Synthesis and properties of amphiphilic poly(methacrylic acid) copolymers possessing uniform polystyrene side-chains

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Poly(methacrylic acid) (PMAA) copolymers with uniform polystyrene (PS) side-chains were synthesized through the macromer technique. The graft copolymers (PMAA-*g*-PS) were purified by extraction with water and hot cyclohexane, and were then characterized by gel permeation chromatography, infra-red spectrophotometry and ^{1}H nuclear magnetic resonance spectroscopy. The average grafting number was determined to be 3–7, and decreases with increasing conversion. The graft copolymers showed good emulsifying properties and high water absorbency, and can be used as a good compatibilizer for blending polystyrene with epichlorohydrin rubber (CHR). Only 2–3 wt% of the graft copolymer based on the blend was needed to enhance the mechanical properties of the blends, and the blends with weight ratio of PS/CHR = 3/7 to 5/5 behave as good thermoplastic elastomers. When PMAA-*g*-PS was mixed with polyoxyethylene (PEO) grafted with PS in molar ratio of PEO/PMAA = 1, a thermoplastic intermolecular complex membrane was formed. This behaved as a chemical valve, as its permeability can be controlled reversibly by changing the pH value.

(Keywords: macromer; graft copolymer; poly(methacrylic acid); polystyrene; amphiphilic copolymer; compatibilizer; intermolecular complex; chemical valve)

INTRODUCTION

Since Milkovich[1] and his coworkers developed the method of synthesizing copolymers with uniform side-chains using the macromer technique, much related research work has been carried out[2]. With respect to copolymerization of a macromer with an acidic-group-containing monomer, Yamashita[3] synthesized copolymers of methacrylic acid (MAA) with polystyrene (PS) side-chains, for use as a surfactant, by the macromer technique, and studied its value in the surface modification of polymer films. We have reported the terpolymerization of butyl acrylate and of acrylic acid with a PS macromer[4], a PMMA macromer[5] or a polyoxyethylene (PEO) macromer[6], followed by neutralization with metal acetates to obtain ionomers.

This paper deals with the copolymerization of PS macromers with MAA. We also consider the characterization and properties of the copolymers (PMAA-*g*-PS) designed to provide an amphiphilic graft copolymer with good emulsifying properties and high water absorbency. Such a system could also be used as a compatibilizer, as in the blending of epichlorohydrin rubber (CHR) and PS. This graft copolymer was also combined with polyoxyethylene grafted with styrene (PEO-*g*-PS) in the formation of an intermolecular complex[7], which behaved as a chemical valve[8,9].

EXPERIMENTAL

Materials

All the solvents used were chemically pure. They were dried over a 4 Å molecular sieve overnight. Methacrylic acid (MAA) was purified by first drying over a 4 Å molecular sieve overnight, followed by distillation over CuCl under reduced pressure. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Styrene was purified by first washing it with 10% NaOH solution and then distilling it under reduced pressure over CuCl. Ethylene oxide was purified by successive distillations over KOH and CaH_2. Methacryloyl chloride was synthesized by reaction of methacrylic acid with SO_2Cl at 65°C. It was purified by vacuum distillation over CuCl. n-Butyllithium 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.

Polystyrene macromers were prepared by the anionic polymerization of styrene initiated with n-butyllithium and tetrahydrofuran (THF), followed by capping with ethylene oxide (EO) and terminating with methacryloyl chloride according to the literature[4].

Synthesis and characterization of the graft copolymers

PMAA-*g*-PS was synthesized by copolymerization of polystyrene macromers with MAA in dimethylformamide (DMF), using AIBN as initiator. The

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copolymerization was terminated with a small amount of *p*-hydroxyphenol. The product was precipitated and washed with water to remove any homopolymer of MAA. The precipitate was dried under vacuum and then extracted three times with cyclohexane at 35°C to remove unreacted macromer. The purified copolymer was characterized. The molecular-weight distribution of the graft copolymer was determined by g.p.c. using an LC-4A liquid chromatography apparatus with THF as the eluant and a differential refractive index detector. The molecular weight of the macromer and of the purified graft copolymer was measured using a Knauer VPO apparatus and a modified Bruss membrane osmometer, respectively. The i.r. spectra of the graft copolymers were obtained with a PE-580B spectrophotometer and the ^{1}H n.m.r. spectra recorded on an AC-80 NMR spectrometer, using tetramethylsilane (TMS) as the internal standard and deuterated dimethylsulphoxide (DMSO-d_6) as the solvent.

The PMAA content of the purified graft copolymer was determined by titration with 0.1 M NaOH in DMF, using phenolphthalein as the indicator, followed by subtracting the blank data. The grafting efficiency (*GE*) or conversion of macromer was calculated using the following equation:

$$GE\ (\%) = \{[(\text{weight of macromer charged}) - (\text{weight of unreacted macromer})] \div (\text{weight of macromer charged})\} \times 100$$

Polyoxyethylene grafted with polystyrene (PEO-*g*-PS) was prepared by the graft copolymerization of styrene onto a copolymer of EO with allyl glycidyl ether (AGE) (containing 10% AGE) in DMF solution at 60°C using AIBN as initiator, followed by extraction with 20% ethanol and cyclohexane at 35°C separately. The copolymer gives an i.r. spectrum showing that the absorption peaks at 1645 and 990 cm^{-1} for the double bonds disappeared and that bands at 1600 and 1500 cm^{-1} for the aromatic phenyl ring appeared. The grafting efficiency of styrene and the PEO content of PEO-*g*-PS can be estimated according to the weight of crude product and extracted products.

Properties of PMAA-g-PS system

The emulsifying properties of the graft copolymer were represented by the emulsifying volume, which was measured as follows. A certain amount of the graft copolymer was dissolved in 10 cm^3 of DMF. The solution was shaken thoroughly with 30 cm^3 of toluene and 60 cm^3 of water for 10 min, followed by pouring into a measuring cylinder with a cover. After settling for 48 h, the total volume and the volume of the water phase were measured. The difference was recorded as the emulsifying volume. Blank tests showed that DMF was soluble in the water layer.

The water absorbency was determined by immersing 1.000 g of hot-pressed film of 0.5 mm thickness in 100 cm^3 of distilled water for 48 h at room temperature. The immersed film was weighed after removing the surface water with filter paper. The water absorbency is given by:

$$\text{Water absorbency, } H_2O\ (\%) = 100(W_a - W_b)/W_b$$

where W_b is the weight of samples before water absorption and W_a is the weight of samples after water absorption.

Blending of epichlorohydrin rubber with polystyrene, the PMAA-*g*-PS being used as a compatibilizer, was carried out on a hot mill at 165°C for 4 min. The blend was hot-pressed between polyester films at 160°C under a pressure of 10 MPa to form a sheet of about 1 mm thickness, which was cut into dumbbell specimens. The mechanical properties of the specimens were measured on a DL-250 tensile tester with an extension rate of 300 mm min^{-1}.

Chemical valves based on intermolecular complex membranes

An intermolecular complex membrane was prepared by dissolving PMAA-*g*-PS and PEO-*g*-PS together in hot DMF, casting the solution on a clean poly(tetrafluoroethylene) plate, followed by slow evaporation and vacuum drying at 50°C for 3 days. The membrane was removed from the plate after immersing it in water. Two pieces of membrane were obtained by mixing PMAA-*g*-PS containing 82.3 and 38.5% PMAA with PEO-*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 600 mm H_2O). The permeation rate (J) was calculated using the following equation:

$$J = [\text{efflux volume (cm}^3)] \div \{[\text{efflux time (min)}] \times [\text{cross-sectional area of membrane (cm}^2)]\}$$

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

RESULTS AND DISCUSSION

Copolymerization of the polystyrene macromer with methacrylic acid

Study of copolymerization conditions showed that, when the total concentration of macromer and monomer is 30 g/100 cm^3, the amount of AIBN used was 0.3% based on total amount of macromer and monomer, the weight ratio of macromer to monomer is less than 40/60, and, when the copolymerization is carried out at 60°C for 24 h, the grafting efficiency can reach over 90%. *Figure 1* indicates the effect of the molecular weight of the macromer on the grafting efficiency and on the molecular weight of the copolymer. One effect of increasing the molecular weight of the macromer is that the grafting efficiency remains almost constant in the range of molecular weight of macromer between 4000 and 10 000 g mol^{-1}, but decreases when the molecular weight of macromer is above 10 000 g mol^{-1}. The former phenomenon implies that the chain length of the macromer within a certain molecular-weight range does not affect the reactivity of the double bond at the chain end. The latter phenomenon is due to the higher viscosity and more difficult diffusion of the macromer possessing much higher molecular weight, resulting in its lower apparent reactivity. On increasing the molecular weight of the macromer, the molecular weight of the graft copolymer increases up to the molecular weight of the macromer of 10 000 g mol^{-1}. Beyond this value, the molecular weight of the copolymer changed only slightly.

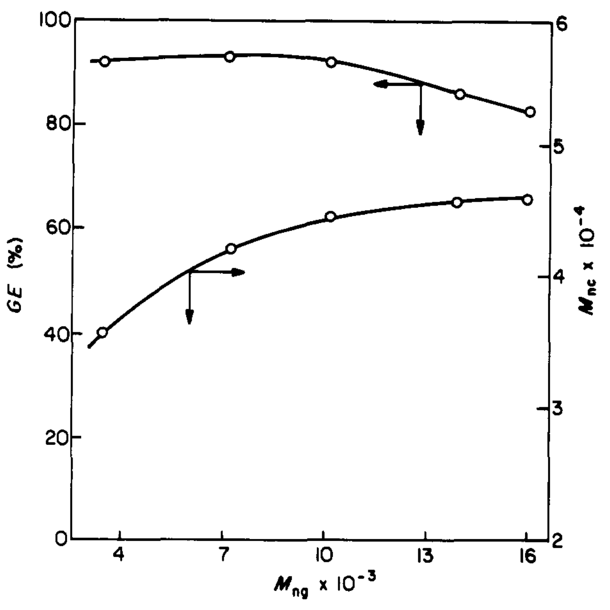

Figure 1 Effect of the molecular weight of polystyrene macromer on the grafting efficiency and on the molecular weight of the copolymer

Table 1 Change of structural parameters of copolymers during copolymerization[a]

Copolym. time (h)	$M_{nc} \times 10^{-4}$ (g mol^{-1})	W_g	N_g
5	3.6	0.711	6.4
10	3.9	0.554	5.4
15	4.2	0.438	4.6
20	4.4	0.355	3.9
25	4.5	0.249	2.8

[a] $M_{ng} = 3.5 \times 10^3$ g mol^{-1}

*Purification and characterization of PMAA-*g*-PS*

G.p.c. curves of PMAA-*g*-PS purified with three water extractions and three cyclohexane extractions at 35°C indicate that the peak for PS macromer at an elution time of 18.2 min disappeared while a peak without a shoulder at an elution time of 9.5 min appeared. This demonstrates that the copolymer after purification contained neither PS macromer nor homopolymer of MAA. The ^{1}H n.m.r. spectrum of the purified product showed peaks at $\delta = 6.6$ and 7.7 ppm due to protons of the phenyl ring, a peak at $\delta = 1.6$ ppm from the CH_2 protons, a peak at $\delta = 0.94$ ppm due to the protons of the methyl group and a small peak at about $\delta = 12$ ppm from the protons of the COOH group, which becomes wider due to hydrogen bonding. The i.r. spectrum of the purified copolymer exhibited absorption peaks of the -OH at 3000 and 1390 cm^{-1}, that of the carbonyl group at 1725-1700 cm^{-1}, that of C-O at 1250 and 1165 cm^{-1} and those of the phenyl ring at 1490, 750 and 700 cm^{-1}. These spectra indicated that the purified product contains both PMAA and PS segments.

Since the side-chains of PMAA-*g*-PS are made from the PS macromer with a uniform molecular weight, the average number of grafts per macromolecule (N_g) can be calculated from the following equation:

$$N_g = \bar{M}_{nc} W_g / \bar{M}_{ng}$$

where $\bar{M}_{nc}$ is the number-average molecular weight of the graft copolymer, $\bar{M}_{ng}$ is the number-average molecular weight of the macromer and W_g is the weight fraction of polystyrene in the copolymer. *Table 1* illustrates the structural parameters of the copolymers obtained at different stages of copolymerization. It can be seen that, with increasing copolymerization time, the average number of grafts per macromolecule decreases. This is attributed to the increase of viscosity of the polymerization system with conversion. This reduces the diffusion of the macromers and their combination with the active centres. It also leads to the increased incompatibility of the copolymer with the macromer, resulting in a lowering of the average number of grafts per macromolecule.

*Properties of the PMAA-*g*-PS graft copolymers*

The graft copolymer can emulsify the water/oil system owing to the hydrophilic properties of the main chains of the PMAA and the hydrophobic properties of the side-chains of the PS. *Figure 2* shows that the emulsifying volume increases with the amount of the graft copolymer used in emulsion and also that the emulsifying volume initially increases with the PMAA content and then decreases. There exists a maximum value at a PMAA content of 58.4%. This is because reduced content of hydrophilic segments makes it difficult for the graft copolymer to enter into the water phase while the reduced portion of hydrophobic segments makes it difficult for the graft copolymer to enter into the oil phase.

The molecular weight of the PS side-chains exerts little effect on the emulsifying volume, as shown in *Figure 3*. The same figure demonstrates that the pH value affects the emulsifying properties of the graft copolymer, since it is an ionic emulsifier. A maximum emulsifying volume appears at pH 7. All of the emulsions are of the oil-in-water type, when the volume ratio of (H_2O + DMF)/toluene is 70/30. However, the emulsion changed to a water-in-oil type when the volume ratio is 30/70.

The PMAA segments in the copolymer can form hydrogen bonds with water. Thus, the copolymers exhibit strong water absorbency, as shown in *Table 2*. This

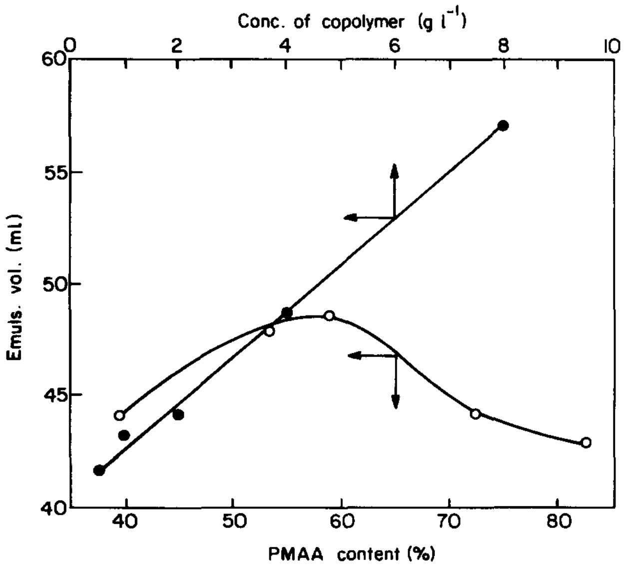

Figure 2 Effect of the PMAA content and the concentration of the graft copolymer on the emulsifying volume

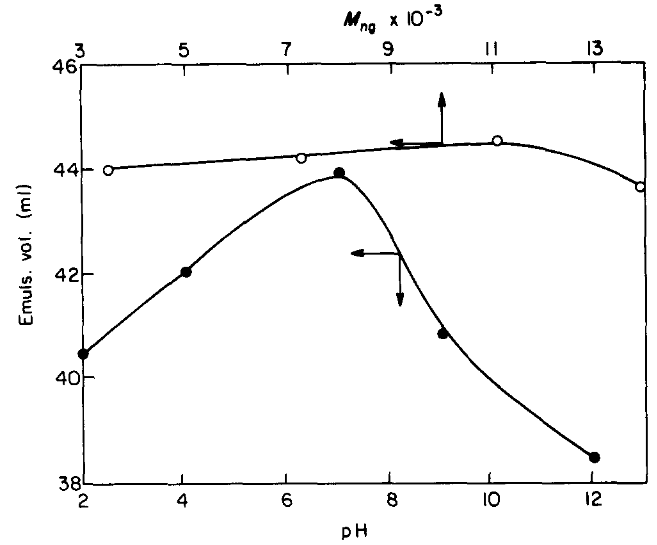

Figure 3 Effect of the pH and of the molecular weight of polystyrene side-chains on emulsifying volume

Table 2 Relationship between the water absorbency and the PMAA content of the graft copolymers[a]

PMAA content (%)	Water absorbency (%)
82.3	2040
71.8	809
58.4	487
53.2	391
39.4	200

[a] $M_{ng} = 10.1 \times 10^3$ g mol^{-1}

Table 3 Effect of the amount of compatibilizer added on the mechanical properties of the PS/CHR blends[a]

Compatibilizer (wt%)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0	4.26	220	36
1	8.34	420	25
2	10.4	700	23
3	9.62	850	17
5	8.77	780	28
7	7.37	750	37
10	7.29	720	49

[a] Weight ratio of PS/CHR = 3/7; PMAA-*g*-PS containing 53.2% PMAA and with $M_{ng} = 10\,100$ g mol^{-1} used as compatibilizer

indicates that the water absorbency of the graft copolymer increases with increase in the hydrophilic PMAA content.

The blend of epichlorohydrin rubber (CHR) with PS shows poor mechanical properties, because the compatibility between CHR and PS is poor. Attempted use of the graft copolymer as a compatibilizer was undertaken, since the COOH groups of the main chain of the copolymer can form hydrogen bonds with ether groups of the CHR phase. Also the PS side-chains are of the same structure as the PS phase. *Table 3* indicates that, when the compatibilizer was added to the blend with PS/CHR = 3/7, the tensile strength and ultimate elongation of the blend increase noticeably, while the permanent set decreases up to compatibilizer content of 2–3%. If the graft copolymer used exceeds 3 wt% based on the blend, both the tensile strength and the ultimate elongation decrease, while the permanent set increases. The blend containing 2 or 3% of graft copolymer behaves as a good thermoplastic elastomer. This is attributed to the adhesion of the interface of the CHR and PS phases due to the compatibilizer.

The effect of a fixed amount of compatibilizer (3% based on the blend) on the mechanical properties of blends with different proportions of PS/CHR is shown in *Table 4*. It can be seen that, with increasing proportion of PS in the blend, the tensile strength increases but the ultimate elongation decreases, while a maximum permanent set appears at a ratio PS/CHR = 3/7. The blends with 3% graft copolymer and PS/CHR = 3/7 to 5/5 exhibit the behaviour of a thermoplastic elastomer, whereas the blend with PS/CHR = 6/4 is a toughened plastic.

Use of the intermolecular complex membrane as a chemical valve

PMAA can form complexes with PEO through hydrogen-bond formation between –COOH groups and $-CH_2OCH_2-$ groups. This complex formation depends on the pH value of the medium. When a membrane was formed by casting a solution of PMAA-*g*-PS and PEO-*g*-PS at a molar ratio of PMAA/PEO = 1 and was set in the ultrafiltration cell assembly, the permeation rate of water through the membrane was found to depend largely on its pH value. On decreasing the pH value of water from 7 to 3 by adding dilute hydrochloric acid, the permeation rate increases gradually at first and then quickly at about pH 4.5 or 5.5 according to the PMAA content of the PMAA-*g*-PS, as illustrated in *Figure 4*. When dilute sodium hydroxide solution was added to the water in the upper reservoir, the permeation rate decreased to less than 0.05 cm^3 cm^{-2} min^{-1} at pH 7 and higher. The process can be carried out reversibly.

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

$$Q = [(\text{weight of swollen membrane}) - (\text{weight of dried membrane})] \div (\text{weight of dried membrane})$$

It can be seen from *Figure 4* that, on increasing the pH value, Q first increased abruptly at about pH 4.5 or 5.5, and then increased slightly up to pH 7.5 or 8.5. It

Table 4 Mechanical properties of the PS/CHR blends with different ratios in the presence of compatibilizer[a]

PS/CHR (wt ratio)	PMAA-*g*-PS (%)	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
0/10	0	1.53	1800	56
10/0	0	49.0	–	–
1/9	3	3.94	1480	50
2/8	3	8.28	1070	26
3/7	3	9.62	850	17
4/6	3	11.4	520	24
5/5	3	13.8	230	28
6/4	3	26.0	140	27

[a] PMAA-*g*-PS containing 53.2% PMAA with $\bar{M}_{ng} = 10\,100$ g mol^{-1}

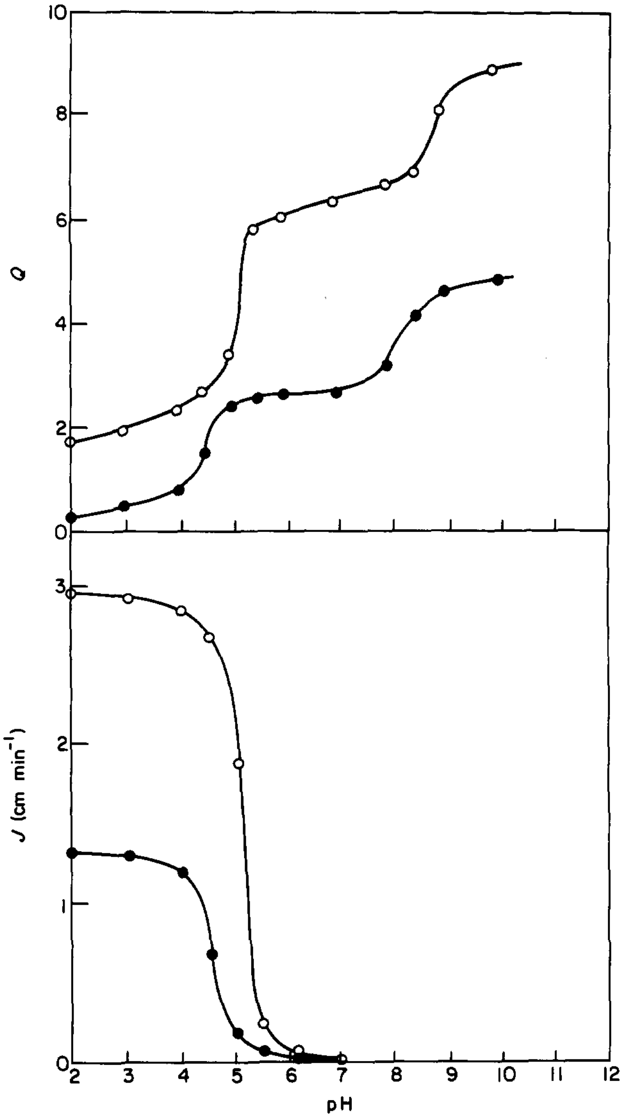

Figure 4 Dependence of the permeation rate of water (J) and of the swelling ratio (Q) of the membrane on the pH value of water: (○) complex membrane containing PMAA-*g*-PS with 82.3% PMAA; (●) complex membrane containing PMAA-*g*-PS with 38.5% PMAA

then again increased abruptly at pH 8 or 9. The pH value for the first abrupt increase of Q coincides with that for the first abrupt increase in J. The greater the PMAA content of PMAA-*g*-PS, 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.

This kind of membrane formed from the complex of the two graft copolymers seems to have a physically crosslinked structure. The PS side-chains of both PMAA-*g*-PS and PEO-*g*-PS can form glassy domains acting as physical crosslinks in the blend, while the PEO of the PEO-*g*-PS complexes with the PMAA of PMAA-*g*-PS to leave channels in the membrane at pH values of about 4.5–5.5. Dissociation of the complex due to deprotonization of PMAA at higher pH 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. It was observed that the chemical valve opened more slowly than it closed. This can be explained by the fact that 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 PEO and PMAA.

The melting peak of crystalline PEO of the PEO-*g*-PS disappeared in the d.s.c. curve of the complex membrane, owing to complex formation between PEO and PMAA via hydrogen bonds.

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