

Adsorption and Desorption Properties of Cationic Polyethylene Film Gels to Organic Anions and Their Regeneration

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ABSTRACT: An investigation was undertaken on the adsorption and desorption properties of 2-(dimethylamino)ethyl methacrylate grafted polyethylene (PE-g-PDMAEMA) films to anionic dye anions with one to three sulfonic groups in response to pH and temperature changes. The amounts of dye anions adsorbed on the PE-g-PDMAEMA films passed through the maximum values at about pH 3 because of an increase in the protonation of dimethylamino groups caused by a decrease in the pH value. The amounts of adsorbed dye anions decreased below pH 3 because the ionic strength increased with the addition of HCl to adjust the initial pH values of the aqueous dye solutions. The amounts of adsorbed dye anions decreased with an increase in the number of sulfonic groups in the dye molecules at the same pH value because electrostatic repulsion was generated between free sulfonic groups of the dye anions adsorbed onto the PE-g-PDMAEMA films and free dye anions in the medium. A large number of dye anions adsorbed were desorbed from the PE-g-PDMAEMA

film with initial pH values above 11.0. The cyclic processes of adsorption at pH 3.0 and desorption at pH 11.0 were repeated without considerable fatigue. The PE-g-PDMAEMA films showed practically regenerative adsorption and desorption behavior in response to the pH changes. In addition, when the dye-anion-adsorbed PE-g-PDMAEMA films were alternately immersed in water at two different temperatures, dye anions were desorbed in water at higher temperatures without any chemical agents because of the deprotonation of dimethylamino groups and thermosensitive contraction of grafted PDMAEMA chains. These results indicate that PE-g-PDMAEMA films can be applied as regenerative ion-exchange membranes for adsorption and desorption processes of anionic compounds in response to the pH and temperature. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 381–391, 2006

Key words: adsorption; membranes; polyethylene (PE)

INTRODUCTION

Wastewater from textile dyeing and finishing factories is a significant source of environmental pollution. Reactive dyes are extensively used fundamentally because of the ability of their reactive groups to bind to textile fibers by covalent bonding. The major environmental problem associated with the use of such reactive dyes is their loss in the dyeing process. The fixation efficiency is limited to the range of 60–90%. Consequently, substantial amounts of unfixed dyes are released in wastewater. Textile wastewater is characterized by high chemical oxygen demand, low biodegradability, and high salt content and is the source of aesthetic pollution related to

color. In addition, it has been stressed recently that color compounds such as dyes and pigments discharged from several industries are very harmful to aquatic life in rivers and lakes. Therefore, it is of great importance to eliminate them from the effluents not only for the removal of the color from water but also for environmental preservation. However, most of them are not oxidized by conventional, biological, and physical treatments because of their complex structure and larger molecular size.^{1–3}

The quantitative and selective separation of color compounds from aqueous environments by a number of sorbents has been extensively investigated by many researchers. The methods of color removal from industrial effluents include biological treatment,⁴ coagulation,^{5,6} adsorption,^{7,8} oxidation,^{9,10} ultrafiltration,^{11–13} and so on. For example, biological treatment is generally cheap and simple to apply, but refractory pollutants caused by textile industries cannot easily be degraded by traditional biological processes and remain in the effluents. In some cases, raw textile wastewater is treated by a combined process of chemical coagulation, electrochemical oxidation, and activated sludge, but the equipment for

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this process is relatively large in scale, and equipment investment is also required.

To the contrary, adsorption appears to have considerable potential for the removal of color from industrial effluents. Many researchers have followed up the possibility of an adsorption process to remove color compounds with ion-exchange membranes, and their advantages for controlling water pollution are less space, lower capital investment, simple design and easy operation of the equipment, and efficient removal of organic waste constituents in comparison with other traditional treatment process.¹⁴

Here we have aimed at the application of grafted polyethylene (PE) films to an ion-exchange membrane for water purification and environmental preservation because membrane separation technologies are promising methods for color removal from the points of view of simplicity and energy savings. A variety of functional membranes with practical mechanical strength were prepared by the photografting of different neutral and ionic monomers throughout PE films in our previous studies.^{15–18} In addition, because polytetrafluoroethylene (PTFE) films are superior to PE films in chemical resistance and stability, the grafting of various monomers onto PTFE films can be expected to widen their application to functional membranes. We have reported that ionic monomers such as methacrylic acid and 2-(dimethylamino)ethyl methacrylate (DMAEMA) can be effectively grafted onto porous polytetrafluoroethylene (pPTFE) and expanded polytetrafluoroethylene (ePTFE) films by the combined use of a plasma treatment and photografting.^{19–23}

Grafted PE, pPTFE, and ePTFE films have promise for various membrane separation techniques such as uphill transport^{17,24} and selective separation.²⁵ Temperature,¹⁸ pH,²⁴ and electric potential differences^{17,23,25} have been applied to the source of the driving force for membrane separation. In addition, weakly basic or acidic polyelectrolytes introduced to the polymer substrates are expected to play an important role in membrane separation by the adsorption process because the positively or negatively chargeable functional groups can be changed reversibly and rapidly in response to a pH change of the surrounding solution.⁸

In this study, an investigation was undertaken on the adsorption and desorption properties of 2-(dimethylamino)ethyl methacrylate-grafted polyethylene (PE-g-PDMAEMA) films to model dye anions with one to three sulfonic groups in response to the pH and temperature changes. In addition, the reusability of the PE-g-PDMAEMA films was also examined by the alternating repetition of the cyclic processes of adsorption and desorption, and their application to a thermally regenerative ion exchange was discussed.

EXPERIMENTAL

Photografting

A PE film (thickness = 30 μm , density = 0.924 g/cm^3), supplied by Tamapoly Co., Ltd. (Tokyo, Japan), was used as a polymer substrate for photografting. The photografting of DMAEMA onto the PE films and the membrane properties of the resultant PE-g-PDMAEMA films are described in our previous publications in detail.^{15,18,26,27} The PE films (60 \times 30 mm) were dipped in an acetone solution containing benzophenone (BP; 0.5 w/v %) as a sensitizer to coat their surfaces with BP. DMAEMA was photografted onto the BP-coated PE films at 60°C by the application of 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 pH 8 with concentrated HCl to increase the solubility of DMAEMA homopolymers during the photografting and to obtain PE-g-PDMAEMA films with higher grafted amounts.

Adsorption and desorption in response to the pH change

The ion-exchange capacity of the PE-g-PDMAEMA films was determined. First, weight-known PE-g-PDMAEMA films of different grafted amounts cut into 10 \times 10 mm^2 pieces in the dry state were immersed in an aqueous 1.0M NaOH solution for 36 h to entirely deprotonate the dimethylamino groups appended to the grafted poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) chains. The PE-g-PDMAEMA films taken from the aqueous NaOH solutions were washed with water to remove the solutions attached on their surfaces and subsequently immersed in an aqueous 0.10M HCl solution (100 cm^3) with moderate stirring at 25°C. The aliquots drawn from the aqueous HCl solutions 36 h after the immersion were titrated with an aqueous 0.0101M NaOH solution with thymol blue as an acid–base indicator. The ion-exchange capacity of the PE-g-PDMAEMA films was calculated from the volume of the titrant and the grafted amount.

The PE-g-PDMAEMA films cut into 10 \times 10 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.¹⁵ Three different types of anion dyes with one to three sulfonic groups were chosen as model compounds [one group, metanil yellow (MY); two groups, sunset yellow (SY); and three groups, amaranth (AM)], as shown in Figure 1. The amounts of dye anions adsorbed on the PE-g-PDMAEMA films were determined by the measurement of the absorbances of the outer solutions at 466, 243, and 475 nm for MY, SY, and AM anions, respectively.

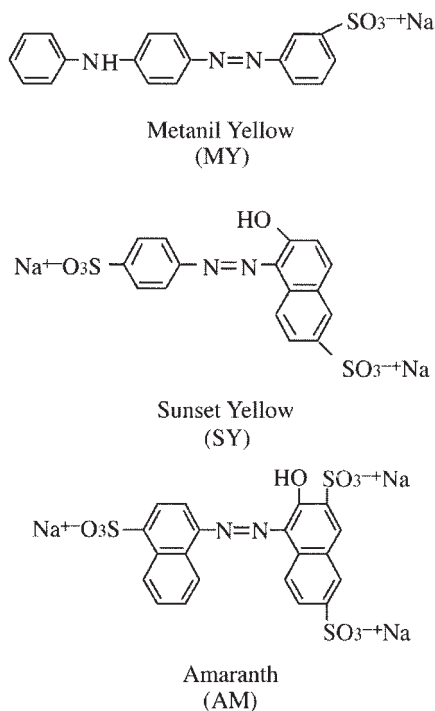


Figure 1 Chemical structures of the dye anions used in this study.

After the dye-anion-adsorbed PE-g-PDMAEMA films were washed with water to remove the solutions attached on their surfaces, they were immersed in the aqueous HCl or NaOH solutions (50 cm³) at the initial pH values of 2.0–12.0 with moderate stirring at 25°C. The amounts of dye anions desorbed from the PE-g-PDMAEMA films were spectrophotometrically measured in the way described previously.

Adsorption and desorption in response to the temperature

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

RESULTS AND DISCUSSION

Langmuir adsorption isotherm

It is reported in our previous article²⁴ that dimethylamino groups appended to the PDMAEMA chains

work as a positively chargeable weak base in response to the pH change from the colloid titration measurement with potassium poly(vinyl alcohol)sulfate (KPVs). Figure 2 shows the ion-exchange properties of the PE-g-PDMAEMA films as a function of the grafted amount. It is of great importance to estimate the ion-exchange properties of the PE-g-PDMAEMA films for applying them to functional membranes for the separation of ionic compounds. The ion-exchange capacity of the PE-g-PDMAEMA films linearly increased with the grafted amounts. The PE-g-PDMAEMA films with grafted amounts higher than 5 mmol/g of PE had higher ion-exchange capacity than the commercially available ion-exchange membranes. The degree of ion exchange of the PE-g-PDMAEMA films went up to over 97% and stayed almost constant, regardless of the grafted amount. These results indicate that almost all of the dimethylamino groups appended to the grafted PDMAEMA chains work as a positively charged adsorption site.

The PE-g-PDMAEMA films with the grafted amount of 10.5 mmol/g of PE were swollen to the

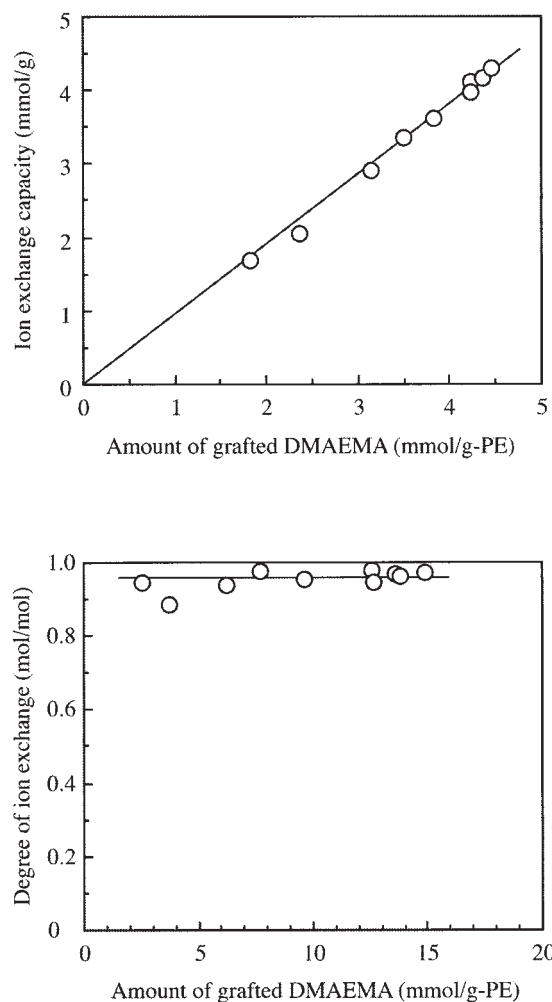


Figure 2 Dependence of the ion-exchange properties on the grafted amount for the PE-g-PDMAEMA films at 25°C.

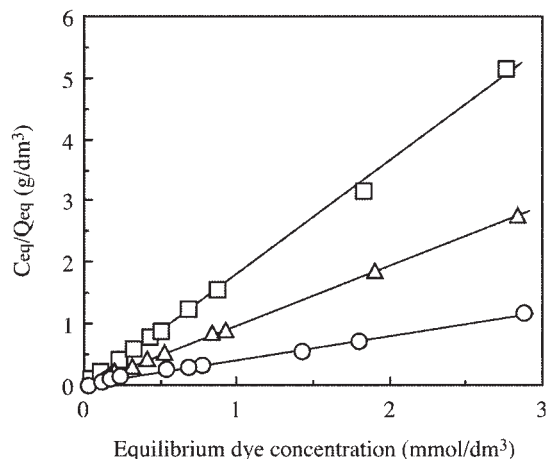


Figure 3 Linear relationship between the equilibrium concentration of (○) MY, (△) SY, and (□) AM anions and the C_{eq}/Q_{eq} value in the Langmuir adsorption isotherm equation at 25°C for a PE-g-PDMAEMA film of 10.5 mmol/g of PE.

equilibrium state in distilled water and then immersed in aqueous solutions of MY, SY, or AM without adjustment of the pH values in the dye concentration range of 0.05–3.0 mM at 25°C. The adsorption of three kinds of dye anions on the PE-g-PDMAEMA films was analyzed according to the Langmuir adsorption isotherm equation:

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{Qb} + \frac{C_{eq}}{Q} \quad (1)$$

where C_{eq} is the free dye concentration in the outer solution at equilibrium (mol/dm³), Q_{eq} is the amount of adsorbed dye anions per gram of PE-g-PDMAEMA film (mol/g), Q is the maximum amount of adsorbed dye anions (mol/g), and b is the Langmuir constant (dm³/mol).^{18,20,28} The equilibrium dye concentration and the amount of adsorbed dye anions bore a linear relationship in the Langmuir adsorption isotherm equation for the three kinds of dyes, as shown in Figure 3. Q , determined from the slopes and intercepts of the straight lines shown in Figure 3, decreased with an increase in the number of sulfonic groups in the dye molecules (2.53 mmol/g for MY, 1.05 mmol/g for SY, and 0.55 mmol/g for AM). The difference in the Q values can be explained as follows: Some of the SY and AM anions adsorbed onto the protonated dimethylamino groups appended to the grafted PDMAEMA chains through ionic bond will have free sulfonic groups. The electrostatic repulsion can take place between the adsorbed SY or AM anions and free SY or AM anions present in the medium, and consequently, the diffusion of IC and AM anions into the grafted layers will be depressed. However, the linear relationship obtained indicates a sulfonic group in the dye

molecules bonds to a protonated dimethylamino group appended to the grafted PDMAEMA chains in 1:1 stoichiometry.

pH dependence of adsorption

The pH dependence of adsorption of three kinds of dye anions on a PE-g-PDMAEMA film of 10.5 mmol/g of PE was investigated in aqueous dye solutions of 0.5 mM in the pH range of 2.0–12.0. The PE-g-PDMAEMA films were swollen to equilibrium in an aqueous solution of HCl or NaOH whose pH values were equal to those of the aqueous dye solutions. Figure 4 shows the variations in the amount of adsorbed dye anions with the equilibrium pH value. The adsorbed amounts of the three kinds of dye anions used here increased with a decrease in the equilibrium pH value. However, the amounts of adsorbed dye anions decreased, although the degree of protonation of dimethylamino groups stayed constant below pH 3. This pH dependence of dye anion adsorption can be

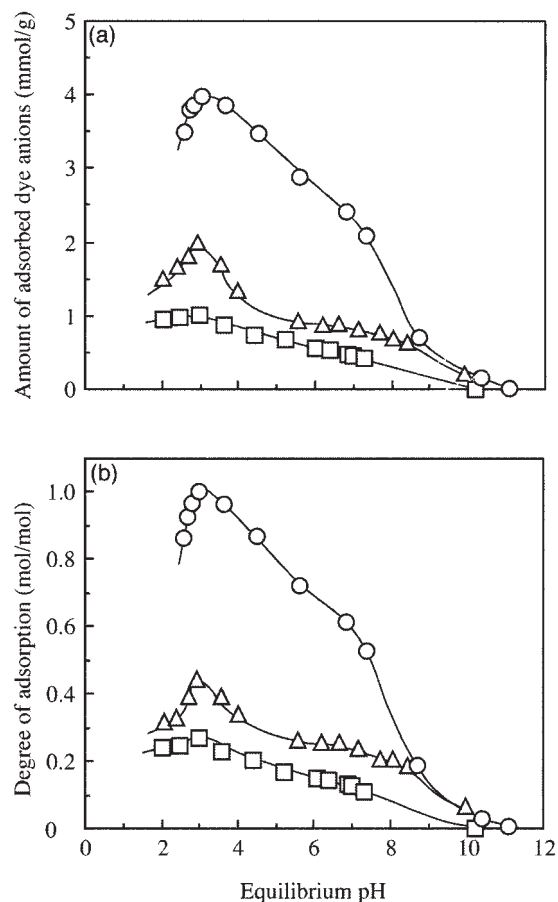


Figure 4 Variations in (a) the amount of adsorbed (○) MY, (△) SY, and (□) AM anions and (b) the degree of adsorption with the equilibrium pH value with an initial dye concentration of 0.5 mM at 25°C for a PE-g-PDMAEMA film of 10.5 mmol/g of PE.

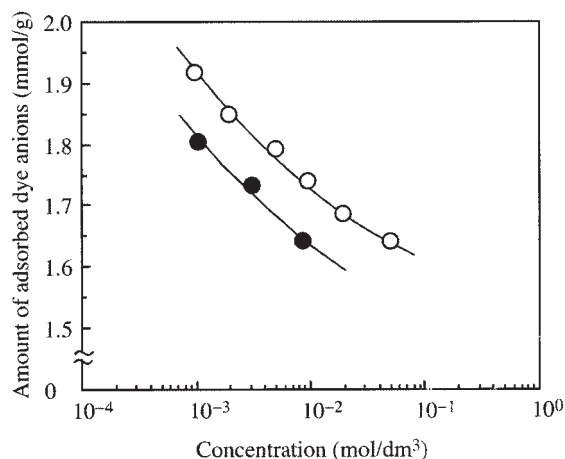


Figure 5 Changes in the amount of adsorbed SY anions with the concentration of (●) HCl and (○) NaCl with an initial dye concentration of 0.5 mM at pH 3.0 and 25°C for a PE-g-PDMAEMA film of 10.5 mmol/g of PE.

explained in terms of the fact that the degree of protonation of dimethylamino groups appended to the PDMAEMA chains determined by colloid titration in ref. 24 increases with a decrease in the pH value. The adsorptivity of a PE-g-PDMAEMA film of 10.5 mmol/g of PE to MY anions was examined in aqueous HCl solutions of pH 3.0 with different NaCl concentrations ranging from 0.01 to 0.1 mol/dm³ to discuss the decrease in the amount of adsorbed SY anions below pH 3. The amount of adsorbed SY anions at pH 3.0 decreased with an increase in the NaCl concentration of the solvent, as shown in Figure 5. The decrease in dye anion adsorption below pH 3 is probably due to the screening effect caused by the addition of HCl for adjusting the initial pH values of the dye solutions. In addition, the difference in the adsorbed amounts for the three kinds of dye anions was discussed in more detail from the changes in the degree of the adsorption as a function of the equilibrium pH value. The degree of adsorption went up to about 100% at pH 3 for MY anions, as shown in Figure 4(b). 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.

Here, the pH dependence of 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 KPVS in our previous article,²³ and the ratio of the protonated dimethylamino groups ionically bonding to dye anions to the protonated dimethylamino groups appended to the grafted PDMAEMA chains (Deg_{pro}^{dye}) was calculated as follows:

$$Deg_{pro}^{dye} = \frac{Q_{eq}}{\frac{W_g - W_0}{M_{DMA}} \times \alpha} \quad (2)$$

where W_g is the weight of the PE-g-PDMAEMA film, W_0 is the weight of an ungrafted PE film, M_{DMA} is the molar mass of the DMAEMA monomer (mol/g), and α is the degree of protonation of dimethylamino groups appended to the PDMAEMA chains.

Figure 6 shows the change in Deg_{pro}^{dye} with the equilibrium pH value. The Deg_{pro}^{dye} value of MY anions stood at about 1.0 and was kept almost constant, regardless of the equilibrium pH value. This result supports the fact that adsorption stoichiometrically takes place between an MY anion and a protonated dimethylamino group through the ionic bond. On the other hand, the Deg_{pro}^{dye} value for SY and AM anions decreased with an increase in the equilibrium pH value. An increase in the pH value led to a decrease in the density of protonated dimethylamino groups appended to the grafted PDMAEMA chains because the degree of protonation of dimethylamino groups increased with a decrease in the pH value. The decrease in the adsorption of SY and AM anions against the equilibrium pH value, as shown in Figure 6, was mainly attributable to the electrostatic repulsion between free sulfonic groups of the SY or AM anions adsorbed onto the protonated dimethylamino groups appended to the grafted PDMAEMA chains and free SY or AM anions in the medium.

The adsorption of dye anions on protonated dimethylamino groups was assumed to proceed in a first-order-like reaction, and the kinetic constant of adsorption (k) was calculated as follows:

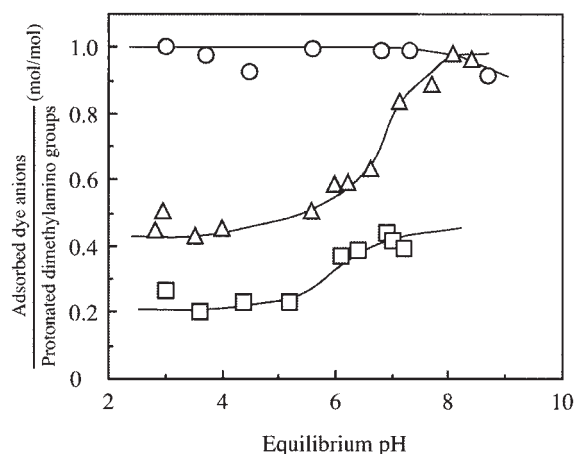


Figure 6 Changes in the ratio of the protonated dimethylamino groups bonding to (○) MY, (△) SY, and (□) AM anions to the protonated dimethylamino groups appended to the grafted PDMAEMA chains with the equilibrium pH value in aqueous dye solutions with an initial concentration of 0.5 mM at 25°C for a PE-g-PDMAEMA film of 10.5 mmol/g of PE.

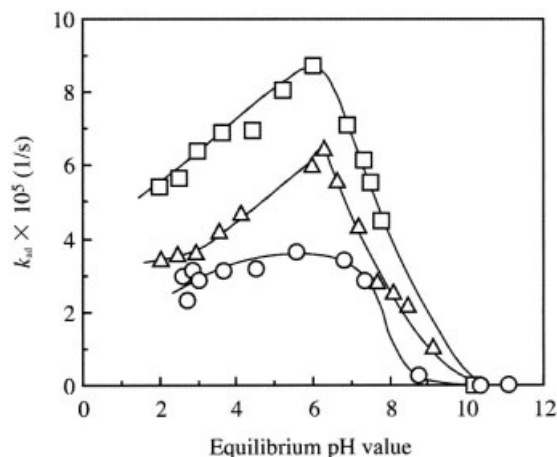


Figure 7 Variations in the kinetic constant of adsorption (k_{ad}) of (○) MY, (△) SY, and (□) AM anions with the equilibrium pH value in aqueous dye solutions with an initial concentration of 0.5 mM at 25°C for a PE-g-PDMAEMA film of 10.5 mmol/g of PE.

$$\ln\left(1 - \frac{Q_t}{Q_{eq}}\right) = -kt \quad (3)$$

where Q_t is the amount of adsorbed dye anions at immersion time t .²⁰ Because a plot of $\ln(1 - Q_t/Q_{eq})$ against the immersion time gave a straight line, the kinetic constants of adsorption were calculated from their slopes. Figure 7 shows the variations in the kinetic constant of adsorption with the equilibrium pH value for the three types of dye anions used here. The kinetic constants of adsorption passed through the maximum values around pH 6, regardless of the type of dye anion used.

In our previous article,¹⁸ the viscometric measurements of PDMAEMA in water as a function of the pH value showed that the reduced viscosity of an aqueous PDMAEMA solution had the maximum value at pH 6. The expansion of grafted PDMAEMA chains caused by the electrostatic repulsion between protonated dimethylamino groups would facilitate the adsorption of dye anions on the protonated dimethylamino groups appended to the grafted PDMAEMA chains. The kinetic constant of adsorption for AM anion was higher than those for MY and SY anions because the adsorption of AM anions with three sulfonic groups was restricted to the surface region of the grafted layers, probably on account of the electrostatic repulsion between sulfonic groups of free AM anions in the medium and sulfonic groups of the AM anions adsorbed onto the protonated dimethylamino groups and their relatively larger molecular size, and the adsorption equilibrium was reached at shorter times in comparison with MY and SY anions.

Grafted amount dependence of adsorption

The adsorption of the dye anions was investigated on PE-g-PDMAEMA films with grafted amounts of 3–15 mmol/g of PE at the initial pH value of 3.0, at which the adsorbed amounts had the maximum values, as shown in Figure 4. Figure 8(a,b) shows the changes in the amount of adsorbed dye anions and the degree of adsorption with the grafted amount, respectively. Although the amounts of adsorbed dye anions increased with an increase in the grafted amount, the degree of adsorption stayed almost constant, regardless of the type of dye anion used here. In addition, the increase in the number of sulfonic groups in the dye molecules resulted in the decrease in the degree of adsorption (97% for MY, 85% for SY, and 30% for AM), as shown in Figure 8(b). It is understandable from the value of the degree of adsorption for MY anions that most of the protonated dimethylamino groups located inside the PE-g-PDMAEMA films also work as the adsorption site for MY anions. The degree of adsorption of 85% for SY anions was higher than the calculated value of 50% obtained for the stoichiometric adsorp-

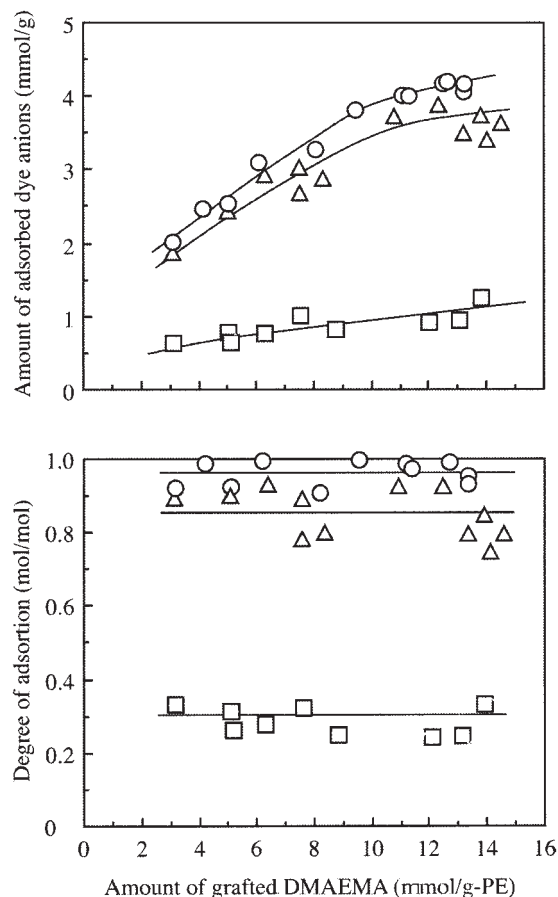


Figure 8 Changes in the amount of adsorbed (○) MY, (△) SY, and (□) AM anions and the degree of adsorption with the grafted amount in aqueous dye solutions with an initial concentration of 0.5 mM at pH 3.0 and 25°C.

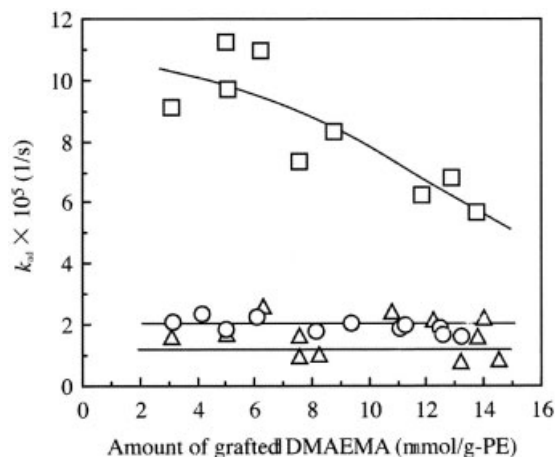


Figure 9 Changes in the kinetic constant of adsorption (k_{ad}) of (○) MY, (△) SY, and (□) AM anions with the grafted amount in aqueous dye solutions with an initial concentration of 0.5 mM at pH 3.0 and 25°C.

tion of an SY anion with two sulfonic groups on two protonated dimethylamino groups through the ionic bond. It can be considered that most of the adsorbed SY anions have free sulfonic groups. On the other hand, the degree of adsorption for an AM anion with three sulfonic groups was quite low because of repulsive interaction between the adsorbed AM anions and free AM anions in the medium as well as the relatively large molecular size. Therefore, the adsorption of AM anions is considered to be restricted to the surface region of the grafted layers of the PE-g-PDMAEMA films. Figure 9 shows the changes in the kinetic constant of adsorption obtained from the slopes of the straight lines of $\ln(1 - Q_t/Q_{eq})$ against the immersion time with the grafted amount for the dye anions used here. The kinetic constant of adsorption for AM anions decreased with an increase in the grafted amount. This result can be explained in terms of the fact that the time required to reach the equilibrium adsorption for AM anions stayed almost unchanged against the grafted amount, although the amount of adsorbed AM anions gradually increased with an increase in the grafted amount, as shown in Figure 8. On the other hand, the kinetic constants of adsorption for SY and MY anions were much lower than that of AM anions and ranged from 1.0 to 2.5×10^{-5} (1/s) independently of the grafted amount. This result supports our consideration that the adsorption of AM anions is restricted in the vicinity of the outer surface region of the grafted layers formed on the PE films.

Temperature dependence of adsorption

The temperature dependence of the amount of adsorbed dye anions and the kinetic constant of adsorption was investigated from 20 to 50°C at pH 3.0, at

which the adsorbed amounts of the three kinds of dye anions had the maximum values. Figure 10 shows the changes in the amount of adsorbed SY anions with the immersion time at different temperatures. As the temperature increased, the adsorbed amount more sharply increased against the immersion time, and the time required to reach the equilibrium adsorption was shortened. The adsorption of MY and AM anions showed a similar tendency against the temperature. In addition, a plot of $\ln(1 - Q_t/Q_{eq})$ against the immersion time t gave a straight line at each temperature, and the kinetic constants of adsorption calculated from their slopes for each dye anion are summarized in Table I.

The slight decrease in the amount of adsorbed dye anions caused by the increase in the temperature was due to the contraction of grafted PDMAEMA chains. It is reported in our previous article²⁵ that a PDMAEMA polymer is a thermosensitive polymer and has a lower critical solution temperature (LCST) of 27°C in a NaHCO₃/NaOH buffer of pH 10. PDMAEMA is insoluble in the temperature range higher than 27°C in a NaHCO₃/NaOH buffer. As the pH value decreased, the LCST gradually increased because of the increase in the protonation of dimethylamino groups appended to the PDMAEMA chains. At pH 9, at which the degree of protonation reached 10%, the contraction of PDMAEMA caused by the increase in the temperature became continuous instead of discontinuous. It can be concluded from these experimental results that although PDMAEMA is soluble at pH 3, it would be gradually contracted with an increase in the temperature from 20 to 50°C. The increase in the temperature led to the decrease in the adsorbed amount and the increase in the kinetic constant of adsorption. In addition, the kinetic constant of adsorption obtained at

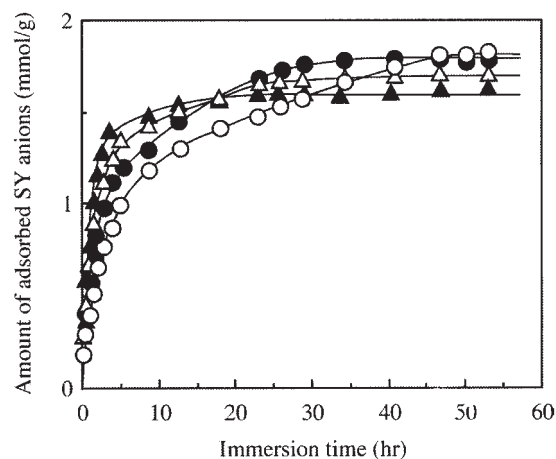


Figure 10 Changes in the amount of adsorbed SY anions with the immersion time in aqueous SY solutions of (○) 20, (●) 30, (△) 40, and (▲) 50°C at pH 3.0 for a PE-g-PDMAEMA film of 10.5 mmol/g of PE.

TABLE I
Adsorption Properties of a 10.5 mmol/g of PE PE-g-PDMAEMA Film to MY, SY,
and AM Anions at Different Temperatures

Temperature (°C)	MY		SY		AM	
	Q_{eq} (mmol/g)	$k_{\text{ad}} \times 10^5$ (1/s)	Q_{eq} (mmol/g)	$k_{\text{ad}} \times 10^5$ (1/s)	Q_{eq} (mmol/g)	$k_{\text{ad}} \times 10^5$ (1/s)
20	3.82	2.56	1.81	4.20	1.26	5.64
30	3.52	4.70	1.78	5.95	1.22	9.14
40	3.48	7.33	1.71	8.60	1.20	12.20
50	3.36	10.77	1.63	11.22	1.18	14.97

k_{ad} , kinetic constant of adsorption.

each temperature was plotted in agreement with the Arrhenius equation as the natural logarithm of the kinetic constant of adsorption versus the reciprocal of the temperature, and the activation energies for adsorption of MY, SY, and AM anions calculated from the slope of the best straight lines were 37.5, 25.6, and 21.70 kJ/mol, respectively. As the number of sulfonic groups in a dye molecule decreased, the temperature dependence of adsorption increased.

Desorption in response to the pH value and repetitive cycles of adsorption and desorption

After the adsorption of dye anions on PE-g-PDMAEMA films of 10.5 mmol/g of PE was equilibrated, the PE-g-PDMAEMA films that adsorbed dye anions were immersed in aqueous solutions of HCl or NaOH ranging from pH 2 to 13. Figure 11 shows the changes in the degree of desorption determined from the adsorbed amount and the desorbed amount for each dye anion with the equilibrium pH value. The degree of

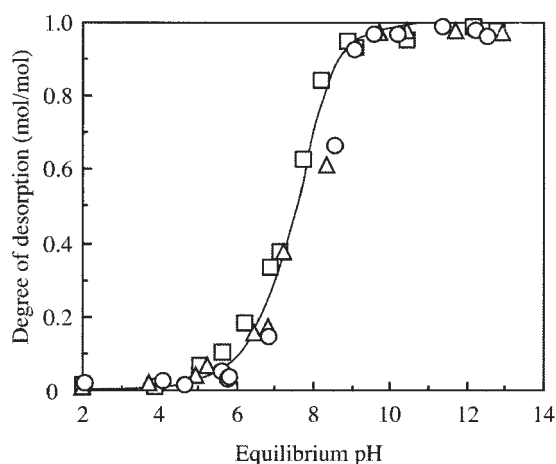


Figure 11 Changes in the degree of desorption of (○) MY, (△) SY, and (□) AM anions with the equilibrium pH value for a PE-g-PDMAEMA film of 10.5 mmol/g of PE. The adsorption of dye anions was carried out on a PE-g-PDMAEMA film of 10.5 mmol/g of PE at pH 3.0 before the desorption experiments.

desorption increased with an increase in the equilibrium pH value, and the quantities of dye anions adsorbed (ca. 100%) were desorbed at the equilibrium pH values above 9, regardless of the dye anions used here. This indicates that liberation of dye anions from the grafted PDMAEMA films is caused by deprotonation of protonated dimethylamino groups.²⁵

On the basis of the results for the pH dependence of adsorption and desorption of dye anions presented in Figures 4 and 11, the reusability of a PE-g-PDMAEMA film of 10.5 mmol/g of PE was examined by the alternating repetition of the cyclic process of adsorption at the initial pH value of 3.0 and desorption at the initial pH value of 11.0. Figure 12 shows three successive MY anion adsorption–desorption cyclic processes in response to the pH change in the medium. When the PE-g-PDMAEMA film was put into an aqueous MY solution at pH 3.0 after the first desorption process, MY anions adsorbed on the PE-g-PDMAEMA film to the same adsorbed amount as that of the first adsorption process. The physicochemical properties obtained for the repeated cyclic process of adsorption and de-

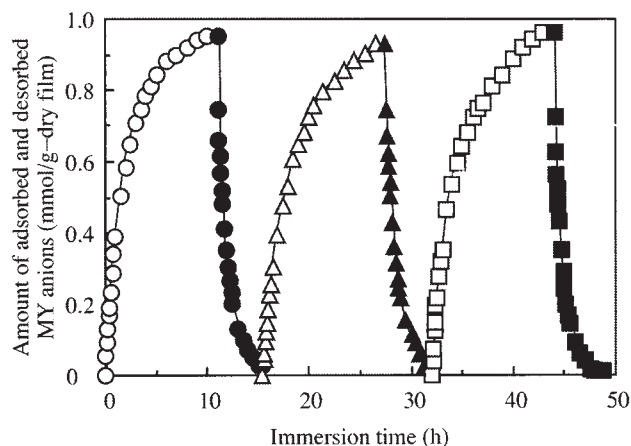


Figure 12 Alternately repeated cyclic process of adsorption at the initial pH value of 3.0 (open symbols) and desorption at the initial pH value of 11.0 (shaded symbols) for a PE-g-PDMAEMA film of 10.5 mmol/g of PE at 25°C: (○,●) first run, (△,▲) second run, and (□,■) third run.

TABLE II

Physicochemical Properties of the Alternately Repeated Cyclic Process of Adsorption at the Initial pH Value of 3.0 and Desorption at the Initial pH Value of 11.0 of MY Anions for a 10.5 mmol/g of PE PE-g-PDMAEMA Film

	First run	Second run	Third run
Adsorbed amount (mmol/g)	0.951	0.937	0.962
Degree of desorption (mol/mol)	0.973	0.952	0.983
Kinetic constant of adsorption $\times 10^5$ (1/s)	13.81	11.78	12.34
Kinetic constant of desorption $\times 10^5$ (1/s)	84.34	76.48	85.72

sorption of MY anions are summarized in Table II. The amounts of adsorbed and desorbed MY anions were almost equivalent, and the kinetic constants of adsorption and desorption stayed unchanged in each adsorption and desorption process. The cyclic adsorption and desorption process was also carried out for SY and AM anions in the same manner, and the obtained physicochemical properties are summarized in Tables III and IV, respectively. The amounts of adsorbed and desorbed anions were almost equivalent, and the quantities of SY and AM anions adsorbed (95–98%) were desorbed in each adsorption and desorption process. These results indicate that the PE-g-PDMAEMA film is practically acid- and alkali-proof and can endure several cycles of the adsorption and desorption process in response to the pH change without considerable fatigue.

Desorption in response to the temperature and repetitive cycles of adsorption and desorption

The PE-g-PDMAEMA film of 10.5 mmol/g of PE that adsorbed dye anions at pH 3 was alternately immersed in water at 20 and 40, 60, or 80°C. As shown in Figure 13, MY anions were desorbed from the PE-g-PDMAEMA film in water at 80°C and not at 20°C. After the desorption process at 80°C for MY anions attained equilibrium, the PE-g-PDMAEMA films were

TABLE III

Physicochemical Properties of the Alternately Repeated Cyclic Process of Adsorption at the Initial pH Value of 3.0 and Desorption at the Initial pH Value of 11.0 of SY Anions for a 10.5 mmol/g of PE PE-g-PDMAEMA Film

	First run	Second run	Third run
Adsorbed amount (mmol/g)	0.841	0.833	0.848
Degree of desorption (mol/mol)	0.966	0.985	0.984
Kinetic constant of adsorption $\times 10^5$ (1/s)	10.20	11.96	13.12
Kinetic constant of desorption $\times 10^5$ (1/s)	59.16	56.67	69.06

TABLE IV

Physicochemical Properties of the Alternately Repeated Cyclic Process of Adsorption at the initial pH Value of 3.0 and Desorption at the Initial pH Value of 11.0 of AM Anions for a 10.5 mmol/g of PE PE-g-PDMAEMA Film

	First run	Second run	Third run
Adsorbed amount (mmol/g)	0.675	0.689	0.674
Degree of desorption (mol/mol)	0.953	0.945	0.939
Kinetic constant of adsorption $\times 10^5$ (1/s)	15.90	17.62	16.21
Kinetic constant of desorption $\times 10^5$ (1/s)	119.5	125.2	123.6

cooled in water of 20°C followed by immersion in water at 80°C. When the cyclic process of immersion in water at 20 and 80°C was repeated, MY anions were desorbed only at 80°C. In addition, the thermosensitive desorption experiments were carried out by the adjustment of the temperature of water to 40 or 60°C. The results of the thermosensitive desorption of MY anions for the PE-g-PDMAEMA film at 40, 60, and 80°C are summarized in Table V. Although the amount of desorbed MY anions decreased with an increase in the run number of the desorption process, the total desorbed amount increased with an increase in the temperature of water from 40 to 80°C. In addition, SY and AM anions were also desorbed from the PE-g-PDMAEMA films upon immersion in water at 40–80°C. The total desorbed amounts for SY and AM anions decreased with an increase in the number of the sulfonic groups in the dye molecules. The desorption of dye anions from the PE-g-PDMAEMA film in water at 40, 60, and 80°C is considered to be acceler-

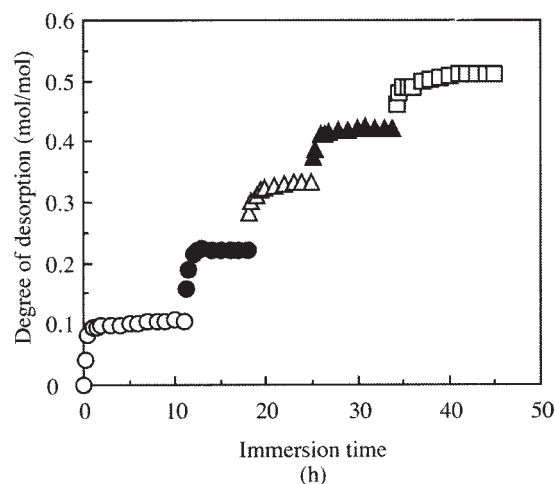


Figure 13 Desorption of MY anions from a PE-g-PDMAEMA film of 10.5 mmol/g of PE at 80°C by fluctuations in the water temperature between 20 and 80°C: (○) first run, (●) second run, (△) third run, (▲) fourth run, and (□) fifth run.

TABLE V
Desorption of MY, SY, and AM Anions from a 10.5 mmol/g of PE-g-PDMAEMA Film at Higher Temperatures with the Water Temperature Alternately Fluctuating Between 20 and 40, 60, or 80°C

Dye anion	Temperature (°C)	First run (%)	Second run (%)	Third run (%)	Fourth run (%)	Fifth run (%)	Total (%)
MY	40	1.8	2.4	2.1	2.2	1.8	10.3
	60	5.2	6.5	7.0	5.7	3.7	28.1
	80	10.5	11.7	10.9	9.0	9.2	51.3
SY	80	13.9	10.8	7.5	6.2	5.9	44.3
AM	80	15.0	9.0	5.9	4.0	3.1	37.0

ated by the squeezing effect caused by the contraction of grafted PDMAEMA chains as well as the deprotonation of protonated dimethylamino groups appended to the grafted PDMAEMA chains. The total degree of desorption for MY anions was limited to about 50% even at 80°C, although it went up to 89% with an increase in the volume of water at 80°C, as shown in Table VI.

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 (< ca. 5%), as mentioned previously.¹⁶ Many workers have reported on the adsorption properties of polymer materials, which were prepared mainly by the copolymerization of both weakly acidic and weakly basic monomers with a crosslinking agent, in response to temperature changes.^{29–31} However, little has been reported on a thermally generative ion-exchange membrane prepared from a single weakly cationic monomer, as described in this study. The photografting technique used in this study can facilitate the preparation of membranes with thermally regenerative ion-exchange properties. In addition, this membrane system is a practical alternative to the bead system conventionally used for adsorption in facile handling.

CONCLUSIONS

We have investigated the adsorption and desorption properties of PE-g-PDMAEMA films in response to pH and temperature changes and their repetitive cycles of adsorption and desorption. From the experi-

mental results mentioned previously, we can conclude the following.

The amounts of dye anions adsorbed onto the PE-g-PDMAEMA films pass through the maximum values at about pH 3 and decrease with an increase in the number of sulfonic groups in the dye molecules at the same pH values because of the electrostatic repulsion between free sulfonic groups of the dye anions adsorbed onto the PE-g-PDMAEMA films and dye anions. A large number of dye anions adsorbed are desorbed from the PE-g-PDMAEMA film with initial pH values above 11.0, and the cyclic processes of adsorption at pH 3.0 and desorption at pH 11.0 are repeated without considerable fatigue.

In addition, when the dye-anion-adsorbed PE-g-PDMAEMA films were alternately immersed in water of two different temperatures (20 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 and thermosensitive contraction of grafted PDMAEMA chains. These results indicate that the PE-g-PDMAEMA films can be applied as regenerative ion-exchange membranes for the adsorption and desorption process of anionic compounds in response to pH and temperature changes.

Since we have shown the regenerative ion-exchange-membrane properties in response to pH and temperature changes for PE-g-PDMAEMA films in this article, we have tried to improve thermally regenerative ion-exchange-membrane properties using an ePTFE film photografted with DMAEMA. The ePTFE film is an appropriate substrate for thermally regenerative ion-exchange membranes because of its high vacancy and chemical stability. Therefore, we will

TABLE VI
Desorption of MY Anions from a 10.5 mmol/g of PE-g-PDMAEMA Film in Water at 80°C with the Water Temperature Alternately Fluctuating Between 20 and 80°C

Volume (cm ³)	First run (%)	Second run (%)	Third run (%)	Fourth run (%)	Fifth run (%)	Total (%)
50	10.5	11.7	10.9	9.0	9.2	51.3
100	25.4	20.7	14.1	11.0		71.2
200	29.3	24.8	19.5	14.7		88.3
300	38.5	30.7	19.6			88.8

publish the regenerative ion-exchange-membrane properties in response to temperature changes for DMAEMA-grafted ePTFE films in the near future.

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