

Preparation and Properties of Negatively Charged Ultrafiltration Membrane: Photografted Sodium Styrene Sulfonate onto Brominated Polyacrylonitrile Membrane

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SYNOPSIS

Charged ultrafiltration membranes were prepared by photografting sodium styrene sulfonate onto photosensitive polyacrylonitrile membrane containing bromine atoms. The degree of the photografting was characterized by contact angles of air or *n*-octane in water and FT-IR spectra for the negatively charged membrane. Permeations of dextran and dextransulfate through the negatively charged membranes were studied by ultrafiltration in the aqueous solutions of both solutes. With an increase of photoirradiation, the permeability of the solutes decreased. Also, an electrostatic repulsion of the solute and the membrane was confirmed by direct comparison between the permeability of the solutes, dextran, and dextransulfate, each having similar molecular size.

INTRODUCTION

Charged ultrafiltration membranes are more interesting than noncharged membranes for practical applications, since they have three variables: sign, density of charges, and pore size. It is therefore useful to apply a charged ultrafiltration membrane to the separation and permeation of constituents, such as proteins, enzyme, and water soluble polymer.

In our previous works,¹⁻³ the charged ultrafiltration membranes were prepared from charged copolymer, synthesized from photosensitive brominated polyacrylonitrile with ionic monomer in DMSO by the photochemical method. We found, by taking scanning electron micrographs, that the prepared ultrafiltration membrane had a heterogeneous porous structure, containing a narrow and tubular pore and a dense pore, similar to a sponge.¹ The pore size of the membrane was controlled by conditions of the membrane preparation. But, it is difficult to prepare the membranes with various amounts of charge, and of similar pore size, because

the ultrafiltration behavior depends on the polymer concentration and PVA concentration in the cast solution,⁴ and also on the amounts of the charge in the polymer. Since the pore size decreases with an increasing amount of fixed charge, a certain ultrafiltration membrane, having a fixed charge of about 1 meq/g-polymer, does not have an efficient permeation of fluid and a macromolecular solute. In addition, membranes prepared from the charged copolymer with the fixed charge contents were not available for the experiments, because these membranes are easily broken.

In this work, in order to obtain a charged ultrafiltration membrane with efficient permeation, and having proper mechanical strength, charged membranes were prepared by photografting an ionic monomer, sodium styrene sulfonate, onto a photosensitive, brominated polyacrylonitrile membrane.

Here, the unirradiated membrane shows efficient permeation and proper cutoff characteristics for a macromolecular solute, such as dextran. The negatively charged membrane obtained was characterized by means of contact angle and FT-IR. The ultrafiltration properties and permeation characteristics of the negatively charged membrane were examined using nonionic and anionic dextrans with similar molecular sizes.

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EXPERIMENTS

Materials and Grafting

Synthesis of the photosensitive polyacrylonitrile (PAN-Br) was carried out by photopolymerization.^{5,6} The ultrafiltration membrane of the PAN-Br, having 0.65 wt % bromine atom, has a molecular cutoff property of about 50% rejection for dextran with the molecular weight 2×10^6 . The preparation and properties of the ultrafiltration PAN-Br membrane were reported previously.^{2,4}

Water, used for dextran solution, was purified using ion-exchange resin and was distilled before experiments.

The photografting of the negatively charged monomer onto the photosensitive ultrafiltration membrane was performed as follows. The PAN-Br membrane, soaked in 10 wt % aqueous solution of sodium styrene sulfonate, was photoirradiated in the presence of air using an 100 w high pressure mercury lamp, where the distance between the source and the membrane was 10 cm. At that distance from the source, the light power was measured by photometer (TPM-316, Gentec) and was checked through the photoirradiation experiments. After irradiation, the membrane was washed with a large quantity of water and was kept in water.

Preparation of Dextransulfate

Dextransulfate, having 1.6 mol % content of sodium sulfonate groups, was synthesized according to the method⁷ of sulfonated poly(vinyl alcohol) with some modifications: To 120 mL of pyridine in a cooled round flask, a 28 mL portion of chlorosulfonic acid was added in 30 min with vigorous stirring. The mixture was stirred for another 1 h. Then, a 10 g portion of dextran (Pharmacia, Mw = 70,000) was added and the mixture was stirred for 1 h at 80°C. After reaction, a 10 mL portion of water was added. The obtained viscous product was purified by reprecipitating the solution into large amounts of ethanol and the product was dissolved in a dilute aqueous sodium hydroxide. This was repeated about five times until there was until no characteristic odor of pyridine. The solution was dialyzed using macroporous dialysis membrane (6000–8000 cutoff mol wt), of Spectrum Medical Industries Inc., against pure water for 10 days. The dextransulfate was recovered by a freeze-drying technique. The amount of the product was 5.5 g. The sulfonation was identified using an IR spectrophotometer. The content of SO_3^- residues was determined by titration with

0.01 N HCl. The molecular size of the dextransulfate was measured by GPC (TOSO Co. Ltd., TSK gel G6000XL).

Properties of Membranes

The amount of charge grafted onto the membrane was measured by an acid-base titration as follows. Accurately weighed, dry samples were soaked in 50 mL of distilled water for 24 h. Then, the solution involving the membrane was titrated, with 0.01 M HCl monitoring the pH, by an Horiba H-7LD pH meter.

Contact angles between the membrane and air or *n*-octane were measured in water with an apparatus of captive air and *n*-octane measurement (Type CA-A, Kyowa Kagaku Co. Ltd.), as reported previously.⁸

IR spectra of charged membranes were recorded by the attenuated total reflection (ATR-IR) technique with a Shimadzu FT-IR 8100 spectrophotometer. Here, membranes dried *in vacuo* at room temperature were used for the measurement. The ATR-IR spectra were taken at a 45° angle to the incident light.

Permeation Measurements

The membranes used were of about 100 μm thickness and 43 mm effective diameter. The ultrafiltration experiments were carried out with an apparatus (Amicon Co. Ltd., type 8050 cell) under an hydraulic pressure of 760 mmH₂O, corresponding to 7.5 kPa.

For measurements of dextran permeation, 0.2 wt % of the aqueous solute solution was used. The amount of the permeated dextran was measured by GPC analysis for the solute.

RESULTS AND DISCUSSION

Characterization of Grafting

The brominated polyacrylonitrile can be used for photocopolymerization with several vinyl monomers in DMSO solution under irradiation of UV light, as reported by Miyama et al.^{5,6,9} In our previous works,^{1,2,4} the charged copolymers of polyacrylonitrile with some ionic monomers, quaternized N,N-dimethylaminoethylmethacrylate and sodium styrene sulfonate, were synthesized by photopolymerization. Accordingly, the photopolymerization technique was available for the preparation of charged ultrafiltration membrane; the brominated polymer membrane was photografted with ionic monomer, sodium styrene sulfonate.

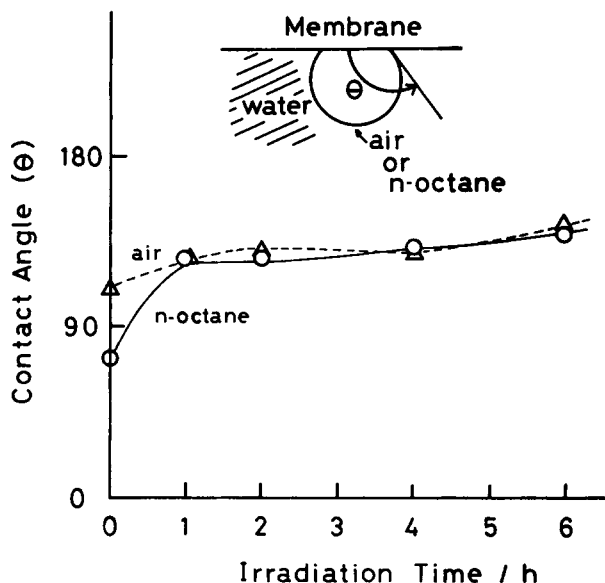


Figure 1 Contact angle of air and *n*-octane in water for ultrafiltration membranes prepared by grafting sodium styrene sulfonate.

To evaluate the grafting, in this work, the contact angle method in water was adopted, as presented in Figure 1. Figure 1 shows the contact angle between the photografted membrane and air or *n*-octane in water with function of irradiation time. The values of the membrane photoirradiated are larger than

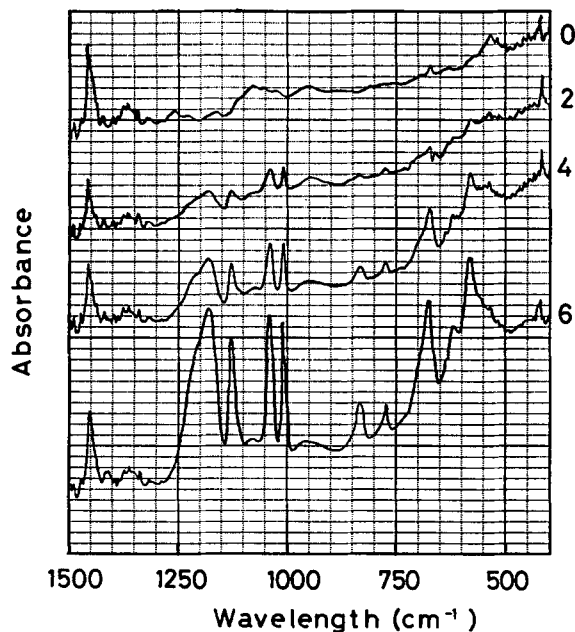


Figure 2 FT-IR spectra of polyacrylonitrile membranes, photografted with sodium styrene sulfonate at various irradiation times, 0, 2, 4, and 6 h.

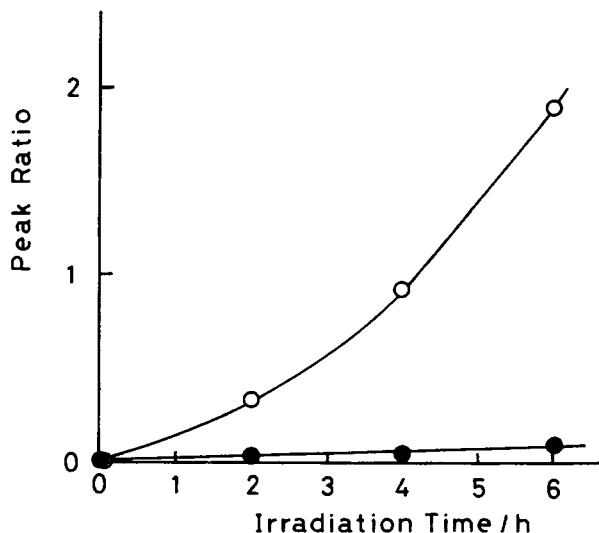


Figure 3 Plots of the ratio of peak intensity at 1170 cm^{-1} to that at 1450 cm^{-1} for FT-IR spectra of unirradiated membrane and irradiated membranes. (○) Photoirradiated side, (●) reverse side of the membrane.

that of the unirradiated membrane. It is clear that photoirradiation enhances the degree of the hydrophilic nature of the membrane because of the graft of sulfonated groups onto the membrane.

FT-IR spectra of the membranes, photoirradiated for various times, are shown in Figure 2. In the spectra of the photoirradiated membrane, the absorption peaks at 670 , 770 , and 830 cm^{-1} are characteristic of a *p*-disubstituted benzene ring by a styrene sulfonate group.^{2,10,11} The peaks, at 1000 – 1250 cm^{-1} , are characteristic of sulfonic acid. The peak inten-

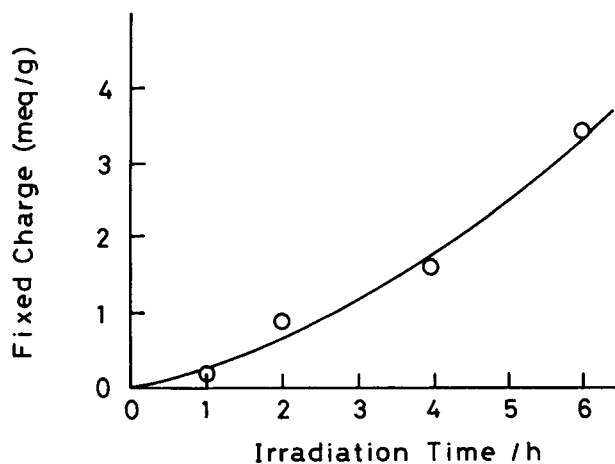


Figure 4 Fixed charges of negatively charged membrane, prepared by photografting with various irradiations. The values were determined by titration with 0.01 N HCl .

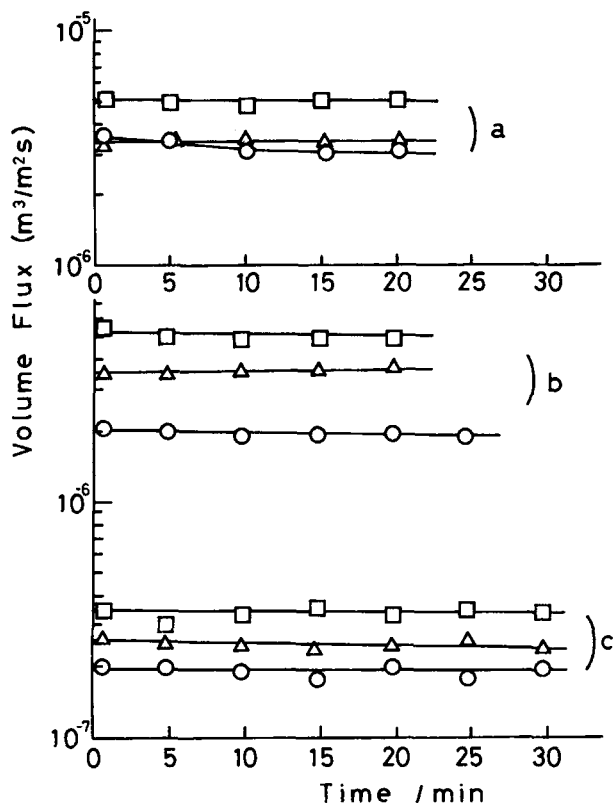


Figure 5 Plots of volume flux of water (□) and 0.2 wt % aqueous solutions of dextran (Δ) and dextransulfate (○) vs. operated time for ultrafiltration. (a) Unirradiated membrane, (b) membrane irradiated for 2 h, (c) membrane irradiated for 6 h. Applied pressure: 7.5 kPa. The mol wt of the dextrans used for experiments was 70,000.

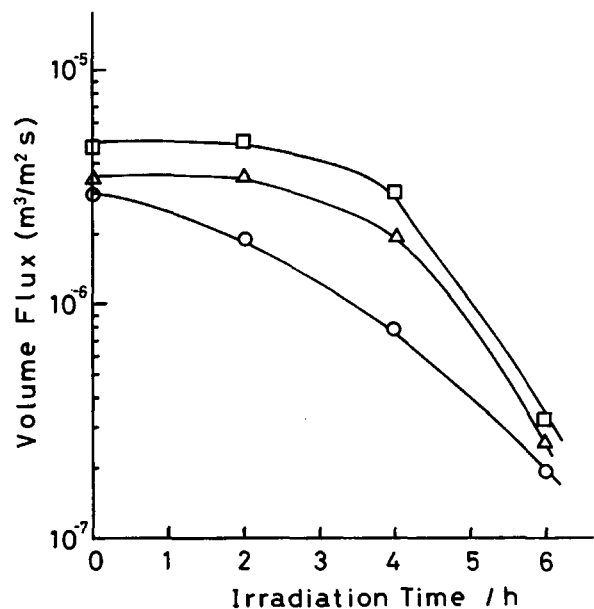


Figure 6 Volume flux of water (□) and 0.2 wt % aqueous solution of dextran (Δ) and dextransulfate (○) for various irradiation times.

sities of the styrene sulfonate group increase with an increase of irradiation time. Also, the CH bending for polyacrylonitrile is observed at 1450 cm^{-1} .¹² Figure 3 shows the ratio of the peak intensity at 1170 cm^{-1} to that at 1450 cm^{-1} . It is shown that the grafting of the monomer to PAN-Br occurs effectively by photoirradiation. On the other hand, in the reverse side of the membranes, the ratio is remarkably lower than that in the photoirradiated side of the membranes. The data show that the monomer is grafted a little in the reverse side.

Figure 4 shows the amounts of fixed charges of SO_3^{2-} (meq/g-polymer) in the membranes by the photoirradiation. The fixed charges of the membranes increase with increasing irradiation time. As mentioned previously, the values of the fixed charges in the membranes, prepared from the charged copolymer, were lower than about 1 meq/g-polymer.⁴

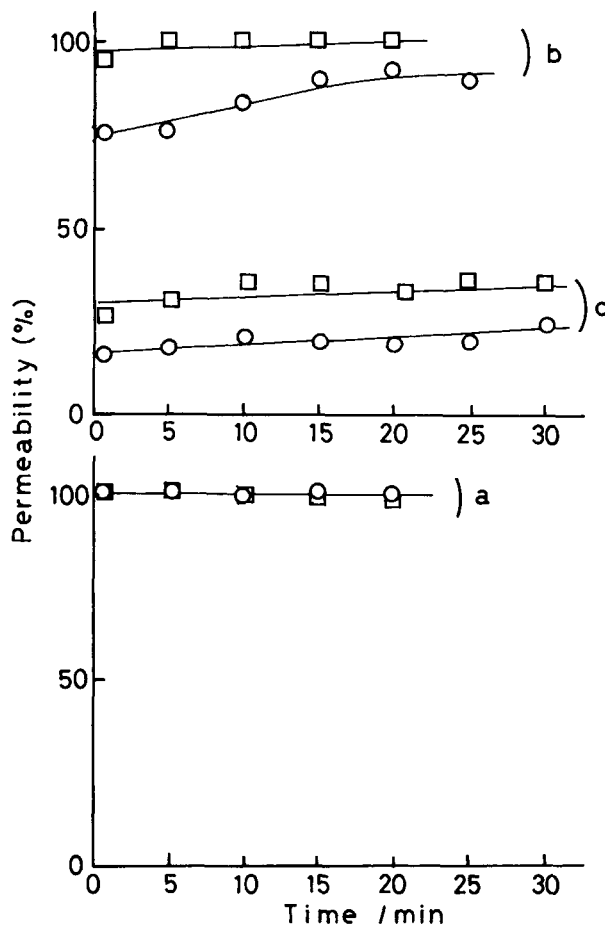


Figure 7 Plots of permeability dextran (□) and dextransulfate (○) vs. operated time for ultrafiltration. (a) Unirradiated membrane, (b) membrane irradiated for 2 h, (c) membrane irradiated for 6 h. Applied pressure: 7.5 kPa. The mol wt of the dextrans used for experiments was 70,000.

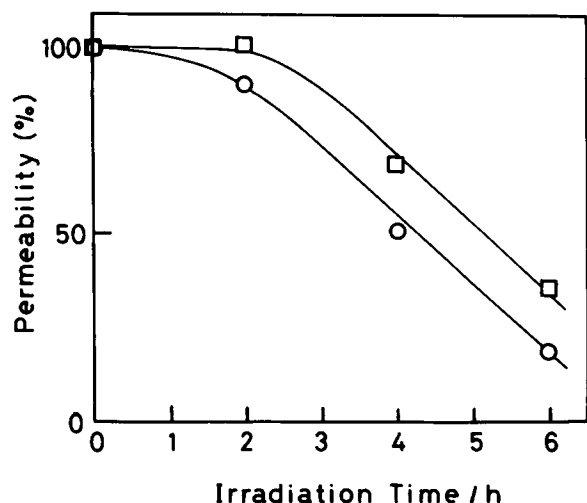


Figure 8 Permeability of 0.2 wt % aqueous solution for dextran (\square) and dextransulfate (\circ) at various irradiation times.

In present work these are higher than 1 meq/g-polymer, except for that of 1 h irradiation. However, these are the average values per whole membrane weight, since the photografting proceeded on the irradiated side of the membrane, as mentioned above. Namely, the charge density is considered to be the irradiated surface, as shown by Figure 4.

Characteristics of Ultrafiltration

As shown in Figure 5, the volume flux of water and aqueous solutions of dextran and dextransulfate were measured at the operated time within the range

of 30 min. Here, the molecular weight of these solutes is 7×10^4 . The values of the volume flux measured were almost constant in the times. The data at 10 min for each solute plotted, vs. irradiation time, are shown in Figure 6. The volume flux gradually decreases with an increase in the irradiation. It is noted that the dependence of the volume flux for dextran shows a similar tendency as that of water. But, for the dextransulfate, the degree of the decrease with the irradiation time is larger than the degrees of decrease for water and dextran.

Figure 7 shows the plots of the permeability of dextran and dextransulfate vs. operating time. The values obtained do not show the large changes with the operated time. These observations imply little fouling in their filtrations. For the unirradiated membrane, the data show that all of the solutes, having the molecular weight of 70,000, permeated through the membrane. The permeability of dextran for the membrane irradiated for 2 h was the same as that for the unirradiated membrane. But, the values of dextransulfate, containing anionic charges in the molecules, were about 70–80%. Since the dextran permeability of the charged membrane was the same as that of the unirradiated membrane, the difference in the permeation of dextransulfate for both membranes indicates the presence of electrostatic repulsion between the negatively charged membrane and the anionic dextransulfate. As shown in Figures 5 and 6, the slow permeation of the dextransulfate solution supports the decrease of the permeability by the electrostatic repulsion. For the membrane of 6 h irradiation, the values are further lowered by the grafting. Figure 8 shows the relationship between the permeability of the solutes and the irradiation

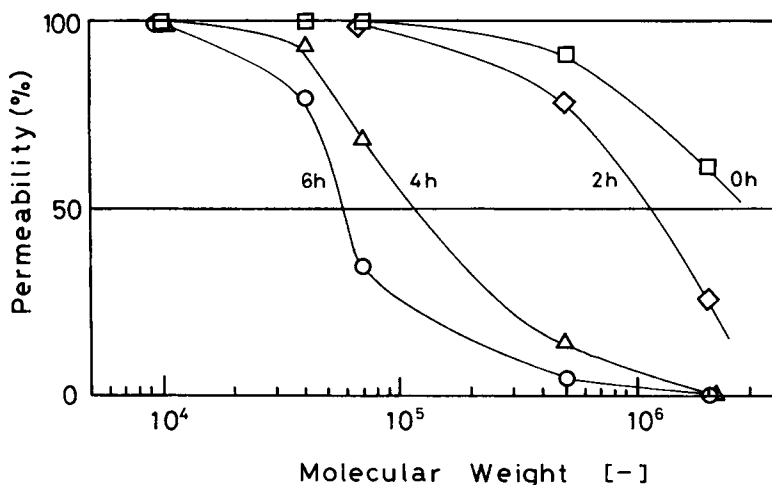


Figure 9 Permeability curves of various mol wts of dextran for unirradiated membranes (\square) and membranes irradiated for 2 (\diamond), 4 (\triangle), and 6 h (\circ).

time by using the data obtained in 10 min operation time. With an increase of the irradiation, the permeability of the solutes decreased clearly.

To estimate the pore size of the photoirradiated membranes, the permeation experiments were carried out using dextrans having various molecular weights, 1×10^4 , 4×10^4 , 7×10^4 , 5×10^5 , and 2×10^6 . Figure 9 shows the permeability curves through unirradiated membrane and membranes irradiated for 2, 4, and 6 h vs. molecular weights. The curves for the irradiated membranes markedly shift toward the low molecular weight side with increasing the irradiation. According to a sieve slit model,^{4,13} the average pore radius can be estimated using 0.8 rejection, corresponding to 20% of permeability in the curves, because the solute rejection relates to the solute size and the pore size of the membrane. Here, the solute radius of the dextrans for the molecular weights are calculated by the Stokes–Einstein equation.^{3,4} The obtained values of the average pore size, obtained for the membranes irradiated for 2, 4, and 6 h, are 106, 149, and 370 Å, respectively.

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