

Synthesis and Properties of Two Kinds of Amphiphilic Graft Copolymers with Well-Defined Structure

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SYNOPSIS

Polyacrylamide with well-defined polystyrene grafts (PAM-*g*-PS) and poly(methacrylic acid) with well-defined poly(methyl methacrylate) grafts (PMAA-*g*-PMMA) were synthesized via macromer techniques. Polymerization conditions and reactivity ratios for the copolymerizations were studied. The graft copolymers were purified by extractions and characterized with IR spectra. Structural parameters of PMAA-*g*-PMMA were determined by measurement of number average molecular weight of both macromers and copolymers. Both kinds of the graft copolymers are amphiphilic, exhibiting good emulsifying properties. When PAM-*g*-PS was mixed with PMAA-*g*-PMMA in a molar ratio of PAM/PMAA = 1, an intermolecular complex membrane was formed. This behaves as a chemical valve; its permeability can be controlled reversibly by changing the pH value. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymers with well-defined polystyrene (PS) grafts were first synthesized by Milkovich and coworkers¹ using the macromer technique in 1974. Oto et al.² synthesized PMMA macromer through radical polymerization of MMA with azobisisobutyronitrile (AIBN) as initiator and thioglycolic acid as chain transfer agent, followed by reaction of the carboxyl-terminated prepolymer with glycidyl methacrylate. Bonordi et al.³ prepared the polydodecylacrylate macromer by radical polymerization using mercaptoethanol as chain transfer agent, followed by reaction of the hydroxyl-terminated prepolymer with methacryloyl chloride (MAC). Yamashita et al.⁴ studied the copolymerization of PS macromer with 2-hydroxyethyl methacrylate and that of PMMA macromer with MAA,⁵ indicating that the graft copolymers are amphiphilic and can be used in surface modification of polymer film. Albrecht and Wunderlich⁶ synthesized amphiphilic graft copoly-

mers through copolymerization of the PMMA macromer with MAA. We have used PMMA macromer in synthesizing graft copolymer of acrylic acid, which was used as compatibilizer for the blending of epichlorohydrin rubber with poly(vinyl chloride) or PMMA.⁷ Recently we have reported the copolymerization of MAA with PS macromer and the properties of the graft copolymer as emulsifier, compatibilizer, and chemical valve, when complexed with polyoxyethylene grafted with PS.⁸ The chemical valves were prepared earlier by Osada⁹ and Nishi,¹⁰ who made some membranes based on chemically crosslinked semi-interpenetrating polymer network (IPN) and full IPN of poly(acrylic acid) and polyoxyethylene and called them chemical valves, because their permeability can be controlled reversibly by adjusting the chemical environment.

This paper deals with the synthesis of polyacrylamide (PAM) with PS grafts and poly(methacrylic acid) with PMMA grafts via the macromer technique, in order to obtain amphiphilic copolymers, since PAM or PMAA is hydrophilic and PS or PMMA is hydrophobic. The emulsifying properties and the behavior of an intermolecular complex membrane made from these two graft copolymers were studied.

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EXPERIMENTAL

Materials

All the solvents used were chemically pure and dried with 4A molecular sieve overnight. MMA was purified by washing with 20% NaOH and water successively, followed by distillation over CuCl under reduced pressure. Styrene was purified by first washing with 10% NaOH solution and water successively and then distilling under reduced nitrogen pressure over CaH₂. MAA was dried over 4A molecular sieve and distilled over CuCl under reduced pressure. Acrylamide was chemically pure and used as received. Ethylene oxide was purified by successive distillation over KOH and CaH₂. MAC was synthesized by reaction of MAA with SO₂Cl at 65°C and purified by distillation over CuCl under reduced pressure. *n*-Butyl lithium was synthesized by reaction of *n*-butyl chloride with lithium chips in cyclohexane at 50°C under nitrogen. Its concentration was determined by double titrations.

Synthesis of the Macromers

PS macromers were prepared by the anionic polymerization of styrene initiated with *n*-butyl lithium and tetrahydrofuran (THF), followed by capping with ethylene oxide and terminated with MAC as follows: An oven-dried serum-capped bottle was charged with dried and purified toluene. After purging with nitrogen, styrene and a small amount of THF (THF/*n*-BuLi = 2.5/1 molar ratio) were added via syringes. The impurities were titrated out by dropping *n*-BuLi slowly via a syringe, until a light orange color persisted for 5 min. Then a calculated amount of *n*-BuLi, depending on the molecular weight of PS macromer needed, was added to the bottle under nitrogen. Polymerization was carried out in a 50°C thermostat bath for 2 h. The living polystyrene thus obtained was capped with ethylene oxide at room temperature. Ethylene oxide was bubbled in until the red color of living polystyrene anions disappeared. The reaction was continued at 50°C for half an hour. Then MAC at a molar ratio of MAC/*n*-BuLi = 1.5/1 was introduced via syringe and reacted with the living anions at 45°C for 2 h. The product was precipitated with ethanol and vacuum-dried.

PMMA macromers were obtained by radical polymerization of MMA in the presence of mercaptoethanol as chain transfer agent, followed by reaction of the hydroxyl-terminated prepolymer with MAC as follows: Radical polymerization of MMA

was carried out in benzene under nitrogen atmosphere using AIBN as initiator and a different amount of mercaptoethanol as chain transfer agent at 65°C for 9 h to obtain prepolymers with different molecular weights, which were then purified by precipitation in benzene with 95/5 petroleum ether-ethanol. Hydroxyl end groups of the prepolymer were determined by isocyanate method.¹¹ The purified prepolymer was then reacted with MAC at a molar ratio of MAC/OH = 2 in xylene in the presence of triethylamine at 70°C for 8 h. The macromer thus obtained was purified by precipitation in xylene with 95/5 petroleum ether-ethanol. Efficiency of the reaction between the prepolymer and MAC was determined to be nearly 100% by titration of the remaining OH group in the macromer. IR spectrum of the macromer showed the presence of double bonds at 840, 960–980 and 1630 cm⁻¹.

Copolymerizations of the PMMA Macromer with MAA and of the PS Macromer with AM

Copolymerization of the PMMA macromer with MAA was carried out by heating MAA, DMF solution of PMMA macromer and AIBN at 75°C under nitrogen atmosphere. The copolymerization was terminated with 1% aqueous solution of *p*-hydroxyphenol. The crude product was dried to constant weight and then purified by successive extractions with toluene and methanol at room temperature three times each to remove untreated macromer and PMAA, respectively.

Conversion of MAA and of the macromer (or grafting efficiency) can be calculated as follows:

% Conv. of macromer

$$= (\text{macromer charged} - \text{macromer unreacted}) \times 100 / \text{macromer charged}$$

% Conv. of MAA

$$= (\text{crude product} - \text{macromer charged}) / \text{MAA charged} \times 100$$

The efficiency of purification was ascertained by extractions of a mixture of PMMA macromer and PMAA in the same way.

Copolymerization of the PS macromer with AM was carried out at 60°C in THF using AIBN as initiator under nitrogen atmosphere. The copolymerization was terminated with a small amount of THF solution of *p*-hydroxyphenol. The crude product was dried to constant weight and purified by successive

extractions with cyclohexane at 35°C and with methanol at room temperature three times each, in order to remove the unreacted PS macromers and AM homopolymer. Conversion of the macromer (or grafting efficiency) and of AM can be calculated according to the similar equations stated above.

Determination of Reactivity Ratios and Structural Parameters

The reactivity ratios of the macromer (r_1) and the monomer (r_2) were determined at different stages of copolymerization. The reactivity ratio (r_2) can be calculated according to Kennedy's equation:¹²

$$r_2 = \frac{\ln(1 - P_2)}{\ln(1 - P_1)}$$

where P_2 and P_1 are the conversion of the monomer and macromer at the same stage of copolymerization.

Average number of PMMA grafts per macromolecule (N_g) can be calculated from the following equation:

$$N_g = \frac{M_{nc} \times W_g}{M_{ng}}$$

where M_{nc} and M_{ng} are the average molecular weights of the graft copolymer (PMAA-*g*-PMMA) and the PMMA macromer, respectively, and W_g is the weight fraction of PMMA grafts in the copolymer.

Characterization

The molecular weights of the macromers were determined by a Knauer VPO apparatus using CHCl_3 as solvent, and those of the copolymers by a modified Bruss membrane osmometer using DMF as a sol-

vent. The PMAA content of the purified PMAA-*g*-PMMA was determined by titration with 0.1 M NaOH in DMF using phenolphthalein as an indicator, followed by subtracting the blank data.

IR spectra of the macromer, the copolymer, and the complex were obtained with an IR-435 spectrophotometer, using a KBr disk coated with the sample.

$[\eta]$ of PAM-*g*-PS was determined with a Ubbelohde viscosimeter using chlorophenol as solvent at 60°C, whereas that of PMAA-*g*-PMMA using DMF as solvent was determined at 35°C.

Emulsifying Properties

Emulsifying properties of the graft copolymers were measured as emulsifying volume, determined as follows: 0.2 g sample was dissolved in 30 ml toluene, which was added to 70 ml distilled water. The mixture was vigorously shaken for 5 min and poured into a 100 ml measuring cylinder. After standing for 24 h, the emulsifying volume was measured by subtracting the volume of the lower water layer from the total volume.

Chemical Valves based on Intermolecular Complex Membranes

An intermolecular complex membrane was prepared by dissolving PMAA-*g*-PMMA and PAM-*g*-PS in THF at 50°C with stirring for 4 h, casting the colloidal solution in a culture dish, followed by slow evaporation. The membrane was removed from the dish after immersing it in distilled water and then dried in vacuum oven at 50°C.

Two pieces of membrane were obtained by complexing PMAA-*g*-PMMA containing about 30% and 60% of PMAA with PAM-*g*-PS in a 1 : 1 molar ratio. Measurement of the permeation rate of water was carried out in an ultrafiltration cell assembly. The membrane was sandwiched between two porous filters mounted on the cell with rubber packages. The driving force is the water head between the water inlet of the ultrafiltration cell assembly and the water level in the reservoir above it (about 582 mm H_2O). The permeation rate (J) was calculated using the following equation:

$$J = \frac{\text{Efflux volume (cm}^3\text{)}}{\text{Efflux time (min)} \times \text{Cross area of the membrane (cm}^2\text{)}}$$

where the cross area of the membrane was 396.7 mm^2 .

Table I Reactivity Ratio (r_2) of MAA during Copolymerization with PMMA Macromer vs Polymerization Time (h)

t (h)	P_1 (%)	P_2 (%)	r_2
2	44.8	3.26	0.66
4	58.2	44.0	0.67
6	69.6	56.0	0.69
8	69.9	70.4	1.01
12	74.0	76.4	1.07
16	76.4	81.9	1.18

Table II Reactivity Ratio (r_2) of AM during Copolymerization with PS Macromer vs Polymerization Time (h)

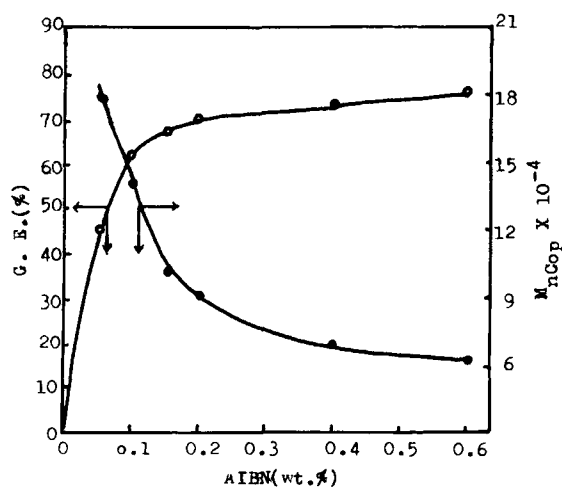
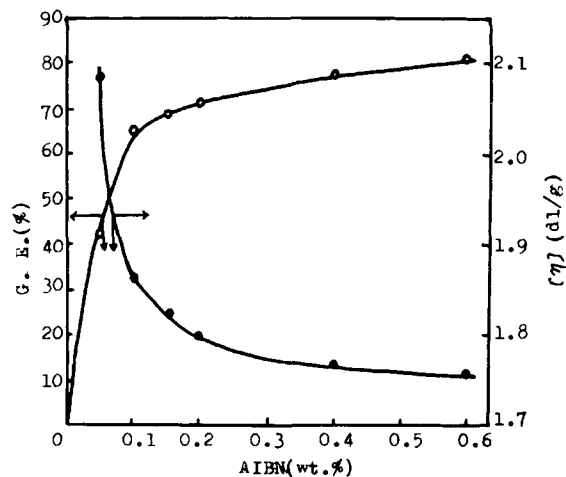
t (h)	P_1 (%)	P_2 (%)	r_2
2	41.0	25.2	0.55
6	58.0	38.4	0.55
8	63.1	43.0	0.57
12	70.9	65.5	0.86
16	76.0	78.0	1.06

RESULTS AND DISCUSSION

Reactivity Ratios

Table I shows the reactivity ratios (r_2) of MAA in its copolymerization with the PMMA macromer, calculated according to the conversion of the monomer and of the macromer. It appears that r_2 is almost constant and equal to 0.67 when the conversions of macromer and monomer are below 70% and 56%, respectively. The r_2 increases abruptly when the conversion of monomer exceeds 60%. Table II indicates the reactivity ratio of AM in its copolymerization with PS macromer. The same phenomenon occurred. Below $P_2 = 43\%$ and $P_1 = 63\%$, r_2 remained almost unchanged and was equal to 0.56, while it increased evidently when the conversion was raised further.

The increase in r_2 is probably due to the fact that with increase of conversion, viscosity of the copolymerization system increased, and the diffusion of

**Figure 1** Effect of amount of initiator used on the grafting efficiency and molecular weight of PMAA-g-PMMA.**Figure 2** Effect of amount of initiator used on the grafting efficiency and $[\eta]$ of PAM-g-PS.

active centers and macromers decreased more evidently than that of the monomers.

These two tables also demonstrate that the conversion of macromer is faster than that of monomer in the earlier stages of the copolymerization. This is apparently due to the higher reactivity of the double bonds of methacryloyl groups than those of acryloyl groups in the case of copolymerization of PS macromer with AM. In the case of copolymerization of PMMA macromer with MAA in DMF, it is probably due to the association of MAA with DMF solvent through hydrogen bonding, which lowers the reactivity of MAA and enhances the conversion of the macromer. However, when viscosity of the copolymerization system became higher at higher conversion of both macromer and monomer, it seems easier for the monomer to diffuse and react with the active centers than for the macromer. Thus the conversion of monomer exceeds that of the macromer and r_2 no longer remains constant.

Factors Affecting Grafting Efficiency and Molecular Weight of the Copolymers

Figures 1 and 2 indicate that either in the copolymerization of MAA with PMMA macromer, or in the copolymerization of AM with PS macromer by increasing the amount of initiator used, grafting efficiency (GE) increases while molecular weight or $[\eta]$ of the graft copolymer decreases, both rapidly at lower AIBN concentration. This is because the active centers increase with an increase of initiator, resulting in a decrease of the molecular weight of

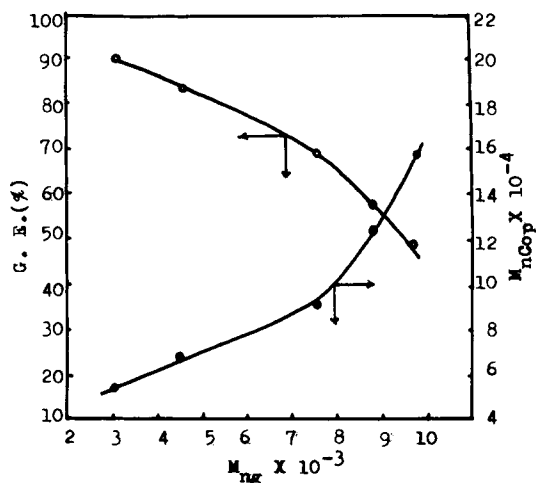


Figure 3 Effect of molecular weight of PMMA macromer on the grafting efficiency and molecular weight of PMAA-*g*-PMMA.

active chains and a decrease of the viscosity of the polymerization system. Lower viscosity is favorable to an increase in GE. This is more evident at lower temperature.

GE decreases with increasing molecular weight of the macromer as shown in Figures 3 and 4. These results may be attributed to more difficult diffusion and larger steric hindrance of the macromer with higher molecular weight, which makes the reaction between active centers and macromer less probable. Figure 3 also indicates that the molecular weight of the copolymer is raised as the molecular weight of the macromer used in copolymerization increases. This is because probability of chain termination or chain transfer is lowered by the increase of viscosity of the polymerization system, resulting in an increase in the molecular weight of the graft copolymer.

Both Figures 4 and 5 illustrate that GE decreases with increment of charging ratio of the macromer to monomer. These results may probably be due to an increase of viscosity of the polymerization system containing more macromers, and also due to the difficulty of homopolymerization of the macromer. Molecular weight of the graft copolymer increases with charging ratio of macromer to monomer. This fact can be explained by the decrease of chain termination probability, owing to the higher viscosity of the polymerization system containing more macromers, and also by the more evident increase of molecular weight of the copolymer when the active center reacts with a macromer as compared with a monomer.

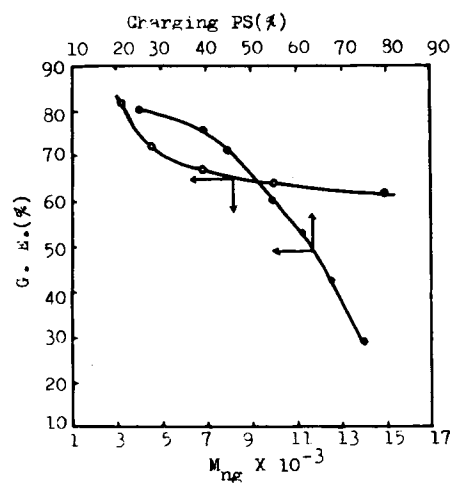


Figure 4 Effects of molecular weight and charging wt % of PS macromer on the grafting efficiency in the copolymerization of PS macromer with AM.

Characterization of the Purified Graft Copolymers

The crude products obtained from the copolymerization were purified by extractions. The efficiency of purification was ascertained by extraction of a mixture of PMMA macromer and PMAA or a mixture of PS macromer and PAM.

The IR spectrum of the purified PMAA-*g*-PMMA showed the characteristic peak at 1730 cm^{-1} for the carbonyl group of ester, a peak at 1400 cm^{-1} for the methyl ester, peaks at $1150\text{--}1200 \text{ cm}^{-1}$ for C—O vibration, and a wide peak at about 3000 cm^{-1} for

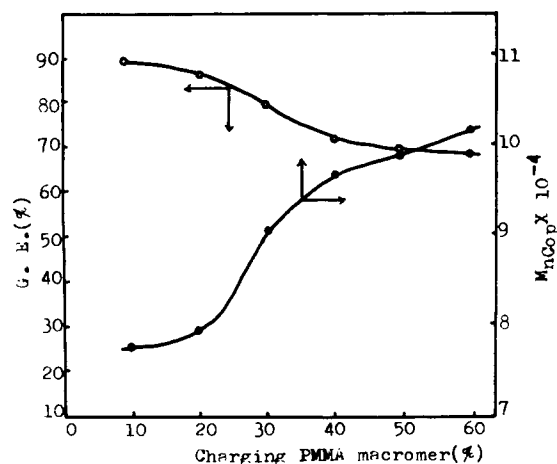


Figure 5 Effect of charging wt % of PMMA macromer on the grafting efficiency and molecular weight of PMAA-*g*-PMMA.

Table III Change of Average Number of Grafting (N_g) with Copolymerization Time (h) during Copolymerization of MAA with PMMA Macromer

t (h)	W_g (%)	$M_{ng} \times 10^{-4}$	N_g
2	37.1	8.6	4.3
4	36.2	8.8	4.2
8	29.9	9.6	3.8
12	29.3	9.7	3.7
16	28.9	9.9	3.7

the carboxylic acid dimer. This spectrum demonstrates that the purified product is composed of both PMAA and PMMA segments.

The IR spectrum of the purified PAM-*g*-PS exhibited absorption peaks of the NH_2 at 1600 cm^{-1} and 3400 cm^{-1} , that of the carbonyl group of amide at 1650 cm^{-1} , and that of C—N at 1400 cm^{-1} , as well as those of the phenyl ring at 690, 1310, 1490, and 3100 cm^{-1} . These absorption peaks indicate that the purified product contains both PAM and PS segments.

Since the side chains of the PMAA-*g*-PMMA are made from the PMMA macromer with molecular weight determined by VPO, and the molecular weight of the graft copolymer can be measured by a membrane osmometer using DMF as solvent, the average number of grafts per macromolecule for PMAA-*g*-PMMA obtained at different stages of copolymerization was estimated in Table III.

It can be seen from Table III that with increasing copolymerization time the average number of grafts

per macromolecule decreases. This is because viscosity of the polymerization system increases with conversion, resulting in a reduction of macromer diffusion and their combination with the active centers. The increase of incompatibility of the copolymer with the macromer with increasing conversion also lowers the average number of grafts per macromolecule. However, the decrease in the average number of grafts per macromolecule in this case seems to be less than that in the copolymerization of the PS macromer with MAA,⁸ probably due to less compatibility of the PS macromer with MAA than that of the PMMA macromer with MAA.

Emulsifying Properties of the Two Graft Copolymers

These two kinds of graft copolymers can emulsify the toluene/water system, since PAM and PMAA are hydrophilic and PS and PMMA are hydrophobic. The effects of the amount of the copolymer used as emulsifier and content of the hydrophilic segments on emulsifying properties are shown in Table IV, where the emulsifying properties were measured as emulsifying volume. It can be seen that the emulsifying volume increases with the amount of the graft copolymer used and that the graft copolymers containing about 50 wt % of hydrophilic segments offers the largest emulsifying volume. The latter may be due to the fact that almost equal portions of hydrophilic and hydrophobic segments benefit the formation of an emulsion.

Table V demonstrates that the emulsifying volume decreases with the raising of molecular weight of the macromer. This result is attributed to the

Table IV Effects of Amount of Graft Copolymer used and of Hydrophilic Segments Content on Emulsifying Volume (E.V.)

PMMA- <i>g</i> -PMMA			PAM- <i>g</i> -PS		
Amount (g/100 ml)	PMAA (%)	E.V. (ml)	Amount (g/100 ml)	PAM (%)	E.V. (ml)
0.05	33.3	47.2	0.05	66.7	37.0
0.10	33.3	50.0	0.10	66.7	37.2
0.20	33.3	51.0	0.20	66.7	46.8
0.40	33.3	54.6	0.40	66.7	55.8
0.80	33.3	58.0	0.80	66.7	59.6
0.20	10.0	40.0	0.20	42.9	43.5
0.20	50.0	51.4	0.20	50.0	46.6
0.20	75.0	42.5	0.20	57.1	46.5
0.20	90.0	41.8	0.20	71.6	40.2
			0.20	85.7	35.6

Table V Effects of Molecular Weight of Grafts and pH Value on the Emulsifying Volume (E.V.)

PMAA- <i>g</i> -PMMA			PAM- <i>g</i> -PS		
$M_{ng} \times 10^{-3}$	pH	E.V. (ml)	$M_n \times 10^{-3}$	pH	E.V. (ml)
3.01	7	51.2	3.25	7	47.6
4.52	7	51.0	4.28	7	46.8
7.50	7	48.2	6.58	7	44.2
8.81	7	46.0	9.65	7	41.8
9.63	7	42.0	14.71	7	39.8
4.52	1	41.0	4.28	1	46.8
4.52	3	46.2	4.28	3	46.8
4.52	7	51.0	4.28	7	46.8
4.52	9	53.5	4.28	9	46.8
4.52	13	40.2	4.28	13	46.8

decrease of hydrophobic sites as the number of grafts diminishes. The same table shows that the emulsifying volume of PMAA-*g*-PMMA depends markedly on pH value of the emulsion, whereas that of PAM-*g*-PS stays almost constant at pH from 1 to 13. This phenomenon is evidently due to the former graft copolymer's being an ionic emulsifier while the latter is nonionic.

Intermolecular Complex Membrane as a Chemical Valve

PMAA can form a complex with PAM through hydrogen bonds formation between the COOH and CONH₂ groups. This complex formation depends on the pH value of the medium. When a membrane was formed by casting a hot THF solution of PMAA-

g-PMMA and PAM-*g*-PS at a molar ratio of PMAA/PAM = 1 and setting it in the ultrafiltration cell assembly, the permeation rate of water through the membrane was found to depend apparently on its pH value. On decreasing the pH value of water from 7 to 3 by adding dilute hydrochloric acid, the permeation rate increased gradually at first and then quickly from pH 5 to 4, as indicated in Figure 6. When dilute sodium hydroxide solution was added to the water in the upper reservoir, the permeation rate decreased to less than 1.3 cm³/cm²·min at pH 7 and higher. The process can be carried out reversibly.

The swelling ratio (Q) of the complex membrane was determined at different pH values in order to explain the above phenomenon. The swelling ratio was defined as follows:

$$Q = \frac{\text{Wt of the swelling membrane} - \text{wt of the dried membrane}}{\text{Wt of the dried membrane}}$$

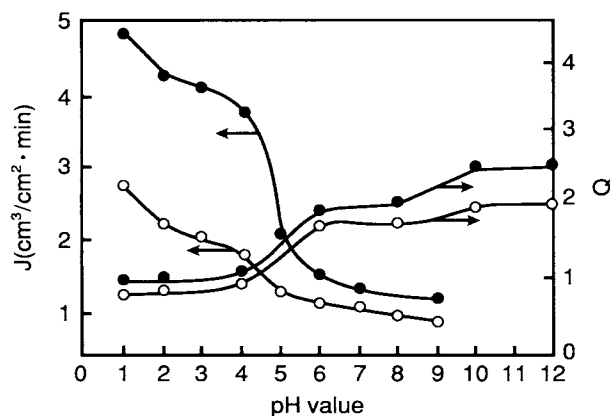


Figure 6 Change of permeation rate of water and swelling ratio of the intermolecular complex membrane vs. pH (○-30 wt % PMAA, ●-60 wt % PMAA).

The same figure shows that on increasing the pH value, Q increased abruptly at pH 4 to 6, then remained almost unchanged up to pH 8. It then again increased abruptly at pH 8 to 10. The pH value for the first abrupt increase of Q nearly coincides with that for the first abrupt increase in J . The greater the PMAA content of the PMAA-*g*-PMMA, the larger is the change of Q and J . This is due to the greater amount of intermolecular complex formed between the two graft copolymers.

In the membrane the PAM of the PAM-*g*-PS complexed with the PMAA of PMAA-*g*-PMMA to leave channels in the membrane at pH values of

about 4 and 5. At higher pH dissociation of the complex due to deprotonization of PMAA causes the membrane to swell, closing the channels. This functions as a chemical valve, because its permeability can be controlled reversibly by adjusting the chemical environment, such as the pH of the medium. The chemical valve opened more slowly than it closed because OH ions are transported quickly through the opened channels formed by the contraction of the complex, thereby causing the complex to dissociate quickly; while H⁺ ions must diffuse through the closed channels, exchanging with Na⁺ and then forming a complex between PAM and PMAA.

IR spectrum of the membrane confirmed the hydrogen bond formation between PMAA-*g*-PMMA and PAM-*g*-PS, since the absorption peak of the amine group became widened at 3100–3500 cm⁻¹ and the absorption peak of carbonyl group widened and shifted to a lower wave number at 1640–1720 cm⁻¹.

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REFERENCES

1. R. Milkovich and M. T. Chiang, U.S. Pat. 3,786,116 (1974).
2. K. Oto, N. Usami, and Y. Yamashita, *Macromolecules*, **13**, 216 (1980).
3. C. Bonordi, B. Boutevin, Y. Pietrasanta, and M. Taka, *Makromol. Chem.*, **186**, 261 (1985).
4. Y. Yamashita, K. Ito, H. Kizuno, and K. Okada, *Polym. J.*, **15**, 443 (1983).
5. Y. Yamashita, *Polym. Prepr.*, **27**(2), 27 (1986).
6. K. Albrecht and W. Wunderlich, *Angew. Chem.*, **145/146**, 89 (1986).
7. H. Q. Xie, G. Z. Xu, and J. S. Guo, *J. Macromol. Sci., Chem.*, **A29**, 263 (1992).
8. H. Q. Xie and Y. Liu, *Polym. J.*, **34**, 182 (1993).
9. Y. Osada and Y. Takeuchi, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 303 (1981).
10. S. Nishi and T. Kotaka, *Macromolecules*, **19**, 978 (1986).
11. H. Q. Xie and X. Chen, *Chinese J. Appl. Chem.*, **4**(2), 22 (1987).
12. J. P. Kennedy and C. Y. Lo, *Polym. Bull.*, **8**, 63 (1982).

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