

# Adsorption and Desorption Properties of Expanded Poly(tetrafluoroethylene) Films Grafted with DMAEMA and Their Regeneration

Kazunori Yamada, Chiyo Takagi, Mitsuo Hirata

Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, Narashino, Chiba 275-8575, Japan

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**ABSTRACT:** An investigation was undertaken on the adsorption and desorption properties of the expanded poly(tetrafluoroethylene) (ePTFE) films grafted with 2-(dimethylamino)ethyl methacrylate (DMAEMA) to anionic dye anions with one to three sulfonic groups in response to temperature changes. The amount of adsorbed metanil yellow (MY) anions increased with the grafted amount and most of the dimethylamino groups appended to the grafted PDMAEMA chains worked as an adsorption site to MY anions for the DMAEMA-grafted ePTFE (ePTFE-g-PDMAEMA) films with the grafted amounts of higher than 1.1 mmol/g. When the dye-anion-adsorbed ePTFE-g-PDMAEMA films were alternately immersed in water at two different temperatures, dye anions were desorbed from the ePTFE-g-PDMAEMA films at higher temperatures without any chemical agents. The amount of desorbed dye anions increased with an increase in the temperature of water from 40 to 80°C. Desorption of dye

anions is caused by either deprotonation of dimethylamino groups appended to the grafted PDMAEMA chains or thermosensitive contraction of the grafted PDMAEMA chains. These results indicate that the ePTFE-g-PDMAEMA films can be applied as a regenerative ion-exchange membrane for adsorption and desorption processes of anionic compounds in response to the temperature change. The thermally regenerative ion-exchange properties of the ePTFE-g-PDMAEMA films was superior to that of the PE-g-PDMAEMA films reported in our previous article in the fact that the total degree of desorption was higher for the ePTFE-g-PDMAEMA films. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3301–3308, 2007

**Key words:** poly(tetrafluoroethylene); photografting; 2-(dimethylamino)ethyl methacrylate; adsorption; desorption; thermally regenerative ion exchange membrane

## INTRODUCTION

Wastewater from textile dyeing and finishing factories is one of the significant sources of environmental pollution. Many reactive dyes are used because they can bind to textile fibers by covalent bonding. One of the major problems in the use of such reactive dyes is their loss in the dyeing process. In fact, substantial amounts of unfixed dyes are released into the environment. Dyes and pigments discharged are very harmful to aquatic life in rivers, lakes, and seas. Textile wastewater is characterized by high chemical oxygen demand, low biodegradability, and high salt content. It is of great importance to eliminate them from industrial wastewater not only for removal of colors from water but also for environmental preser-

vation.<sup>1,2</sup> Removal of dyes and pigments from industrial wastewater was carried out by biological treatment,<sup>3–5</sup> coagulation,<sup>6,7</sup> adsorption,<sup>8–10</sup> ultrafiltration,<sup>11–13</sup> and so on, but the equipment for some of these process is relatively large in scale and high investment on equipment is frequently required. Since the adsorption process appears to have a considerable potential for removal of color compounds, many researchers have followed up on the possibility of the adsorption process to remove color compounds with ion-exchange membranes.<sup>10,14,15</sup> The advantages of the use of the ion-exchange membranes are less space, lower capital investment, simple design, and easy operation.

We have aimed at the application of the polyethylene (PE) and poly(tetrafluoroethylene) (PTFE) films modified by the photografting of hydrophilic or reactive monomers and particularly at the subsequent functionalization to various functional membranes for removal of undesirable chemical compounds or water purification.<sup>16–21</sup> In addition, weakly acidic polyelectrolytes introduced to the polymer films are expected to play an important role in membrane separation by the adsorption process. Some researchers have reported on the thermally regenerative ion-

Correspondence to: K. Yamada (k5yamada@cit.nihon-u.ac.jp).

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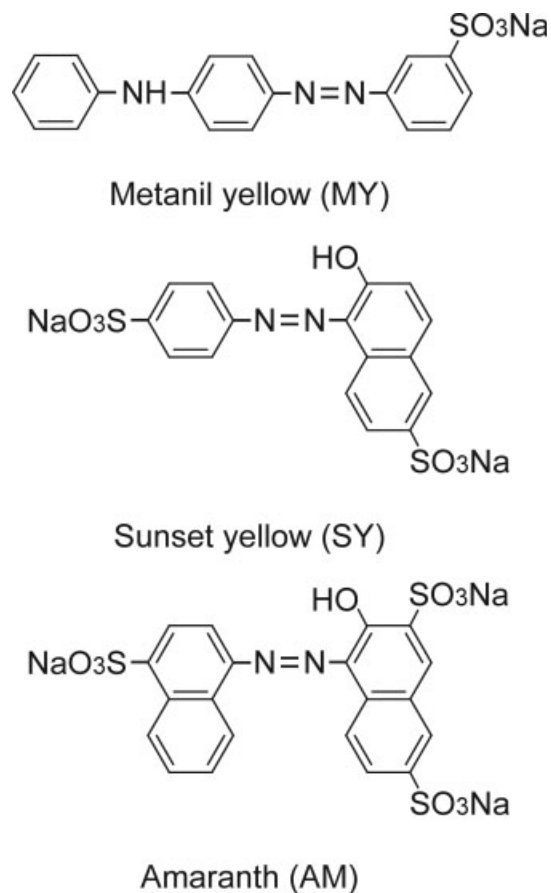
exchange properties of polymer materials, which were prepared by copolymerization of both weakly acidic and weakly basic monomers with a crosslinking agent, in response to temperature changes.<sup>22–24</sup> However, little has been reported on a thermally generative ion-exchange membrane prepared from a single weakly ionic monomer. In our previous paper,<sup>25</sup> we investigated the regenerative ion-exchange properties in response to the temperature changes for the 2-(dimethylamino)ethyl methacrylate (DMAEMA)-grafted PE (PE-g-PDMAEMA) films. When the dye-anion-adsorbed PE-g-PDMAEMA films were alternately immersed in water of two different temperatures, dye anions were desorbed from the PE-g-PDMAEMA films in water at higher temperatures without any chemical agents because of the deprotonation of dimethylamino groups appended to the grafted PDMAEMA chains and thermosensitive contraction of grafted PDMAEMA chains. In addition, since the PTFE films are superior to the PE films in chemical and thermal resistance and stability, the grafting of various monomers onto the PTFE films can be expected to widen their application as functional membranes.<sup>2,26–31</sup> We have also reported that hydrophilic methacrylic monomers such as methacrylic acid, acrylic acid, and DMAEMA can be effectively grafted onto porous PTFE (pPTFE) and expanded PTFE (ePTFE) films by the combined use of the plasma treatment and photografting.<sup>26–28</sup> The ePTFE-g-PDMAEMA films possessed high water absorptivity and practical strength for functional membranes in the water-absorbed state. In addition, The ePTFE film is an appropriate substrate for the thermally regenerative ion-exchange membranes in its high vacancy and chemical stability.

In this study, an investigation was undertaken on adsorption and desorption of the ePTFE-g-PDMAEMA films to model dye anions with one to three sulfonic groups in response to temperature changes. In addition, the reusability of the ePTFE-g-PDMAEMA films was examined by the alternating repetition of the cyclic processes of adsorption and desorption. From the obtained experimental results, their application to a thermally generative ion exchange membrane will be discussed.

## EXPERIMENTAL

### Materials

An ePTFE film (diameter: 47 mm, thickness: 83  $\mu\text{m}$ , pore size: 3.0  $\mu\text{m}$ , vacancy: 83%), obtained from Toyo Roshi (Tokyo, Japan) was used as a polymer substrate for the photografting of DMAEMA. Three different types of anion dyes with one to three sulfonic groups were chosen as model compounds [one group, meta-



**Figure 1** Chemical structures of the dye anions used in this study.

nil yellow (MY); two groups, sunset yellow (SY); and three groups; amaranth (AM)], as shown in Figure 1.<sup>8</sup>

### Plasma treatment and photografting

The plasma treatment and photografting of DMAEMA onto the ePTFE films were carried out in the same manner described in our previous publications.<sup>8,26,28</sup> Both surfaces of the ePTFE films were treated with oxygen plasmas for 120 s at an output of 200 W and a frequency of 15 kHz under a vacuum of 6.67 Pa (0.05 Torr) using a Shimadzu LCVD 20 type plasma treatment apparatus. Then, the plasma-treated ePTFE films were dipped in an acetone solution containing benzophenone (BP; 0.5 (w/v)%) as a sensitizer to coat their surfaces with BP.<sup>27</sup> DMAEMA was photografted onto the plasma-treated ePTFE films at 60°C by radiating UV rays emitted from a 400-W high pressure mercury lamp in an aqueous DMAEMA monomer solution at a monomer concentration of 1.0M. The pH value of the aqueous DMAEMA solution was adjusted to 8.0 with concentrated HCl to increase the solubility of PDMAEMA homopolymers and to obtain ePTFE-g-PDMAEMA films with higher grafted

amounts.<sup>25</sup> The amount of grafted DMAEMA was calculated from the weight increase in mmol/g-ePTFE after photografting using eq. (1).

$$\begin{aligned} \text{Amount of grafted DMAEMA (mmol/g)} \\ = \frac{(W_g - W_0/157.21)}{W_0} 1000 \quad (1) \end{aligned}$$

where  $W_0$  and  $W_g$  denote the weight of the ungrafted ePTFE and ePTFE-g-PDMAEMA films, respectively. The quantity of 157.21 is the molecular mass of DMAEMA.

### Ion-exchange properties of ePTFE-g-PDMAEMA films

The ion-exchange capacity of the ePTFE-g-PDMAEMA films was determined. First, weight-known ePTFE-g-PDMAEMA films of different grafted amounts cut into  $10 \times 10 \text{ mm}^2$  pieces in the dry state were immersed in an aqueous 1.0M NaOH solution for 24 h to entirely deprotonate the dimethylamino groups appended to the grafted PDMAEMA chains because the photografting of DMAEMA onto the ePTFE films were carried out at pH 8 as mentioned above. The ePTFE-g-PDMAEMA films taken from the aqueous NaOH solutions were immersed in an aqueous 0.101M HCl solution ( $100 \text{ cm}^3$ ) with moderate stirring.<sup>8</sup> The aliquots taken from the aqueous HCl solutions after immersion for 36 h were titrated with a 0.0101M NaOH solution with thymol blue as an acid-base indicator. The ion-exchange capacity and degree of ion-exchange of the ePTFE-g-PDMAEMA films were calculated from the volume of the titrant and the grafted amount using eqs. (2) and (3), respectively.

$$\begin{aligned} \text{Ion exchange capacity (mmol/g)} \\ = \frac{(0.101 - C_{\text{eq}})0.100}{W_g} 1000 \quad (2) \end{aligned}$$

$$\begin{aligned} \text{Degree of ion exchange (mol/mol)} \\ = \frac{(0.101 - C_{\text{eq}})0.100}{(W_g - W_0)/157.21} \quad (3) \end{aligned}$$

where  $C_{\text{eq}}$  denotes the equilibrium HCl concentration after immersion of ePTFE-g-PDMAEMA films.

### Determination of amounts of adsorbed dye anions

The ePTFE-g-PDMAEMA films cut into  $10 \times 10 \text{ mm}^2$  pieces were immersed in the aqueous anion dye solutions in the pH range of 2.0–12.0 with appropriate stirring at 25°C. The amounts of dye anions adsorbed on the ePTFE-g-PDMAEMA films were determined by the measurements of the absorbances of the outer

solutions at 466, 243, and 475 nm for MY, SY, and AM anions, respectively.

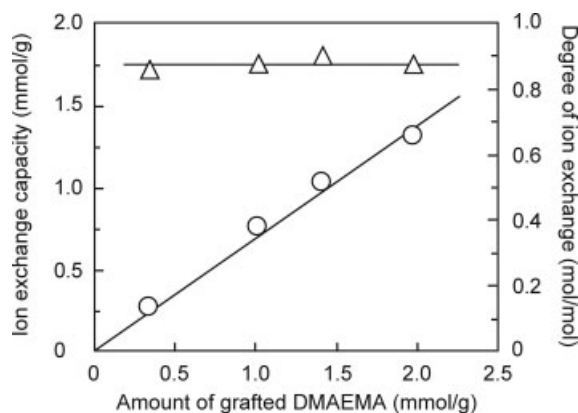
### Desorption in response to temperature

The dye-anion-adsorbed ePTFE-g-PDMAEMA films were alternately immersed in water at 20°C and 40, 60, or 80°C, and the amounts of dye anions desorbed from the ePTFE-g-PDMAEMA films were spectroscopically measured at a prescribed time interval. After the desorption equilibrium was attained at 40, 60, or 80°C, the dye-anion-adsorbed ePTFE-g-PDMAEMA films were transferred to water at 20°C and then immersed in water at 40, 60, or 80°C again. This cyclic procedure was repeated until desorption of dye anions at higher temperature came to a full stop.

## RESULTS AND DISCUSSION

### Membrane properties

The surface analysis by ESCA and membrane properties of the ePTFE-g-PDMAEMA films determined by ESCA were discussed in detail in our previous papers.<sup>26,28</sup> Both O1s/C1s and N1s/C1s values increased and F1s/C1s value decreased with an increase in the grafted amount, and their intensity ratios stayed constant at the grafted amount of 0.01 mmol/g. This indicates that the fabric ePTFE surfaces were fully covered with grafted ePTFE chains. It was found from the SEM pictures of the ePTFE-g-PDMAEMA films measured in the dry state that the pore size of the ePTFE film decreased with an increase in the grafted amount. We can safely say that the photografting of DMAEMA also occurred on the fabric surfaces in the inside of the ePTFE films. In addition, the photografting of DMAEMA made the ePTFE film considerably hydrophilic. The amount of absorbed water sharply increased in a low grafted amount region (<5 mmol/g). However, in the same grafted amount region the area ratio for the ePTFE-g-PDMAEMA films gradually decreased in comparison with the original size of the ungrafted ePTFE film even in the water-adsorbed state. The slight area contraction of the ePTFE films by the photografting of hydrophilic monomers such as MAA and DMAEMA is caused by hydrogen bonding between the polar functional groups appended to the grafted polymer chains. Mechanical strength of the ePTFE-g-PDMAEMA films was equivalent to or a little higher than the original ungrafted ePTFE film. This indicates that the ePTFE-g-PDMAEMA films possess mechanical strength adequate to be used for various functional membranes in the water-adsorbed state. A slight increase in mechanical strength for the ePTFE-g-PDMAEMA films in the water-adsorbed state is considered to be due to hydrogen bonding between the dimethylamino groups appended to the grafted polymer chains.



**Figure 2** Dependence of the ion-exchange capacity (○) and degree of ion exchange (△) on the grafted amount for the ePTFE-g-PDMAEMA films at pH 3.0 and 25°C.

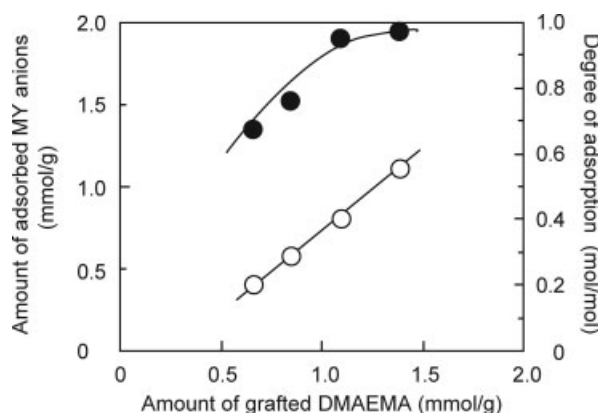
### Ion-exchange properties

When the ePTFE-g-PDMAEMA films were immersed in an aqueous HCl solution of 0.101M, the HCl concentration decreased with an increase in an immersion time, and then the equilibrium was reached at about 30 h. Figure 2 shows the changes in the ion-exchange capacity and the degree of ion exchange with the grafted amount for the ePTFE-g-PDMAEMA films.

The ion exchange capacity approximately linearly increased against the grafted amount. On the other hand, the degree of ion exchange reached up to 0.97 irrespective of the grafted amount. This means that most of the dimethylamino groups appended to the grafted PDMAEMA chains work as a positively charged adsorption site.

### Adsorption of MY anions

Adsorption of MY anions on ePTFE-g-PDMAEMA films with different grafted amounts was carried out



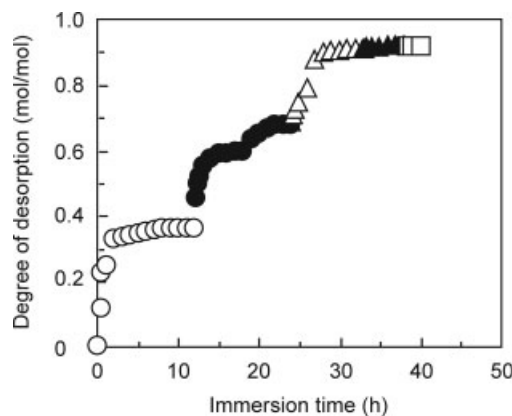
**Figure 3** Changes in the amount of adsorbed MY anions (○) and the degree of adsorption (●) with the grafted amount in an aqueous MY solution of the initial concentration of 0.20 mM at pH 3.0 and 25°C.

at pH 3.0 at which adsorption of MY anions had the maximum value for the PE-g-PDMAEMA films in our previous particle.<sup>8</sup> The amount of adsorbed MY anions for the PE-g-PDMAEMA films increased with a decrease in the pH value. The protonation of dimethylamino groups appended to the grafted PDMAEMA chains also increased with a decrease in the pH value, and all dimethylamino groups were positively charged at pH 3.0.<sup>16</sup> The degree of adsorption defined by eq. (4) increased up to 1.0 at pH 3.0 for adsorption of MY anions to the PE-g-PDMAEMA films. This indicates that all protonated dimethylamino groups appended to the grafted PDMAEMA chains work as the adsorption site and a sulfonic group in an MY molecule bonds to a protonated dimethylamino group appended to the grafted PDMAEMA chains in 1 : 1 stoichiometry through the ionic bond.

On the basis of a series of experimental results obtained for adsorption of MY anions on the PE-g-PDMAEMA films, adsorption of MY anions on the ePTFE-g-PDMAEMA films was carried out at pH 3.0. The amount of adsorbed MY anions for the ePTFE-g-PDMAEMA films in a 0.20 mM MY solution at pH 3.0 and 25°C increased with an increase in the immersion time, and then the adsorption equilibrium was attained at about 24 h. The degree of adsorption was calculated from the amounts of adsorbed MY anions and grafted DMAEMA using eq. (4).

$$\text{Degree of adsorption (mol/mol)} = \frac{Q_{\text{eq}}}{(W_g - W_0)/157.21} \quad (4)$$

where  $Q_{\text{eq}}$  is the amount of adsorbed dye anions per gram of ePTFE-g-PDMAEMA film (mol). Figure 3 shows the changes in the amount of adsorbed MY



**Figure 4** Desorption of MY anions from an ePTFE-g-PDMAEMA film of 1.09 mmol/g at 80°C by fluctuations in the water temperature between 20 and 80°C: (○) first run, (●) second run, (△) third run, (▲) fourth run, and (□) fifth run.

**TABLE I**  
**Desorption of MY Anions from ePTFE-g-PDMAEMA Films of Different Grafted Amounts at 80°C by Fluctuations in the Water Temperature Between 20°C and 80°C**

Grafted amount (mmol/g)	Amount of adsorbed MY anions (mmol/g)	Degree of desorption (%)	Degree of desorption				Total (%)
			First run (%)	Second run (%)	Third run (%)	Fourth run (%)	
0.33	0.303	97.6	19.4	2.4			21.8
0.85	0.707	94.4	43.2	27.3	9.6	4.8	84.9
1.09	0.908	97.7	36.5	31.5	22.6	1.2	91.8

anions and the degree of adsorption with the grafted amount. The amount of adsorbed MY anions increased over the grafted amount. The degree of adsorption to MY anions increased with an increase in the grafted amount, and then went up to 0.95 at the grafted amounts of 1.1 mmol/g or higher. The water-absorptivity measurements and surface analysis by ESCA were carried out for the ePTFE-g-PDMAEMA films in our previous articles.<sup>8,26</sup> As the ePTFE surfaces were covered with grafted PDMAEMA chains, the amount of absorbed water increased. The increase in the water-absorptivity shows hydrophilization of the ePTFE films by the photografting of DMAEMA. Here, we can safely say that the increase in the amount of adsorbed MY anions mainly due to hydrophilization by coverage of the surface of the ePTFE film with grafted PDMAEMA chains. It was found from Figure 3 that MY anions was ionically bonded to almost all of the protonated dimethylamino groups appended to the grafted PDMAEMA chains in the range of the grafted amounts higher than 1.1 mmol/g.

#### Dependence of desorption of MY anions on the grafted amount

The ePTFE-g-PDMAEMA films that adsorbed MY anions were alternately immersed in water at 20 and 80°C. Figure 4 shows desorption of MY anions from the ePTFE-g-PDMAEMA films of the grafted amount of 1.09 mmol/g at 80°C by fluctuations in water temperature between 20 and 80°C. When the MY anion-adsorbed ePTFE-g-PDMAEMA film was immersed in water at 80°C, MY anions were desorbed from the ePTFE-g-PDMAEMA film. When the ePTFE-g-PDMAEMA film was cooled in water at 20°C followed by immersion in water at 80°C after the desorption equilibrium at the first desorption process at 80°C, MY anions were desorbed again. The quantities of MY anions adsorbed of 91.8% were desorbed by alternately repeating the immersion in water at 20 and 80°C four times.

The temperature of an aqueous PDMAEMA solution of 1 w/v% (pH = 9.3) was increased at the rate of heating of 1°C/10 min and the transmittance at 650 nm was measured at different temperatures. The

transmittance of the aqueous PDMAEMA solution discontinuously decreased at 33°C. It was reported in our previous article<sup>25</sup> that PDMAEMA is a thermosensitive polymer and has a lower critical solution temperature (LCST) of 27°C in a NaHCO<sub>3</sub>/NaOH buffer. As the pH value of an aqueous PDMAEMA solution decreases, the LCST gradually increases because of the increase in the protonation of dimethylamino groups appended to the PDMAEMA chains.<sup>16</sup> Here, the pH dependence of the protonation of the dimethylamino groups appended to the grafted PDMAEMA chains was taken to be the same as that of the PDMAEMA homopolymers determined by colloid titration with potassium poly(vinyl alcohol)sulfate (KPVs) in our previous article.<sup>25</sup> The degree of protonation of the dimethylamino groups which work as a positively chargeable weak base in response to the pH change increases with a decrease in the pH value. At pH 9.3 at which the degree of protonation reaches about 7%, the discontinuous contraction of PDMAEMA was observed at 33°C.

It is apparent from the above experimental results that desorption of MY anions from the ePTFE-g-PDMAEMA films in water at 80°C is due to the squeezing effect caused by the contraction of grafted PDMAEMA chains in addition to deprotonation of protonated dimethylamino groups appended to the grafted PDMAEMA chains. The total degree of desorption of MY anions reached 91.8% by repeating the fluctuations in the water temperature between 20 and 80°C four times. The thermosensitive desorption of MY anions from ePTFE-g-PDMAEMA films of different grafted amounts at 80°C are summarized in Table I. Although the amount of desorbed MY anions decreased with an increase in the run number of the desorption process, the total desorption amount increased with an increase in the grafted amount. This indicates that the isotonic contraction of the ePTFE-g-PDMAEMA films caused by the rise in the temperature more effectively occurs at higher grafted amounts. In addition, the thermosensitive desorption properties of the ePTFE-g-PDMAEMA films obtained here were compared with those of the PE-g-PDMAEMA films.<sup>8</sup> The degree of desorption of MY anions for the ePTFE-g-PDMAEMA films at 80°C was

**TABLE II**  
**Desorption of MY Anions from an ePTFE-g-PDMAEMA Film of 0.85 mmol/g at Higher Temperatures by Fluctuations in the Water Temperature Between 20°C and 40, 60, or 80°C**

Temperature (°C)	Degree of adsorption (%)	Degree of desorption					Total (%)
		First run (%)	Second run (%)	Third run (%)	Fourth run (%)	Fifth run (%)	
40	70.1	30.3	25.3	3.6			59.2
60	93.4	42.9	23.8	9.3	4.6	2.3	82.9
80	84.4	43.2	27.4	9.5	4.8		84.9

higher than that for the PE-g-PDMAEMA films, although the ePTFE-g-PDMAEMA films had lower amounts of adsorbed MY anions than the PE-g-PDMAEMA films. These results are explained in terms of the following contributions: (1) the location of the photografting of DMAEMA was restricted to the fibrous surface of the ePTFE films; (2) the ePTFE films used had high porosity, although the specific surface area is not determined in this study; (3) the ePTFE-g-PDMAEMA films contracted in water at 80°C because of a high porosity of the ePTFE film and the thermosensitivity of grafted PDMAEMA chains.

Desorption of MY anions at 80°C proceeded more effectively and higher degree of adsorption was obtained for the ePTFE-g-PDMAEMA films than for the PE-g-PDMAEMA films, while the net amount of adsorbed MY anions for the ePTFE-g-PDMAEMA films was lower than that of the PE-g-PDMAEMA films.

#### Dependence of desorption of MY anions on the temperature

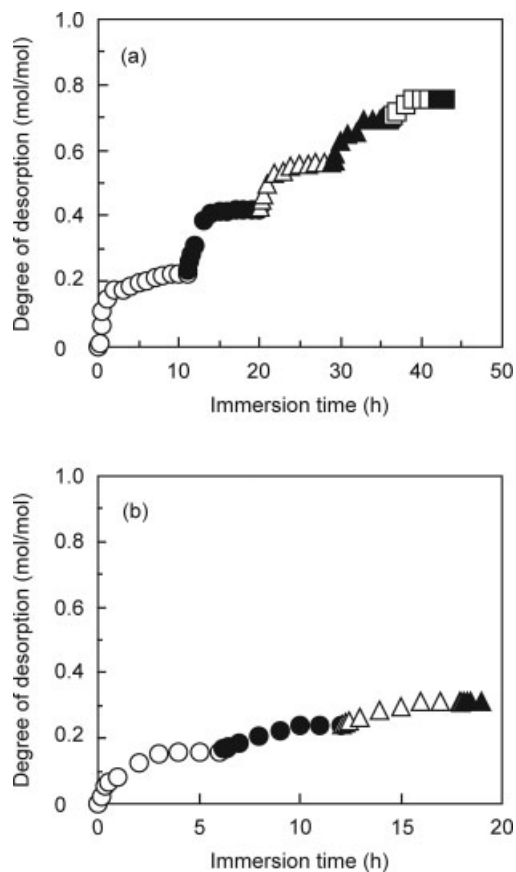
The ePTFE-g-PDMAEMA films of the grafted amount of 0.85 mmol/g that adsorbed dye anions at pH 3 were alternately immersed in water at 20°C and 40, 60, or 80°C. MY anions were desorbed in water at higher temperatures and not at 20°C. After the desorption process at 40, 60, or 80°C attained equilibrium, the ePTFE-g-PDMAEMA films were cooled in water at 20°C followed by immersion in water at 40, 60, or 80°C. The results of thermosensitive desorption of MY anions for the ePTFE-g-PDMAEMA film at 40, 60, or 80°C are summarized in Table II. The total amount of desorbed MY anions increased with an increase in the water temperature. Release of MY anions from the ePTFE-g-PDMAEMA films in water at 40, 60, and 80°C is considered to be accelerated by the squeezing effect. Mechanism of the release of MY anions from the ePTFE-g-PDMAEMA or PE-g-PDMAEMA films at higher temperatures is similar to that of various chemical compounds such as drugs from the thermosensitive hydrogels.<sup>32–34</sup>

Since the amount of desorbed MY anions was low at each desorption process for the PE-g-PDMAEMA films, the total degree of desorption increased by increasing the volume of water of 80°C.<sup>8</sup> On the other

hand, as shown in this study a high degree of desorption was obtained only by increasing the temperature of water for the ePTFE-g-PDMAEMA films. This would be attributed to a high porosity of the ePTFE films used.

#### Thermosensitive desorption of SY and AM anions

The desorption experiments of SY and AM anions was also carried out from an ePTFE-g-PDMAEMA film in response to the temperature changes, since total amount of desorbed MY anions increased with an



**Figure 5** Desorption of (a) SY and (b) AM anions from an ePTFE-g-PDMAEMA film of 1.09 mmol/g at 80°C by fluctuations in the water temperature between 20 and 80°C: (○) first run, (●) second run, (△) third run, (▲) fourth run, (□) fifth run, (■) sixth run.

**TABLE III**  
Desorption of SY Anions from an ePTFE-g-PDMAEMA Film of 1.09 mmol/g at Higher Temperatures by Fluctuations in the Water Temperature Between 20°C and 40, 60, or 80°C

Temperature (°C)	Degree of adsorption (%)	Degree of desorption					Total (%)
		First run (%)	Second run (%)	Third run (%)	Fourth run (%)	Fifth run (%)	
40	34.6	10.9	10.2				21.1
60	32.4	29.1	20.7	16.6			66.4
80	32.9	22.4	19.5	14.1	13.3	6.2	75.5

increase in the grafted amount as shown in Table I. Figure 5 shows desorption of SY and AM anions from an ePTFE-g-PDMAEMA film of the grafted amount of 1.17 mmol/g at 80°C by fluctuations in water temperature between 20 and 80°C. When the SY and AM-adsorbed ePTFE-g-PDMAEMA films were immersed in water at 80°C, SY and AM anions were desorbed from the ePTFE-g-PDMAEMA films. Although the amount of desorbed SY and AM anions decreased with an increase in the run number of immersion in water at 80°C, the total degree of desorption for SY and AM anions went up to 75.5 and 30.8%, respectively. In addition, the results of thermosensitive desorption of SY and AM anions at 40, 60, and 80°C are summarized in Tables III and IV, respectively. The amounts of desorbed SY and AM anions increased with an increase in the temperature of water from 40 to 80°C. However, the number of sulfonic groups in the dye molecules resulted in the decrease in the total degree of desorption.

Although PDMAEMA is a weakly cationic polyelectrolyte, it possesses the thermosensitivity to be soluble and insoluble at temperatures lower and higher than the LCST under conditions in which the degree of protonation is very low (less than ~5%), as mentioned previously.<sup>16,25</sup> Many researchers have reported on the thermally regenerative ion-exchange properties of polymer materials, which were prepared mainly by copolymerization of both weakly acidic and weakly basic monomers with a crosslinking agent, in response to temperature changes.<sup>25,35,36</sup> However, little has been reported on a thermally regenerative ion-exchange membrane prepared from a single weakly cationic monomer as described here.

### Repetitive cycles of adsorption and desorption

After the total degree of desorption of 91.8% was obtained by fluctuations in the water temperature between 20 and 80°C four times for the ePTFE-g-PDMAEMA film of the grafted amount of 1.10 mmol/g, the rest of MY anions adsorbed were removed by washing the ePTFE-g-PDMAEMA film with an aqueous NaOH solution at pH 10. Subsequently, MY anions were adsorbed on the ePTFE-g-PDMAEMA film, and then MY anions were desorbed from the ePTFE-g-PDMAEMA films by fluctuations in water temperature between 20 and 80°C. The repetitive cycles of adsorption and desorption were summarized in Table V. The amount of adsorbed MY anions at pH 3 and the total degree of desorption at 80°C were almost equivalent in three successive MY anion adsorption-desorption cyclic process. These results indicate that the ePTFE-g-PDMAEMA films little undergo considerable fatigue.

### CONCLUSIONS

We have investigated the thermally regenerative ion-exchange properties of the ePTFE-g-PDMAEMA films in response to the temperature changes and their repetitive cycles of adsorption and desorption. From the experimental results mentioned above, we can conclude the following.

When the dye-anion-adsorbed ePTFE-g-PDMAEMA films were alternately immersed in water of two different temperatures (20°C and 40, 60, or 80°C), dye anions were desorbed in water at 40, 60, or 80°C without any chemical agents because of the deprotonation of dimethylamino groups appended to the grafted

**TABLE IV**  
Desorption of AM Anions from an ePTFE-g-PDMAEMA Film of 1.09 mmol/g at Higher Temperatures by Fluctuations in the Water Temperature Between 20°C and 40, 60, or 80°C

Temperature (°C)	Degree of adsorption (%)	Degree of desorption				Total (%)
		First run (%)	Second run (%)	Third run (%)	Fourth run (%)	
40	26.3	10.3	2.8			21.1
60	28.4	16.6	6.2	3.7	1.9	28.4
80	26.5	16.0	7.9	6.9		30.8

**TABLE V**  
**The Repetitive Cycles of Adsorption and Desorption for an ePTFE-g-PDMAEMA Film of 1.10 mmol/g by Fluctuations in the Water Temperature Between 20°C and 80°C**

	Degree of adsorption (%)	Degree of desorption			Total (%)
		First run (%)	Second run (%)	Third run (%)	
1st desorption	88.2	55.3	28.4	14.2	91.8
2nd desorption	82.1	53.9	30.1	7.6	91.6
3rd desorption	83.0	53.8	29.0	7.5	90.3

PDMAEMA chains and the thermosensitive contraction of the ePTFE-g-PDMAEMA films. These results indicate that the ePTFE-g-PDMAEMA films can be applied as a thermally regenerative ion-exchange membrane for the adsorption and desorption process of anionic compounds in response to the temperature changes. Dye anions were more effectively desorbed from the ePTFE-g-PDMAEMA films than the PE-g-PDMAEMA films because of high vacancy and good chemical stability of the ePTFE film. This indicates that the ePTFE film is an appropriate polymer substrate for a thermally regenerative ion-exchange membrane.

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