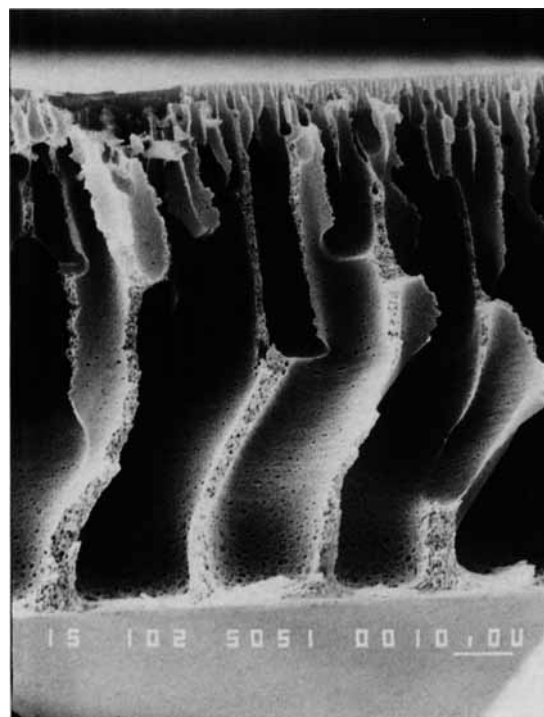
20 μm

Figure 3 SEM photograph of cross section of P(AN-co-SSS) membranes prepared from the casting solution containing 1 wt % of PEG. The charge content of P(AN-co-SSS) membrane is 0.03 mmol/g. The M_w of PEG added is 5×10^4.
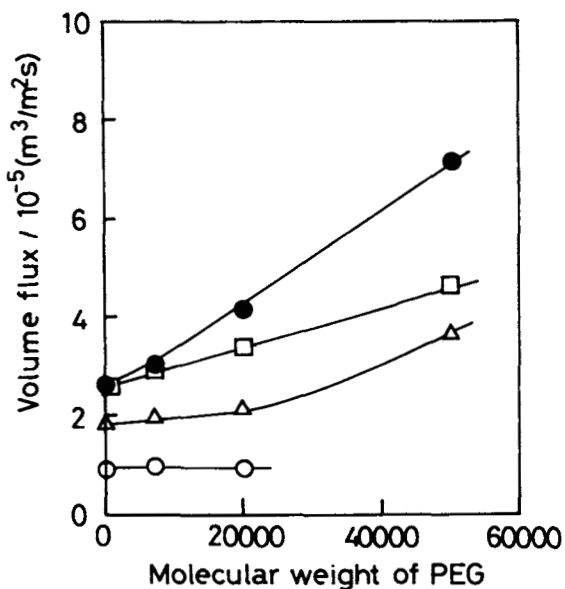
Figure 4 Plots of volume flux of water for P(AN-*co*-SSS) membranes vs. PEG molecular weight added to the casting solution with 1 wt %: (○) 0.51, (△) 0.11, (□) 0.058, and (●) 0.03 mmol/g for the charge content in the membrane.

On the contrary, the polymer having no charges or a low charge contents strongly aggregates in the coagulation medium. In this case, the precipitation of the polymer easily occurs in water. In addition, the chain expansion of the aggregated polymer is very low. This brings about a large pore size in the support layer and thin top layer.

Effect of PEG Addition on Properties of Ultrafiltration Membranes

We reported that the ultrafiltration rate was controlled by adding water-soluble polymer such as poly(vinyl alcohol) (PVA) to the casting solution.[4,5,7] In this work, poly(ethylene glycol) (PEG) having various M_w's of 7×10^3, 2×10^4, and 5×10^4 was used instead of PVA.

Figure 3 shows an SEM photograph of the cross section of P(AN-*co*-SSS) membrane (0.11 mmol/g) prepared from the casting solution containing 9 wt % of the base copolymer and 1 wt % of PEG ($M_w = 5 \times 10^4$). In the presence of hydrophilic PEG in the casting solution, the obtained membrane has asymmetric structure, as well as the membranes without addition of PEG. As compared with the cross section of membrane without the additive, the membrane appears to somewhat swell in the top layer and the support. This suggests that the aggregation of the copolymer was inhibited in the presence of the hydrophilic PEG. In addition, the change of the dense skin structure in the top surface with addition of PEG is observed as shown in the photograph; the skin structure has many and narrow tubular macropores. Furthermore, in cases of the PEG addition, the water contents of the membranes for the SSS content of 0.03, 0.058, 0.11, and 0.51 mmol/g is 89.0, 86.9, 87.8, 92.8%, respectively. These values are slightly larger than those prepared without the addition of PEG in Table I, indicating that the porosity becomes large with the addition of PEG.
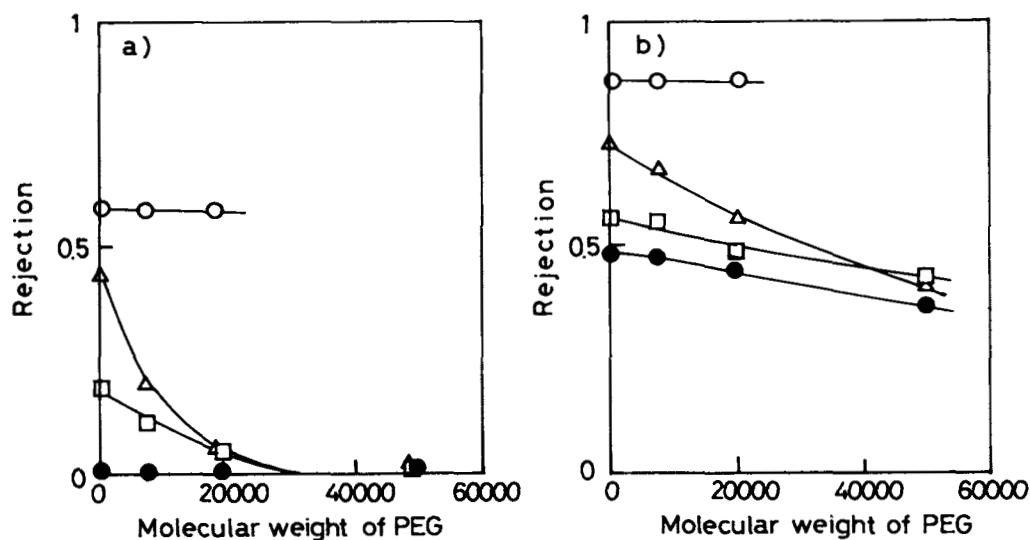
Figure 4 shows volume flux of water for P(AN-

Figure 5 Plots of rejection for (a) D ($M_w = 1 \times 10^4$) and (b) D ($M_w = 2 \times 10^6$) vs. M_w of PEG added to the casting solution with 1 wt %: (○) 0.51, (△) 0.11, (□) 0.058, and (●) 0.03 mmol/g for the SSS contents of the membrane. The feed concentration is 0.1 wt %.
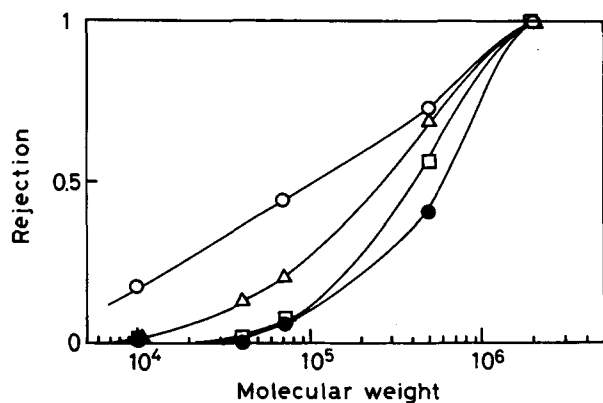
Figure 6   MWCO curves of P(AN-co-SSS) membranes prepared from the casting solution containing 9 wt % P(AN-co-SSS) for the SSS content of 0.11 mmol/g and 1 wt % PEG having various M_w's: (O) no addition; (△) PEG $M_w = 7.5 \times 10^4$, (□) 2×10^4, and (●) 5×10^4.

co-SSS) membranes prepared from the casting polymer solution containing 1 wt % of PEG, which has various molecular weights. When the M_w of the added PEG was increased, the ultrafiltration rate of the membrane increased. This suggests that the permeation is controlled by the PEG addition, as well as by PVA.[5] The large permeation rate of the membrane prepared by the addition of PEG results from the increase of the porosity. However, with an increase in the charge content, the effect of the PEG addition on ultrafiltration rate lowered, especially in the membrane for the SSS content of 0.51 mmol/ g. In this copolymer, the change of morphology for the cross section in the photograph and water content with the addition of PEG was not observed. This suggests that there is little change of the porosity with the addition of PEG.

By washing the membrane with water, the water-soluble additive is removed and then the micropores are retained, probably in the dense layer of the membrane. However, in the copolymer for 0.51 mmol/g, the microscopic voids retained in the membrane may be reduced by the expanded coil conformation of the charged segments surrounding the aggregated AN segments, despite the addition of PEG.

The effect of the M_w of PEG on the performance of dextran rejection is shown in Figure 5. None of P(AN-co-SSS) membranes for the SSS content of 0.03 mmol/g has significant rejections for D having a M_w of 7×10^4. With the increase of the charge content, there is a tendency for the rejection to become large. In the membranes having the charge content for 0.058 and 0.11 mmol/g, the rejection of both D depended on the M_w of PEG added, whereas the rejection for the membrane having the SSS content of 0.51 mmol/g was independent of the M_w of PEG, as well as the permeation rate in Figure 4.

Figure 6 shows the dependence of MWCO curves on the M_w of PEG with the SSS content of 0.11 mmol/g. With the increase of the M_w of PEG added, the curve shifts toward the high molecular weight side of D. This indicates that the pore size of the membranes becomes large with the increase of the PEG M_w. For the membrane having the charge content of 0.51 mmol/g, we also measured the effect of the PEG addition on the cutoff curves of the membrane. However, the cutoff curves did not change regardless of the PEG M_w.

Table III shows volume flux of water and 0.1 wt % of aqueous solutions of D for P(AN-co-SSS) membrane having the SSS content of 0.11 mmol/ g. The permeation rates of water and the solute solution for D of $M_w = 1 \times 10^4$ increased with increase

Table III   Permeation Properties of P(AN-co-SSS) Membrane Prepared with Addition of PEG Having Various M_w's[a]

| | Volume Flux/10^{-6} (m³/m² s) | | | |
PEG M_w	Water	D ($M_w = 1 \times 10^4$)	D ($M_w = 2 \times 10^6$)	MWCO[b]
None	1.2	1.2	0.65	0.88×10^6
7.5×10^3	1.8	1.6	0.70	1.05×10^6
2×10^4	2.1	1.8	0.62	1.15×10^6
5×10^4	3.6	3.1	0.64	1.3×10^6

[a] The charge content of P(AN-co-SSS) used is 0.11 mmol/g. The membranes were prepared from the casting solution containing 9 wt % of the copolymer and 1 wt % of PEG.
[b] MWCO was estimated from 0.85 rejection of the cutoff curves.

of the M_w of PEG added. But in the case for the M_w = 2 × 10⁶ D solution, the value was almost similar, regardless of the PEG M_w. This is responsible for the high rejection of D of M_w = 2 × 10⁶ by the membrane.

Table III also lists the values of MWCO of the membranes. Here, MWCOs are defined as the M_w of D at 0.85 rejection in the cutoff curves of the figure. The result suggests that the pore size of the membrane increases with the increase of the M_w of PEG added.

Restricted Permeation of Dextransulfate (DS)

Figure 7 shows rejection of DS and D for P(AN-co-SSS) membranes having various amounts of the SSS content. Here, D and DS with the M_w of 1 × 10⁴ and the membrane with MWCO of 1.1 × 10⁶ were used, respectively; the MWCO value of the membrane with various charge contents was controlled by adding PEG. Whereas the solute D is not rejected by any membranes, the permeation of the anionic DS is effectively restricted for those membranes. It is noted that the degree of the rejection of DS increased with an increase in the fixed content in the membrane. Especially, the P(AN-co-SSS) membrane with an SSS content of 0.11 mmol/g highly rejected DS. It is known that, when the sign of the charges in the membrane is the same as that of the solute, the electrostatic barrier of the membrane ef-
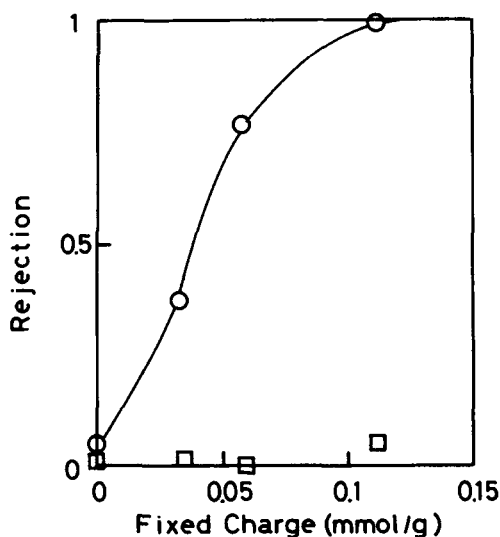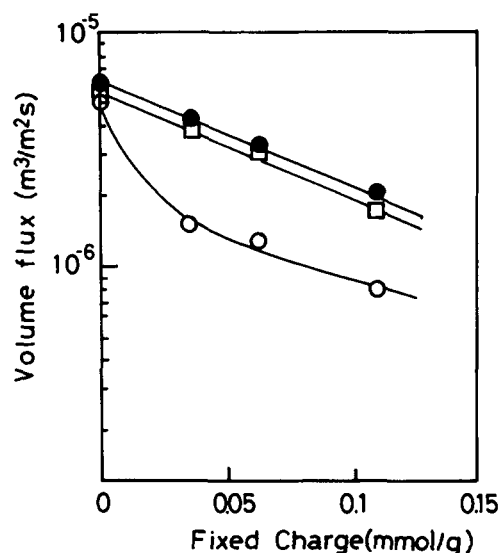

Figure 8 Volume flux of water and 0.1 wt % of the solute solution for P(AN-co-SSS) membranes having various amounts of the SSS group: (●) water; (○) DS (M_w = 1 × 10⁴); (□) D (M_w = 1 × 10⁴). The concentration of the feed solution is 0.1 wt %. P(AN-co-SSS) membranes having MWCO = 1.1 × 10⁶ were used.

fectively acts on the restricted permeation of the ionic solute.[4,13]

Figure 8 shows volume flux of water and 0.1 wt % of aqueous solution of 0.1 wt % D and DS. Although the MWCO curves of the P(AN-co-SSS) membranes are similar, the hydraulic permeation rate of the feed solutions decreased with increase in the charge content. As compared with the flux of the D solution, the value of the DS solution is small, because of the high rejection of DS by the electrostatic repulsion between the membrane containing negatively charged groups and the anionic solute.

To check the molecular size of DS of M_w = 1 × 10⁴ and 4 × 10⁴ and DS of M_w = 1 × 10⁴, the values of reduced viscosity ($\eta_{sp/c}$) for 0.1 wt % aqueous solution measured at 30°C were 8.9, 19, and 11, respectively. The data suggest that the molecular size of DS is slightly smaller than that of D having similar M_w.

According to the sieve slit model,[15,16] the average pore size of the asymmetric membrane can be estimated from the MWCO value of the membrane. In addition, the solute size of D is calculated for the molecular weights from the Stokes–Einstein equation.[17,18] The apparent pore size calculated for a membrane having an MWCO of 1.1 × 10⁶ is 200 Å. The solute size of D and DS having 1 × 10⁴ M_w is 23 and 34 Å, respectively. Accordingly, the apparent

Figure 7 Rejection of D and DS with P(AN-co-SSS) membranes having various amounts of SSS content: (○) DS (M_w = 1 × 10⁴); (□) D (M_w = 1 × 10⁴). The concentration of the feed solution is 0.1 wt %. The membranes for MWCO = 1.1 × 10⁶ were used.

pore size of the membrane is much larger than the molecular size of DS.

Furthermore, to examine the contribution of the electrostatic barrier to the restricted permeation of DS, permeation experiments of DS and D through P(AN-co-SSS) membranes having various MWCOs were carried out. The increase of MWCO of the ultrafiltration membrane implies that pore size in the top layer of the asymmetric membrane increases. For preparation of P(AN-co-SSS) membranes having various MWCOs, the amount of PEG added to the casting polymer solution was changed. For example, P(AN-co-SSS) membranes with the SSS content of 0.51 mmol/g were prepared from the casting solution containing 1, 2, and 3 wt % of PEG with 5×10^4 M_w. Other membranes with SSS content of 0.03, 0.058, and 0.11 mmol/g were prepared from the casting solution without and with 1 wt % of PEG having 2×10^4 and 5×10^4 M_w.

Figure 9 shows plots of the rejection of DS and D vs. the MWCO of the membrane. The values of the rejection for D having no charge group are very low and about zero in their membrane. In contrast, these membranes for the SSS content of 0.11 and 0.51 mmol/g have high rejection to DS, despite their larger pore size. However, the rejection of DS for 0.03 mmol/g gradually decreased with increases of MWCO. In the membrane having a low SSS content, the effect of the electrostatic barrier of the P(AN-co-SSS) membrane to the rejection of DS is lowered by the increase of the pore size of the membrane.
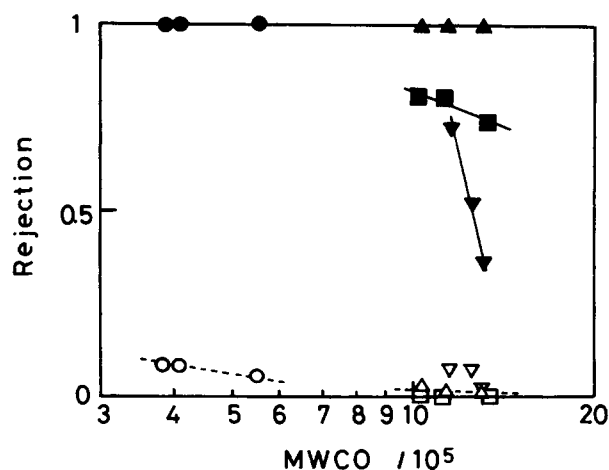

Figure 9 Relationship between rejection of D and DS and MWCO of P(AN-co-SSS) membranes: (○, ●) 0.51, (△, ▲) 0.11, (□, ■) 0.058, and (▽, ▼) 0.03 mmol/g for the charge content in P(AN-co-SSS) membrane. Open and closed symbols are for D and DS. The M_w of D and DS is 4×10^4 and 1×10^4, respectively.
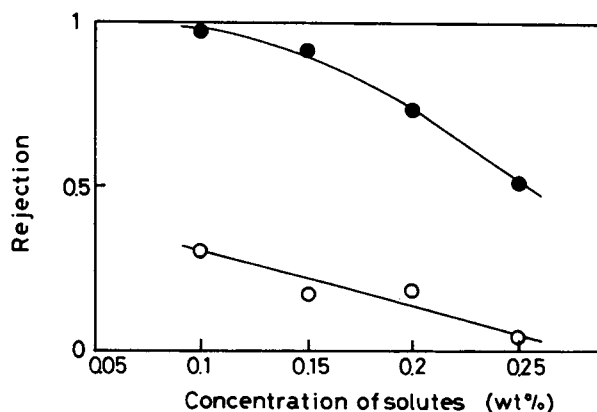

Figure 10 Rejection of (●) DS and (○) D for the P(AN-co-SSS) membrane at various feed concentrations of the D/DS mixture. The charge content and MWCO of the P(AN-co-SSS) membrane are 0.11 mmol/g and 1.1 $\times 10^6$, respectively. The weight fraction of D/DS in the feed is 1/9 (w/w).

However, in the P(AN-co-SSS) membranes having SSS content of 0.058, 0.11, and 0.51 mmol/g, although the pore size in the top layer of the membrane is much larger than the molecular size of DS, electrostatic barrier of the membrane is effective on the restricted permeation of DS.

Separation of DS and D by Ultrafiltration Membrane Containing Charges

We previously reported the electrostatic sieve separation of DS and D by P(AN-co-SSS) membranes.[13] To examine the electrostatic charge effect of P(AN-co-SSS) membrane on the separation of D/DS mixture in detail, the ultrafiltration membranes of PAN-co-SSS and PAN having the identical MWCO of 1.1 $\times 10^6$ were used. These membranes almost permeate both D having 4×10^4 and 1×10^4 M_w with rejection of zero. For the separation of the D/DS mixture, the feed solution of D and DS having 4×10^4 and 1×10^4 M_w, respectively, was used in 0.1 wt % of the total concentration (D/DS = 1/9 [w/w]).

Figure 10 shows the rejection of DS and D over the feed concentration range of 0.1 to 0.25 wt %. With increasing total concentration, each rejection of DS and D decreased. As mentioned, the D or DS solute having 4×10^4 M_w is not rejected by these membranes used. However, in the presence of both DS and D in the feed, D was rejected by the membranes. This tendency is significant in the low concentration of the feed. In this case, the rejection value for DS is very high. Therefore, the reason for

the rejection of D is explained by the decrease of pore size of the membrane, owing to the deposition of DS molecules highly rejected by the membrane.

Figure 11 shows plots of volume flux of the feed mixture solution vs. feed concentration of the D/DS mixture. The values of the feed solution are smaller than those of water. Then, the values for the feed solution slightly increased in the range between 0.15 and 0.25 wt %. By the solute molecules rejected, the electrostatic barrier of the ultrafiltration membrane containing negatively charged groups is considered to be masked. Therefore, the decrease of the rejection is markedly in the high concentration of the feed.

Membrane selectivity toward mixtures of organic molecules is usually expressed in terms of a separation factor, α.[1] For the D/DS mixture, the selectivity factor, $\alpha_{D/DS}$, is given by $\alpha_{D/DS} = (y_D/y_{DS})/(x_D/x_{DS})$, where y_D and y_{DS} are the D and DS concentrations in the permeate and x_D and x_{DS} are the D and DS concentrations of the components in the feed, respectively. The values of $\alpha_{D/DS}$ are plotted vs. the feed concentration of D/DS as shown in Figure 12. The separation factor of the P(AN-co-SSS) membrane with the SSS content of 0.11 mmol/g is approximately 25, indicating that the separation of D and DS highly takes place, namely, the component D permeates preferentially. In ultrafiltration membrane made of PAN having no charges, no separation is achieved: $\alpha_{D/DS} = 1$. As shown, the selectivity of the membrane for 0.11 mmol/g is significantly
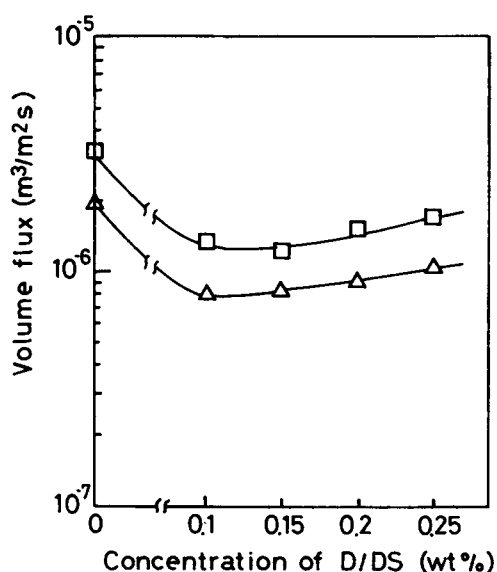
Figure 12   Separation factor of the D/DS mixture at various concentrations of the feed: ($\triangle$) 0.058 and ($\bigcirc$) 0.11 mmol/g for the charge content of the membrane.

higher than that of 0.058 mmol/g at a dilute feed concentration. But the electrostatic effect on the separation of D/DS is lowered, when the feed concentration increased.

CONCLUSION

Ultrafiltration membranes, having negatively charged groups, of P(AN-co-SSS) were prepared. The ultrafiltrate rate of the membranes was controlled by adding PEG of various molecular weights to the casting solution of the copolymer. By using the P(AN-co-SSS) membranes having various MWCO properties, the permeation behavior of dextran (D) and dextransulfate (DS) and separation of the D/DS mixture were studied. P(AN-co-SSS) membranes markedly restricted the permeation of only DS, owing to electrostatic barrier of the membrane containing negatively charged groups to the DS permeation. The electrostatic sieve separation of DS and D, each having similar molecular size, with P(AN-co-SSS) membranes was carried out. The charged membrane effectively rejected to DS with a high permselectivity.

Figure 11   Volume flux of the D/DS mixture solutions at various concentrations: ($\square$) 0.058 and ($\triangle$) 0.11 mmol/g for the SSS content of the membrane.
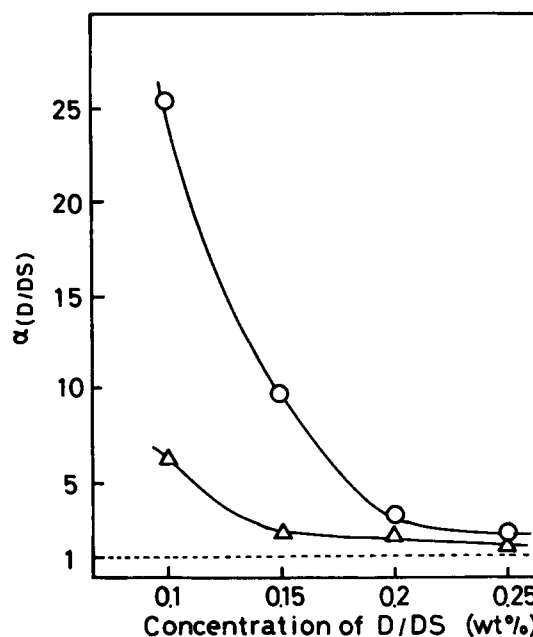
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