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Photocontrolled Gating by Polymer Brushes Grafted on Porous Glass Filter

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ABSTRACT: Polymethacrylate-containing spiropyran was grafted on a glass filter to control permeation of organic liquid by photoirradiation. The glass filter was at first coupled with octadecyldimethyl-*N*,*N*-diethylaminosilane and next subjected to glow-discharge treatment for graft copolymerization of spiropyran-substrated methyl methacrylate (SPMA), (1-(β-methacryloylethyl)-3,3-dimethylindoline-2,2′-spiro-6′-nitrospirobenzopyran, and methyl methacrylate (MMA). The surface modifications were monitored by X-ray photoelectron spectroscopy. The surface wettability was altered by these treatments. An SPMA/MMA copolymer in toluene was soluble under irradiation of ultraviolet light but was insoluble under irradiation of visible light, while the copolymer was soluble in *N*,*N*-dimethylformamide (DMF) irrespective of photoirradiation. Toluene permeation through a glass filter grafted with SPMA/MMA copolymer increased by ultraviolet-light irradiation, and decreased by visible-light irradiation. DMF permeation did not depend on the photoirradiation. These results demonstrated that the permeation of organic liquid through a glass filter can be controlled by the solubility, i.e., the extension/contraction of polymer chains grafted on the surface.

Introduction

Extension and contraction of polymer chain on a microscopic or macroscopic level can be magnified by fabricating a three-dimensional polymer network in hydrogels[1−7] or membranes having a “chemical gate” or “chemical valve” function.[8−20] The latters consist of porous membranes to which stimuli-responsive polymers are graft-polymerized. These materials have been investigated extensively in the field of drug-delivery systems.

When photochromic molecules are bound to a macromolecular chain, their photoisomerization may induce structural variations of the macromolecular chain.[21−24] Therefore, photochromic polymers may be one of the more highly promising materials for development of photomodulation devices. It has been reported that a polymer containing spiropyran residues in the side chains was grafted on a porous polymeric membrane to have water permeation through the graft membrane be photocontrollable.[18] However, the graft membrane was not appropriate for the permeation of organic liquid. In the present study the photochromic polymer was grafted on a glass filter, which is not invasive by organic liquid.

Experimental Section

Materials. A glass filter (diameter, 30 mm; thickness, 3 mm; average pore size, 5 μm) was purchased from Sansyo Co. (Tokyo, Japan). Methyl methacrylate (MMA) was purchased from Nacalai Tesque Ltd. (Kyoto, Japan) and purified by distillation under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Wako Pure Chem. Ind. (Osaka, Japan) and recrystallized from acetone. Solvents used in the present investigation were purified by conventional methods.

Table 1. Content of the Spirobenzopyran Unit in Copolymer

sample abbreviation	content of spirobenzopyran unit in the feed (mol %) (SPMA:MMA molar ratio)	content of spirobenzopyran unit in copolymer (mol %)[a]	M_w[b] ($\times 10^4$)
SPMA/MMA1	3.2 (1:30)	2.6	2.6
SPMA/MMA2	4.7 (1:20)	4.3	2.8
SPMA/MMA3	9.1 (1:10)	11.8	2.3
SPMA/MMA4	20.0 (1:4)	21.6	2.1

[a] Calculated from UV absorbance of spirobenzopyran unit in the copolymer. [b] Average molecular weight was obtained by gel-permeation chromatograph (standard, polystyrene).

Preparation of Spiropyran-Containing Methacrylate Monomer and the Copolymer. A spiropyran-substituted methyl methacrylate (SPMA) was synthesized as previously reported.[18]

SPMA was copolymerized with methyl methacrylate. A methanol solution containing SPMA and MMA of various molar ratios (the total monomer concentration, 20 wt %) was polymerized by AIBN (0.05 wt %) under a nitrogen atmosphere at 60 °C. After 2 h, the precipitate was recovered and dissolved in *N*,*N*-dimethylformamide (DMF). The solution was added into methanol to precipitate the product. The precipitate was dried in a vacuum and used for further experiments.

The content of SPMA in the copolymer was determined by ultraviolet absorption. The molecular weight of copolymers was estimated by gel permeation chromatography using a Shodex K-804 (Showa Denko Co., Tokyo, Japan). A calibration curve was obtained using commercial polystyrenes of known molecular weights.

Ultraviolet spectra were measured using a Hitachi spectrophotometer. To measure the turbidity, the transmittance of solution was determined by the intensity of 750-nm light as reported previously.[22] Since no absorption of the copolymers was observed at 750 nm, the wavelength was chosen to determine the transmittance. The turbidity of solution was the reciprocal of transmittance.

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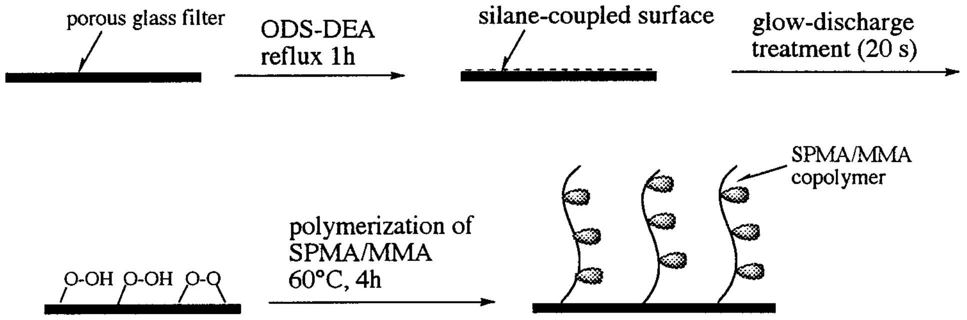


Figure 1. Preparation scheme of surface-grafted glass filter.

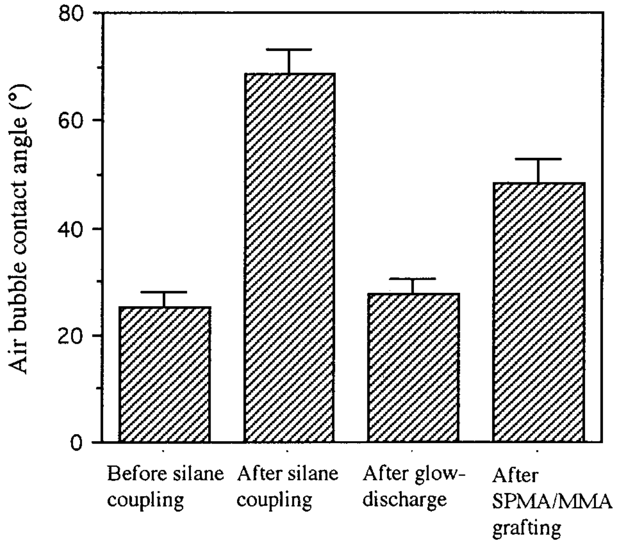


Figure 2. Contact angle of air bubble on the treated surface of glass filter.

Table 2. X-ray Photoelectron Spectroscopy Analysis of the Surface of Treated Glass Filter

	composition (%)			
treatment	Si_{2p}	O_{1s}	C_{1s}	N_{1s}
no treatment	29.9	63.8	6.3	0.0
silane coupling	19.0	27.7	53.3	0.0
grafting	8.0	26.9	64.1	1.0

Graft Polymerization onto a Porous Glass Filter. The preparation scheme is shown in Figure 1. A porous glass filter was incubated in 0.1 M HNO_3 at 70 °C for 3 h and was washed with distilled water several times. The glass filter was dried in a vacuum at 140 °C for 6 h. The treated glass filter was incubated in a toluene solution containing octadecyldimethyl-*N*,*N*-diethylaminosilane (ODS−DEA) synthesized as previously reported.[25,26]

The silane-coupled filter was glow-discharged in air by a high-frequency wave generator, HSF-005 type (200 W, Nihon Koshuha Co., Yokohama, Japan), for 20 s under a pressure of 6.7 Pa. The voltage was 15 kV, and the frequency was 13.56 MHz. The glow-discharged filter was immersed in a DMF solution (40 mL) containing SPMA (2.5 g, 5.95 mmol) and MMA (5.95 g, 59.5 mmol), and the mixture was left to stand at 60 °C under a nitrogen atmosphere. After 4 h, the glass filter was taken out and repeatedly washed with DMF until the 350-nm absorbance of the spiropyran group became undetectable in the washing liquid. The washed filter was dried in a vacuum.

The dried filter was analyzed by X-ray photoelectron spectroscopy (Perkin-Elmer 5500-Series Multi-Technique, Norwalk, CT). The contact angle of the air bubble on the filter surface was measured in pure water. The roughness of the glass filter (micrometer order) was so small in comparison with the size of air bubble (millimeter order) that no significant data distribution was observed. The measurement for one sample was repeated 25 times.

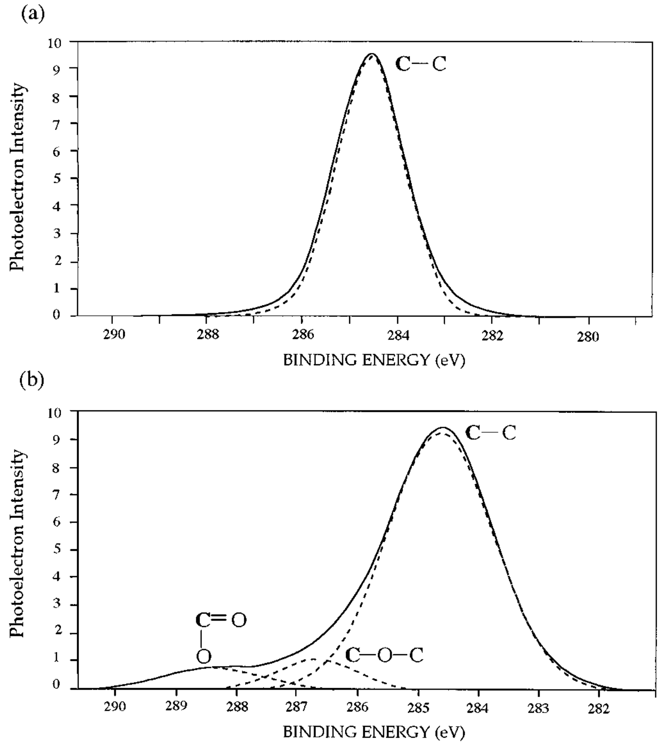


Figure 3. X-ray photoelectron spectra data of (a) silane-coupled and (b) copolymer-grafted glass filter.

Photoirradiation Experiments. A high-pressure mercury lamp equipped with an optical fiber (Hamamatsu Photonics Co., Hamamatsu, Japan) was used. The wavelength of an ultraviolet region ($320 < \lambda < 380$ nm) or a visible region ($\lambda > 380$ nm) was selected with the aid of cutoff filters UV-D36C or L-39 (Toshiba, Tokyo, Japan), respectively.

Permeation Measurements. Permeation experiments were performed as previously reported.[18] Permeabilities of organic liquids were determined by the volume of liquid permeated in a standard time interval under photoirradiation. The measurement for one sample was repeated five times.

Results and Discussion

Solution Polymerization. The content of SPMA in the copolymer and the molecular weight of the copolymer are summarized in Table 1. It is found that a nearly azeotropic copolymerization is attained between SPMA and MMA and that the molecular weight of copolymer is not strongly dependent on the copolymer composition.

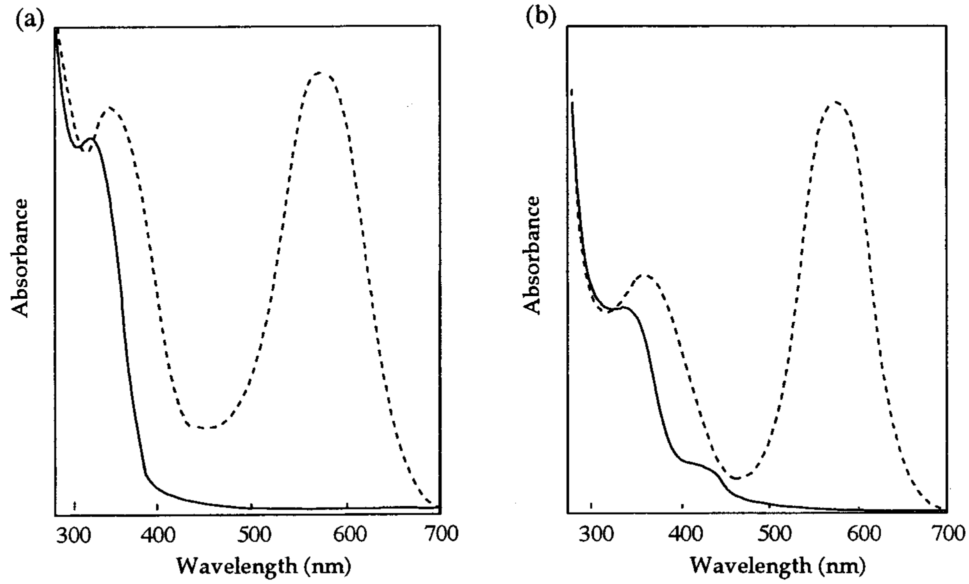


Figure 4. Absorption spectra of SPMA/MMA1 copolymers in (a) toluene and (b) *N*,*N*-dimethylformamide. The solid and dotted lines represent the spectra under irradiation of visible light and ultraviolet light, respectively.

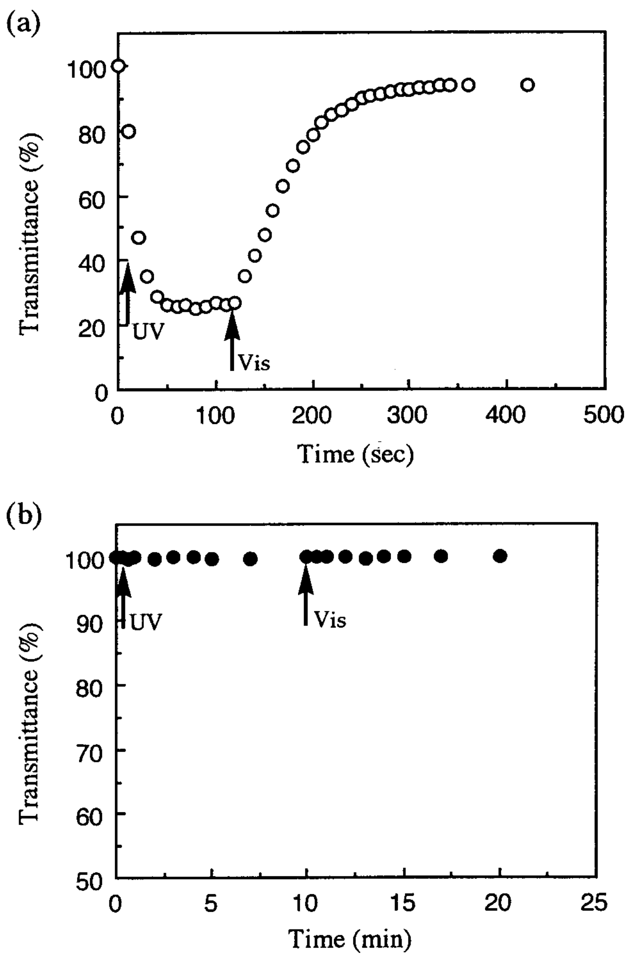


Figure 5. Transmittance of SPMA/MMA3 copolymer at 750 nm in (a) toluene and (b) *N*,*N*-dimethylformamide solution on alternate irradiation of ultraviolet (UV) and visible (Vis) light. The concentration of the copolymer was 5 mg/mL.

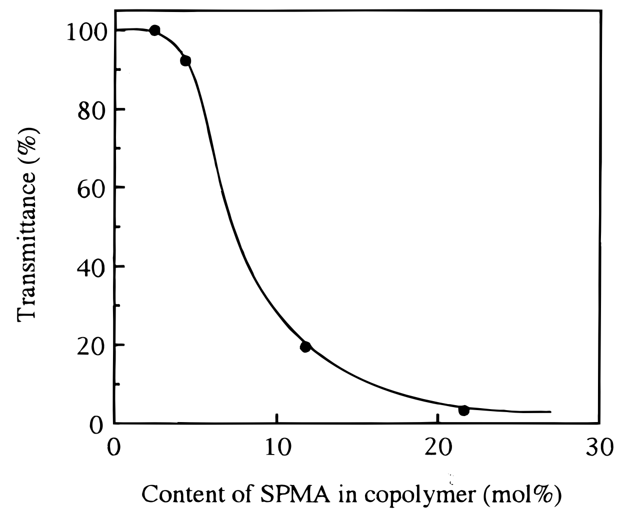


Figure 6. Solubility in toluene of SPMA/MMA copolymers of various compositions, as measured by the 750-nm transmittance, under ultraviolet-light irradiation. The copolymer concentration was 5 mg/mL.

Graft Polymerization. The wettability of the surface of glass filter changed by the surface treatments (Figure 2). The wettability decreased by the silane coupling treatment and increased by the glow-discharge treatment. Graft polymerization reduced the wettability. No siginificant difference of wettabilities of graft-polymerized membrane was observed before and after ultraviolet-light irradiation (data not shown).

Table 2 shows the elemental analysis of the surface of treated glass filter by X-ray photoelectron spectroscopy. After the silane-coupling treatment, the carbon content of the surface significantly increased and the contents of silicon and oxygen decreased. The presence of nitrogen became detectable by the graft polymerization, which may be due to introduction of SPMA unit. In addition, new peaks appeared in the range from 290 to 285 eV, which could be ascribed to the carbon atoms involved in the side chains of graft polymers (Figure 3).

SPMA/MMA Copolymer in Organic Solvent. The spiropyran-containing copolymer was soluble in various organic solvents including toluene, chloroform and DMF at room temperature. Figure 4 shows the alteration of ultraviolet spectra of the SPMA/MMA1 copolymer in toluene and DMF. The appearance of blue color upon ultraviolet-light irradiation indicates isomerization of the pendant spiropyran group to the merocyanine group

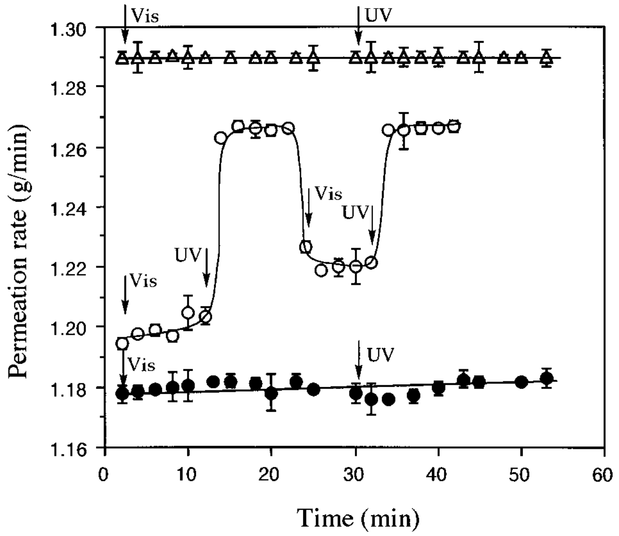
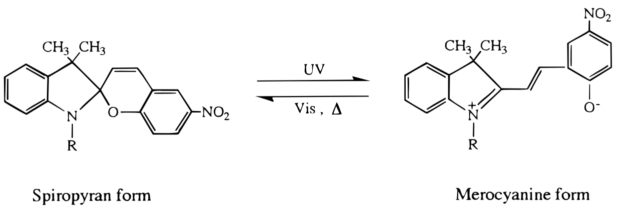


Figure 7. Permeation rate of (○) toluene and (●) *N*,*N*-dimethylformamide through the copolymer-grafted glass filter, and (△) toluene through the silane-coupled glass filter with alternate irradiation of ultraviolet (UV) and visible (Vis) light.

as explained in eq 1. The color change of copolymer solution occurred reversibly upon ultraviolet-light and visible-light irradiations.



(1)

According to the color change, the turbidity of a toluene solution of the SPMA/MMA3 copolymer changed as shown in Figure 5a. On the other hand, no solubility change was observed in DMF as shown in Figure 5b, despite the spectral change occurring. Irie et al.[21,22] reported that the solubility alteration by photoirradiation of polystyrene carrying spiropyran group in the side chains occurred in cyclohexane but not in benzene. It was considered that the critical solubility change of the copolymer did not occur in good solvents.

Figure 6 shows the solubility in toluene of SPMA/MMA copolymers of various compositions under ultraviolet-light irradiation. The copolymers containing spiropyran of more than 10 mol % were insoluble in toluene under ultraviolet-light irradiation.

Permeation of Organic Liquid through the Grafted Glass Filter. The permeation of organic liquid through the glass filter with or without surface grafts was studied with or without photoirradiation, and the results are shown in Figure 7. The permeation of toluene through the silane-coupled glass filter was not influenced by photoirradiation. On the other hand, the glass filter with the copolymer grafts changed the permeability of toluene in response to photoirradiation. The permeation of DMF through the same glass filter was not influenced by photoirradiation.

These results demonstrate that the graft polymer chain can control the permeation of organic liquid through the glass filter. The permeability is obviously related to the solubility of the graft copolymer. The absence of solubility change in DMF led to the absence of permeability change by photoirradiation. The copolymer graft in either the zwitterionic or the neutral state is soluble in DMF, so that the graft chains are well extended in DMF to close pores on the glass filter with unchanged DMF permeation irrespective of photoirradiation. In nonpolar toluene, the zwitterionic merocyanine form of the copolymer grafts, which is produced by UV-light irradiation, makes the graft chains contracted to open pores on the surface of glass filter, thus

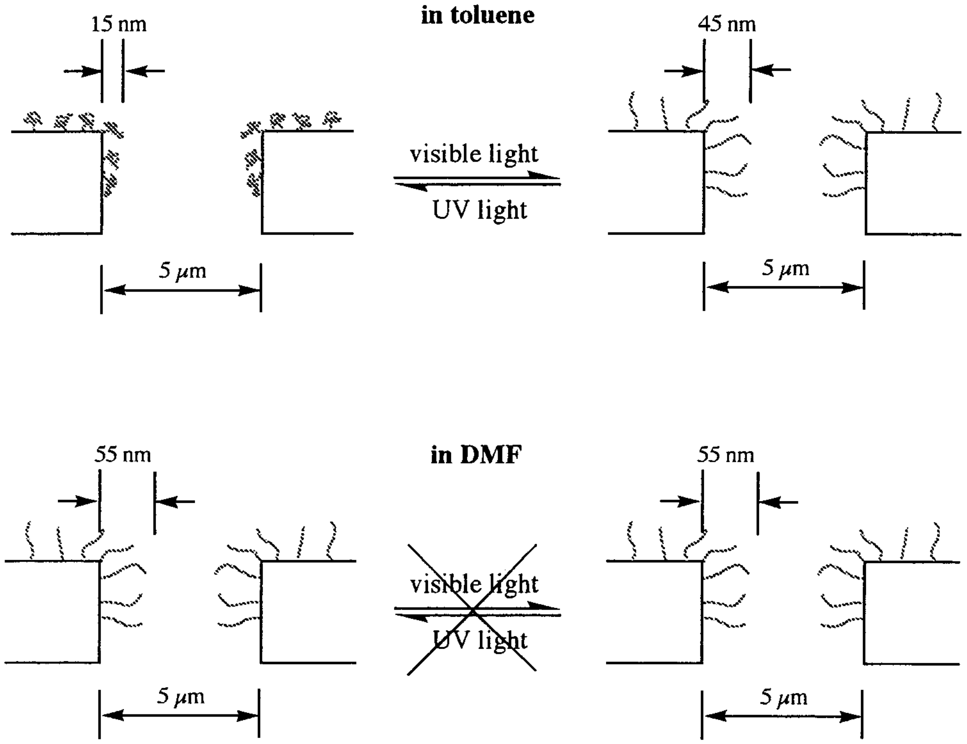


Figure 8. Schematic illustration of thickness of graft layer estimated by Hagen–Poiseuille's equation. The shrinked graft chains open pores to increase permeation, and extended chains cover pores to decrease permeation.

increasing permeation of toluene. The neutral spiropyran form of the copolymer graft under visible-light irradiation is soluble in toluene. The graft chains are extended in toluene to cover pores of the glass filter, reducing the permeation of toluene.

The thickness of graft polymer layer was simply estimated by Hagen–Poiseuille's equation and the result is shown in Figure 8. Although the thickness of graft layer was thin, the spreading of the graft polymer chain significantly changed in response to the photoirradiation in toluene. The graft chains extended in DMF more than in toluene, because DMF was a better solvent for the polymer than toluene.

Recently we[27,28] and Iwata et al.[29] reported that the extension and contraction of pH-responsive polymer grafted on a polymeric porous membrane was observed by an atomic force microscope. Although various types of hydrogels are being developed as signal-responsive materials,[1–7] the mechanical fragility and slow kinetics of the swelling and deswelling processes have limited the number of paractical applications. The filter grafted with signal-responsive polymers as investigated in the present study has a strong enough mechanical property by itself, and it rapidly responds to the environmental signals becuase of the direct contact of graft polymers with the environment. The signal-responsive polymer-grafted porous membrane is a new class of intelligent materials obtained by fabrication of a polymer.

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