

Preparation of Porous Membranes Grafted with Poly(spiropyran-containing methacrylate) and Photocontrol of Permeability

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SYNOPSIS

Graft copolymerization of spiropyran-containing methacrylate (SPMMA) and acrylamide (AM) onto the surface of a porous polymer membrane was carried out. The permeability of the graft membrane varied with ultraviolet (UV)- or visible-light irradiation. It was found that the change by UV-light irradiation of the permeability of the H₂O/CH₃OH mixture through the SPMMA/AM-grafted membrane is related to the change by UV-light irradiation of the solubility, i.e., the chain extension, of the graft copolymer in the mixed solvent. When the free SPMMA/AM copolymer becomes insoluble in the H₂O/CH₃OH mixture by UV-light irradiation, the permeability of the H₂O/CH₃OH mixture through the SPMMA/AM-grafted membrane is increased. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

We have been interested in the synthesis of a membrane device that changes its porosity (permeability) in response to external chemical signals, e.g., pH and glucose concentration change.¹⁻⁴ In the present investigation, the preparation of polymer membrane that changes permeability in response to photoirradiation was attempted.

A conformational change of polymer by photoirradiation can be induced by photoisomerization of a photoresponsive functional group in the side chain. For example, *trans/cis* isomerization or cyclization/ring opening isomerization of a photofunctional group brings about a change of the dipole moment or structure, the formation of zwitterion, or the dissociation into ions of the chromophore, and this changes the properties of the polymer chain. Studies of this kind include the helix/coil transition⁵ or association/dissociation conversion⁶ of poly(L-glutamic acid) in solution due to a *cis/trans* photoisomerization of azobenzene groups attached to the polymer, the compatibility increase of poly(methyl vinyl ether)/polystyrene blends using *cis/trans* photoisomerization of stilbene,⁷ the change of properties of methyl methacrylate copolymers,⁸ the association of polystyrene containing spiropyran by UV-light irradiation,⁹ and the extension/contraction of polymer chains of polyacrylamide containing leucotoluene according to the formation/disappearance of electric charges by photoirradiation.¹⁰ Recently, a change in membrane permeability controlled by photoirradiation has also been reported.^{11,12}

However, no attempt has been reported to photocontrol the permeability of the porous membrane by direct covalent attachment of such photofunctional polymers. A methacrylate containing a spiropyran group is known to produce a zwitterionic merocyanine form under UV-light irradiation, which isomerizes back to the neutral spiropyran under visible-light irradiation as shown in Figure 1. It occurred to us that the spiropyran-containing polymer-grafted porous membrane should photocontrol the pore size (permeability) of the membrane because of the solubility (extension) difference of the graft chains as shown in Figure 2.

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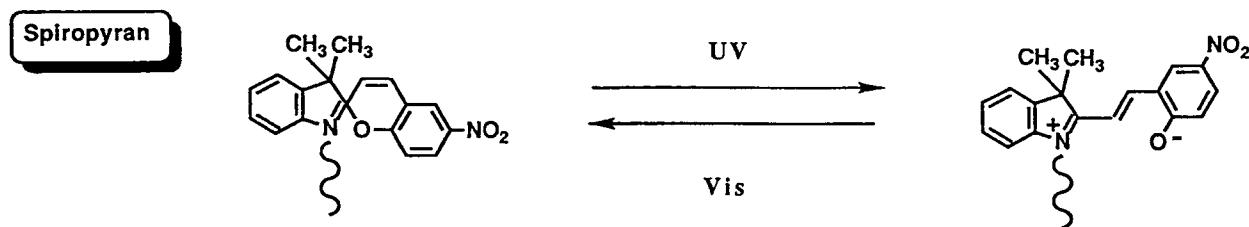


Figure 1 Photoisomerization of spiropyran group.

EXPERIMENTAL

Materials

2,3,3-Trimethylindoline, 2-iodoethanol, 5-nitrosalicyl-aldehyde, and methacryloyl chloride were purchased from Tokyo Kasei (Tokyo, Japan) and used without further purification. Acrylamide (Nacalai Tesque, Kyoto, Japan) was recrystallized from acetone. 2,2'-Azobisisobutyronitrile (AIBN) (Wako Pure Chem. Ind., Osaka, Japan) was recrystallized from methanol. Kieselgel 60 for a silica gel column was a product of Merck (Darmstadt, Germany). A porous polytetrafluoroethylene (PTFE) membrane with a 25 mm diameter, a 75 μm thickness, and a 0.8 μm average pore diameter was purchased from Advantec-Toyo Co. (Tokyo, Japan).

Synthesis of Spiropyran-containing Methacrylate

A spiropyran-containing methacrylate (1- $[\beta$ -(methacryloyl)ethyl]-3,3'-dimethyl-6-nitrospiro(indoline-2,2'-[2H-1]benzopyran,SPMMA) was synthesized by the scheme illustrated in Figure 3 (Ref. 13) and recrystallized from a benzene/*n*-hexane (1/2 v/v) mixture.

ANAL: Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5$: C, 67.8%; H, 5.7%; N, 6.7%.

Found: C, 67.7%; H, 5.7%; N, 6.4%.

Preparation of SPMMA-grafted Porous Membrane

Copolymers of SPMMA and acrylamide (AM) were grafted onto a porous PTFE membrane to render it permeable to $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ mixtures. The surface graft polymerization was carried out as follows: A

porous PTFE membrane was treated by glow discharge under a 0.05 mmHg pressure with a 350 W electric power for 15 s by using a high-frequency wave generator HSF-005 type (Nihon Koshuha, Yokohama, Japan). The glow-discharged membrane, which carries radicals of a 1.9×10^{-10} mol/ cm^2 density (measured by using 1,1-diphenylpicrylhydrazyl as previously reported^{1,2}), was immersed in a methanol solution containing SPMMA (50 mg/mL)/AM (36.5 mg/mL) (1/4 mol/mol) mixture. The solution containing the PTFE membrane was heated at 60°C for 2 h under a nitrogen atmosphere. After the polymerization, the membrane was taken out and washed repeatedly with the solvent used for the polymerization until the absence of spiropyran absorption at 350 nm in the washing liquid was confirmed by UV spectroscopy.

Solution Polymerization

A methanol solution containing an SPMMA (50 mg/mL)/AM (36.5 mg/mL) (1/4 mol/mol) mixture was polymerized by AIBN (0.05 wt %) under nitrogen at 60°C for 2 h. Polymers were precipitated in *n*-hexane and dried *in vacuo* at 40°C. To remove acrylamide homopolymers from the product, the dried polymer was suspended in a $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1/9 v/v) mixture and irradiated by UV light, which caused a precipitation of SPMMA/AM copolymers. The copolymer molecular weight was determined by GPC with Cosmosil 5diol-120 (Nacalai Tesque, Kyoto, Japan). A calibration curve was obtained by using proteins of known molecular weights. The contents of SPMMA in the copolymers were determined by elemental analysis.

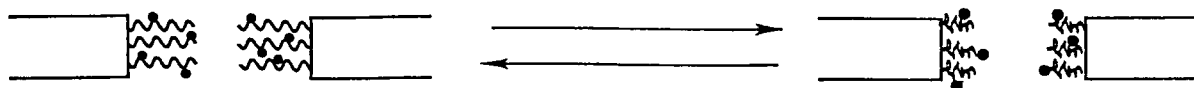


Figure 2 Change of pore diameter of porous PTFE membrane grafted with polymers containing stimuli-responsive groups (●).

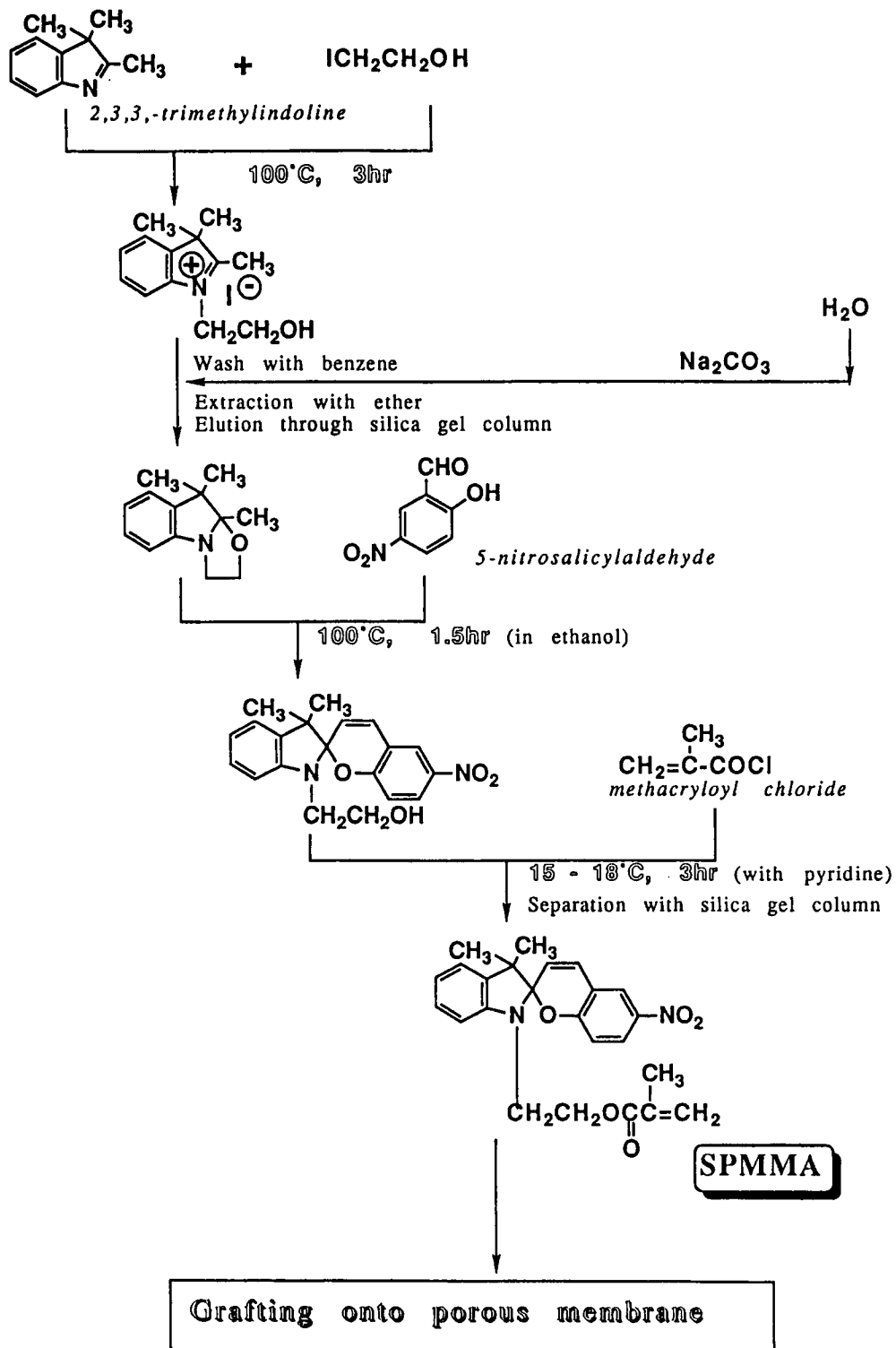


Figure 3 The synthetic scheme of photoresponsive spiropyran-containing methyl methacrylate.

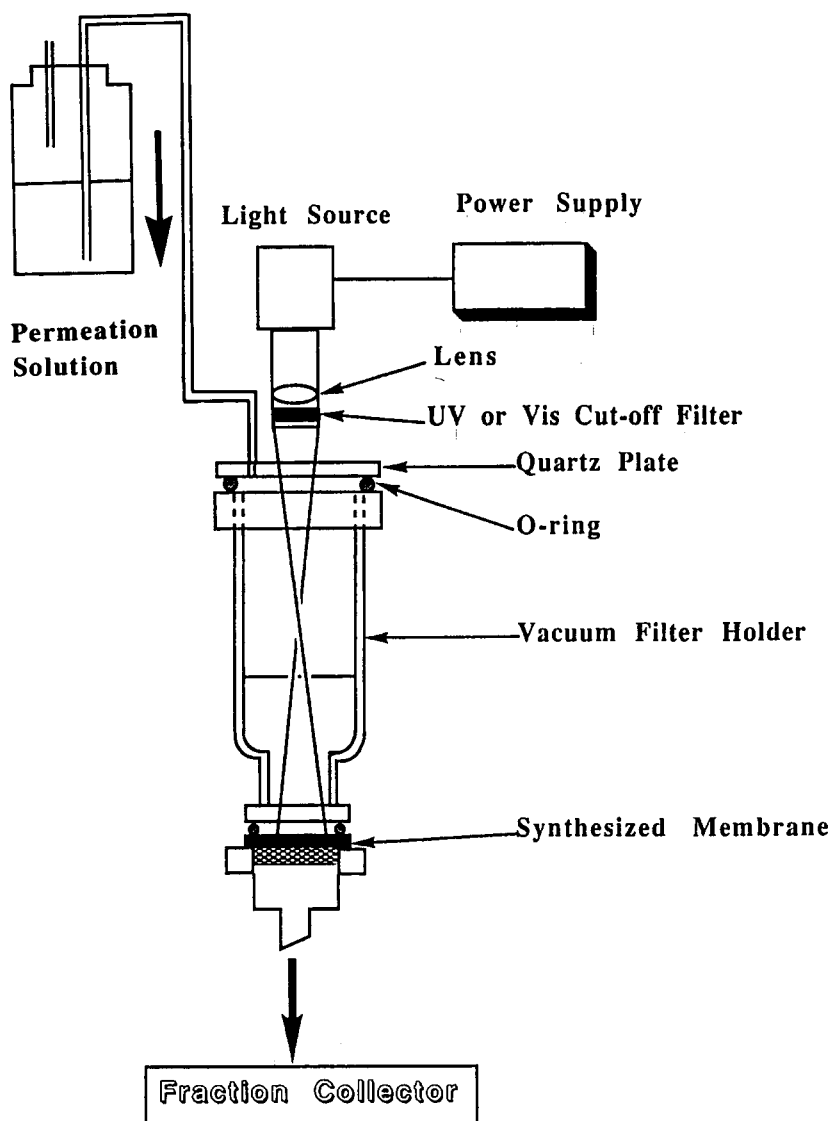


Figure 4 The apparatus for permeation experiments under irradiation of UV or visible light.

Photoirradiation Experiments

A halogen lamp (100 W, Olympus, Tokyo, Japan) equipped with UV-D23C (for visible light irradiation > 370 nm) or UV-37 filter (for irradiation of UV light between 230 and 400 nm) (both filters were made by Hitachi, Tokyo, Japan) was used.

Permeation Experiments

Permeabilities of H₂O/CH₃OH mixtures of different compositions were determined by measuring the amount of permeation over suitable time intervals using the apparatus shown in Figure 4. The influx

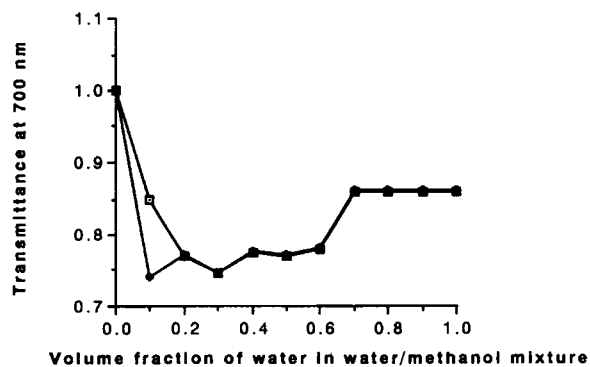


Figure 5 Solubility change of the SPMMA/AM copolymer (5/95 mol/mol; M_n , 37,000) in the H₂O/MeOH mixture of different compositions (■) before and (□) after UV-light irradiation (250–400 nm).

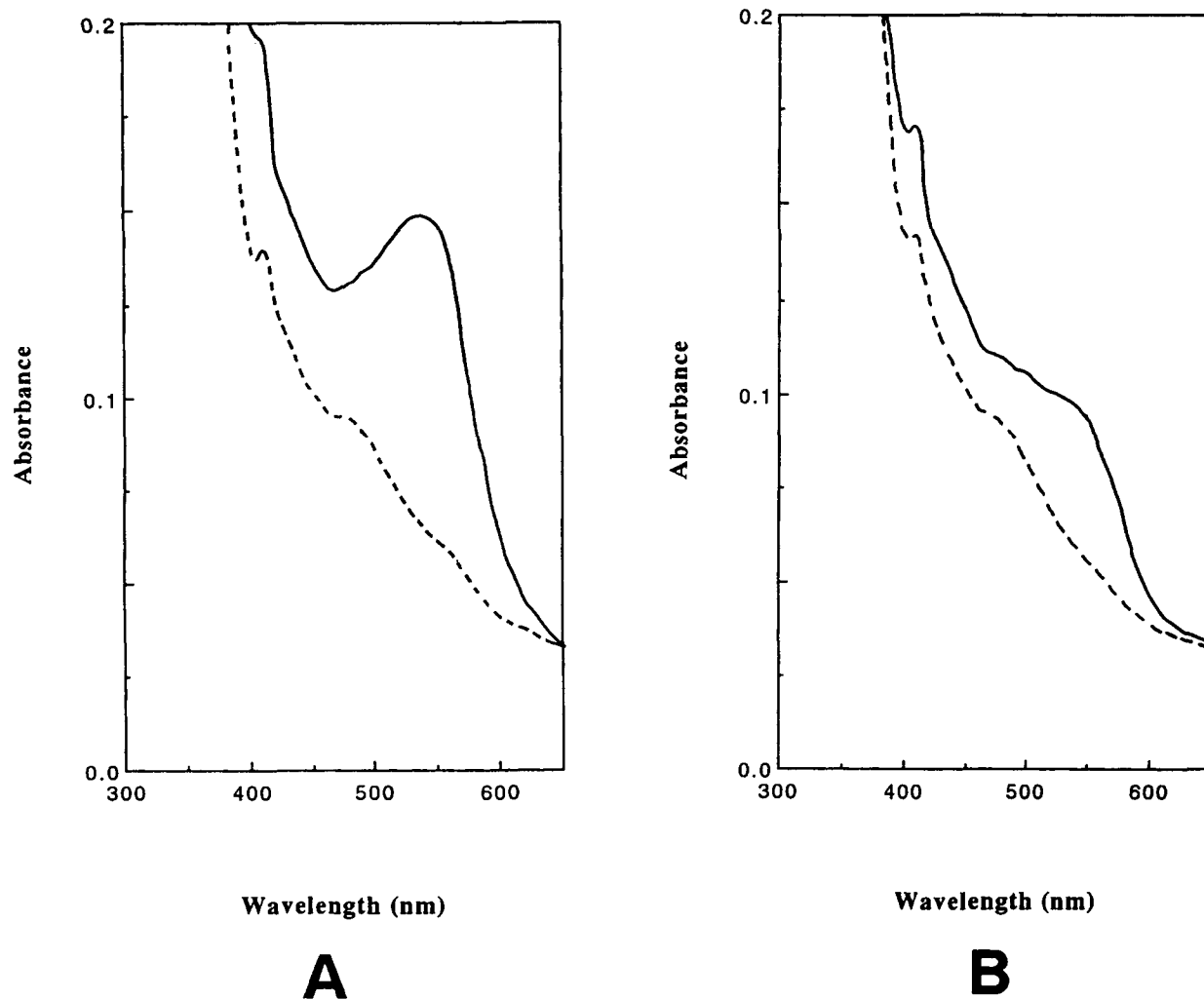


Figure 6 UV spectra of SPMMA/AM copolymer (5/95 mol/mol; M_n , 37,000) in the H₂O/MeOH mixture of different compositions (···) before and (—) after UV-light irradiation (250–400 nm). The volume percentages of MeOH in the MeOH/H₂O mixtures, A, B, C, and D, are 100, 50, 0 and 90, respectively.

rate of the permeation liquid was kept constant to keep constant the inner pressure of the apparatus by equalizing the input and output volumes of the permeation solution.

Spectroscopic Measurements

The UV and ESCA spectra were measured by U-best 50 (JASCO, Tokyo, Japan) and ESCA-750 (Shimadzu, Kyoto, Japan), respectively. The solubility change of the SPMMA/AM copolymer in the H₂O/CH₃OH mixtures of various compositions by photoirradiation was determined by measuring the turbidity of solution (700 nm).

RESULTS AND DISCUSSION

Synthesis of SPMMA/AM Copolymer and Its Solubility in H₂O/CH₃OH Mixtures of Various Compositions

The molecular weight of the copolymer was about 37,000 and the content of SPMMA in the copolymer was 5 mol %. The solubility of the copolymer in the H₂O/CH₃OH mixtures depended on the mixture compositions as shown in Figure 5. The biggest turbidity difference induced by photoirradiation was observed in the mixture including 10 vol % of water. The UV spectral change of the supernatant by pho-

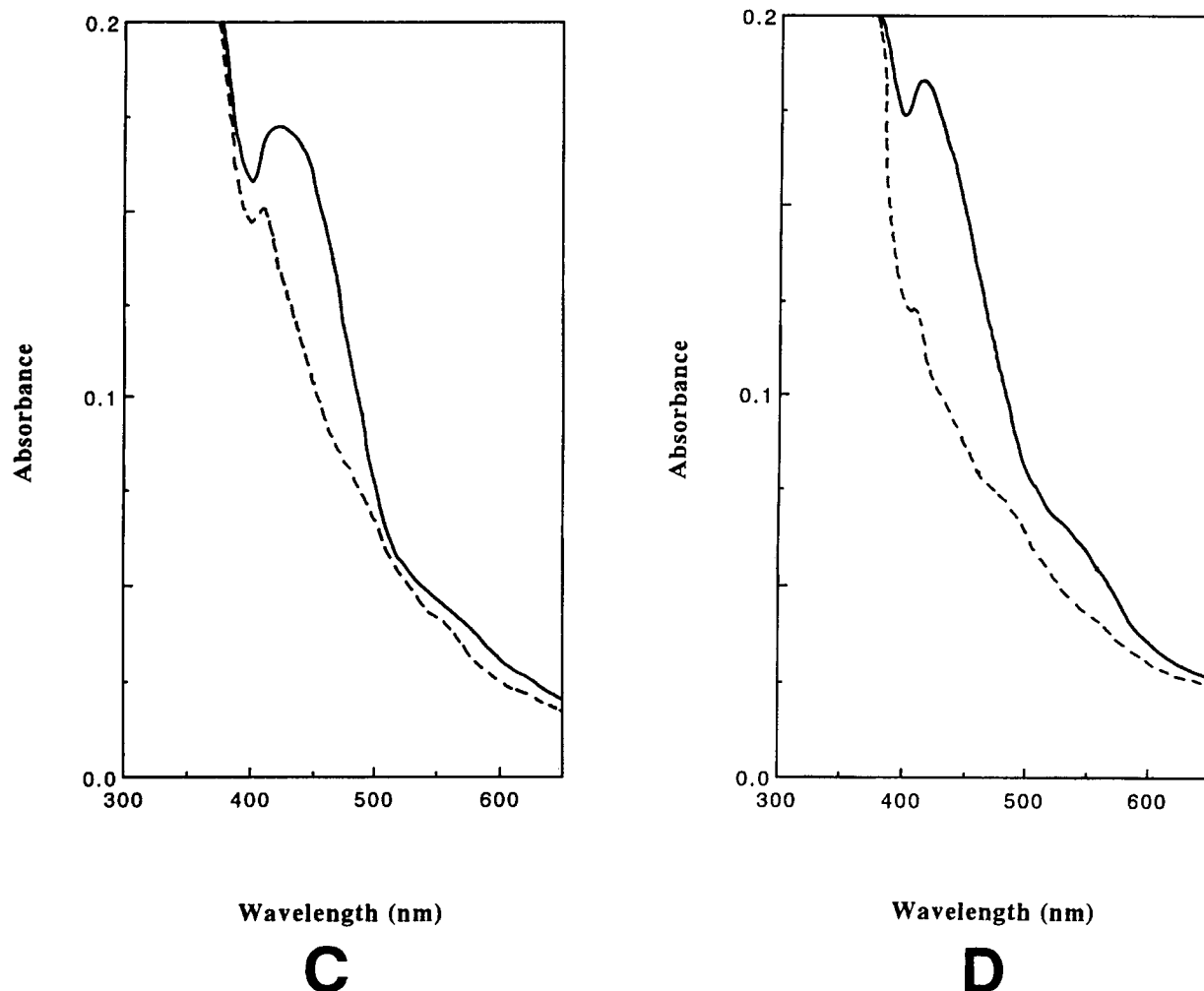


Figure 6 (Continued)

toirradiation was observed in the four mixture compositions shown in Figure 6, although the degree of spectral difference depended on the compositions of the mixture.

Surface Graft Polymerization

The ESCA spectrum (B) of SPMMA/AM-grafted PTFE membrane shows a peak at 287 eV, which is assignable to the C—O bond of the SPMMA unit and absent in the ESCA spectrum (A) of the AM-grafted PTFE membrane, as shown in Figure 7. These observations show the occurrence of surface graft polymerization involving SPMMA. However, the surface of the PTFE membrane was not completely covered with SPMMA, considering that spectrum (B) shows a peak at 294 eV assignable to the C—F bond of PTFE.

Permeabilities of Grafted Membranes

The permeability of a H₂O/CH₃OH (1/9 v/v) mixture through a PTFE membrane grafted with polyacrylamide or SPMMA/AM copolymer containing 5 mol % SPMMA was investigated under photoirradiation, and the results are shown in Figure 8.

Very little effect of the irradiation of UV or visible light on the permeation through the polyacrylamide-grafted PTFE membrane was observed. On the other hand, with the SPMMA/AM-grafted membrane, UV-light irradiation increased the permeation, whereas visible-light irradiation decreased it. These changes of permeability suggest that the graft chains contract to open pores of the membrane by a decreased solubility of the graft chains carrying merocyanine (ionized spiropyran) groups, which were generated by the UV-light irradiation, in the H₂O/

CH₃OH (1/9 v/v) mixture. The graft chains turn to a neutral spiropyran form by visible-light irradiation and extend to close pores of the membrane, decreasing the permeability. In addition, this permeability change by photoirradiation was observed only in the mixture, in which the biggest solubility change by photoirradiation was observed as shown in Figure 5. This result demonstrated that the permeability change of grafted porous membrane should be based on the solubility change of the polymer chain, i.e., the spreading change of polymer chain in the solution.

Reversible permeability changes of the H₂O/CH₃OH (1/9 v/v) mixture were observed six times by alternating UV- and visible-light irradiations of the SPMMA/AM-grafted PTFE membrane. This study shows a new type of intelligent membrane that controls permeability by photoirradiation.

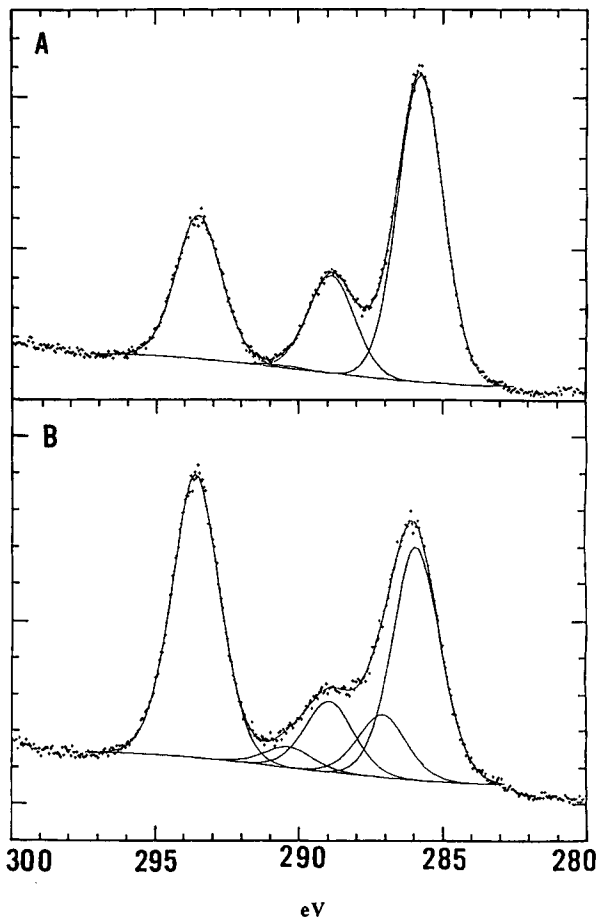


Figure 7 ESCA spectra (C_{1s}) of grafted porous PTFE membranes: (A) PTFE membrane grafted with acrylamide only; (B) PTFE membrane grafted with copolymer of acrylamide and spiropyran-containing methyl methacrylate.

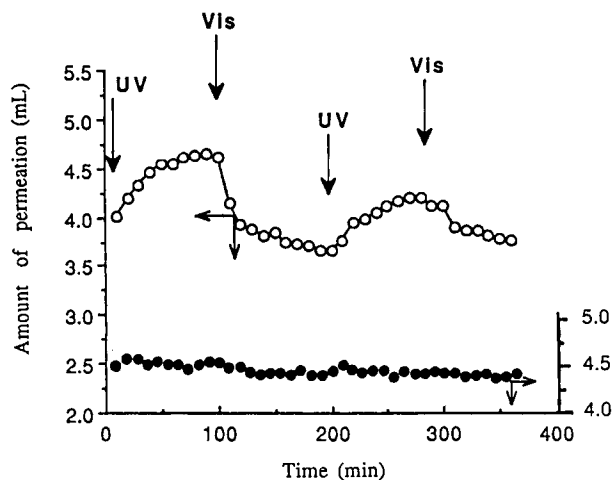


Figure 8 Permeability change of H₂O/MeOH (1/9 v/v) mixture through the (○) SPMMA/AM (5/95 mol/mol)-grafted PTFE membrane or (●) AM-grafted PTFE membrane by UV- or visible-light irradiation.

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