

# Polyacrylamide-Reactive Styrene/Unsaturated Polyester Microgel Composites

E. RUCKENSTEIN\* and L. LIANG

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

## SYNOPSIS

Reactive microgels (RM) were prepared by the copolymerization of styrene and an unsaturated polyester in an emulsion of oil (styrene + unsaturated polyester) in water. The adsorption of the unsaturated polyester on the water-oil interface ensured the stability of the emulsion. Furthermore, polyacrylamide (PAAM) crosslinked with RM was obtained by suspending RM particles in an aqueous AAM solution and polymerizing the system at 70°C to obtain a PAAM-RM composite. The extraction experiments of the RM with dioxane and of the PAAM with water indicated the presence of small amounts of soluble PAAM homopolymers and negligible amounts of free RM, the materials being PAAM crosslinked by RM. The extent of swelling of these materials in water decreased with increasing weight ratio of RM/AAM and was independent of the composition of RM. When the final polymerization temperature was increased to 130°C, RM reacted not only with AAM to form a crosslinked polymer, but also with itself to form semi-interpenetrating reactive polymer networks (SIRPN). The extent of swelling of PAAM-RM SIRPN in water was much lower than that of the PAAM-RM material. Membranes were also prepared by hot pressing at 200°C the PAAM-RM and PAAM-RM SIRPN composites. The swelling behavior of these membranes in water, acetone, tetrahydrofuran, acrylic acid, ethyl alcohol, and dioxane, as well as in the mixtures of ethyl alcohol-water, acetone-water, tetrahydrofuran-water, and acrylic acid-water, was investigated. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Crosslinked polyacrylamide (PAAM) is used as films,<sup>1</sup> coatings,<sup>2</sup> and adhesives<sup>3</sup> and as a medium for electrophoresis of macromolecules, especially proteins.<sup>4,5</sup> Crosslinked PAAM chelating resins have been employed for separation of different metal ions or ions in different valence states.<sup>6</sup> In most cases, *N,N'*-methylenebisacrylamide was used as the crosslinking agent. The crosslinked material is, however, brittle. In the present article, reactive microgels (RM), synthesized from styrene and unsaturated polyester by an emulsion pathway, are employed as crosslinking agents to generate PAAM-RM composites. The RM are intramolecularly crosslinked macromolecules with carboxyl groups and double bonds located on their surface.<sup>7</sup> The PAAM chains are crosslinked by these microgel

particles, generating a material which is less brittle than that crosslinked via the *N,N'*-methylenebisacrylamide and can be more easily processed by hot pressing.

Another advantage of selecting RM as a crosslinking agent instead of *N,N'*-methylenebisacrylamide is that RM is not only a crosslinking agent but also a hydrophobic giant macromolecule. Consequently, the PAAM-RM composites constitute a new kind of amphiphilic polymer.

## EXPERIMENTAL

### Materials

Styrene (St, Aldrich) was distilled before use. Azobisisobutyronitrile (AIBN, Alfa), acrylamide (AAM, Aldrich), and potassium persulfate ( $K_2S_2O_8$ , Aldrich) were purified by recrystallization in methanol and water, respectively. 1,6-Hexanediol (Aldrich, 97%), maleic anhydride (Aldrich, 99%), ethyl al-

\* To whom correspondence should be addressed.

**Table I** Intrinsic Viscosities and Molecular Weights of Different RM

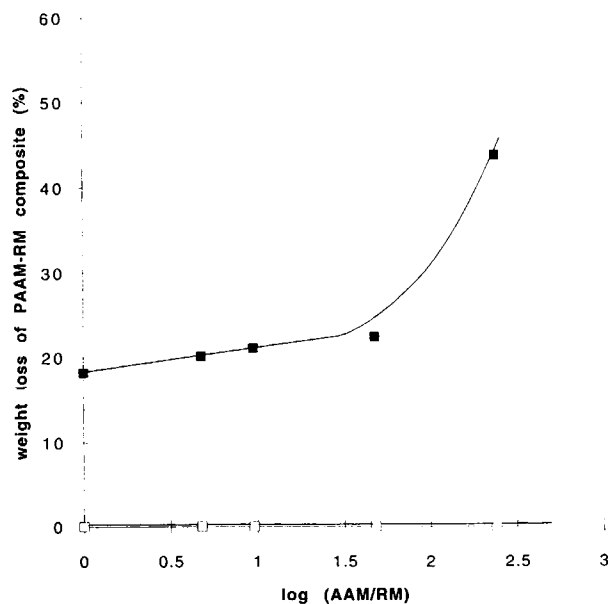
St/UP (g/g)	Intrinsic Viscosities [ $\eta$ ] (mL/g)	Molecular Weight $M \times 10^{-6}$ (g/mol)
10/90	5.2	0.93
20/80	5.8	1.50
40/60	8.2	6.24

Solvent: dioxane; temperature:  $20 \pm 0.2^\circ\text{C}$ .

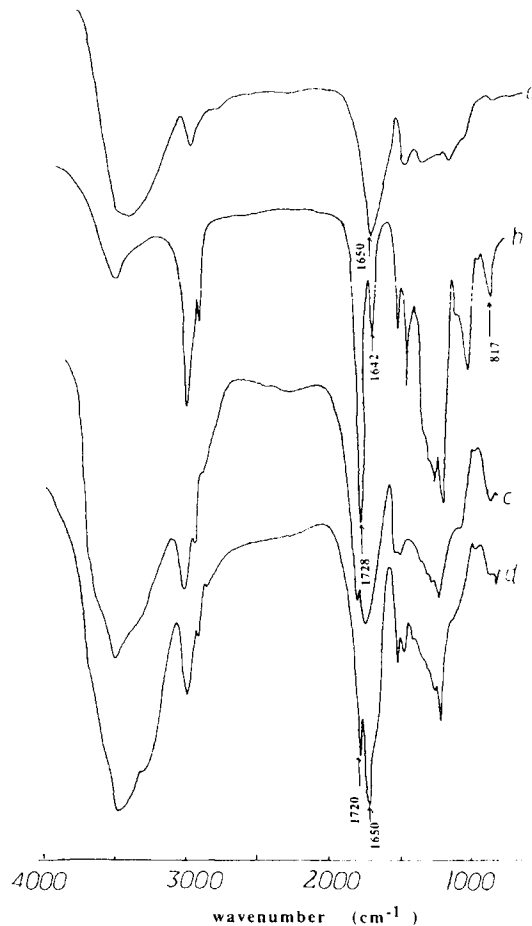
cohol (Aldrich, 99%), acetone (Aldrich, 99%), tetrahydrofuran (Aldrich, 99%), and acrylic acid (Aldrich, 99%) were used without further purification. Water was deionized and double-distilled.

### Preparation of the Unsaturated Polyester<sup>8</sup>

The unsaturated polyester (UP) was prepared by condensation as follows: 2 mol of 1,6-hexanediol and 2.3 mol of maleic anhydride were introduced under a nitrogen atmosphere into an 1 L reaction vessel fitted with a mechanical stirrer and heated to  $100^\circ\text{C}$ . After melting, the above mixture was stirred for 24 h at  $100^\circ\text{C}$ , for 3 h at  $130^\circ\text{C}$ , and for another 15 h at  $150^\circ\text{C}$ . Subsequently, the temperature was decreased to  $100^\circ\text{C}$ , additional maleic anhydride (0.5 mol) added, and the system kept for 21 h at  $100^\circ\text{C}$  to ensure that all the terminal hydroxyl groups were



**Figure 1** Relationship between the weight losses of PAAM-RM composites in dioxane and water and the weight ratio of AAM to RM (temperature of crosslinking reaction:  $70^\circ\text{C}$ ). (■) extracted with water; (□) extracted with dioxane.

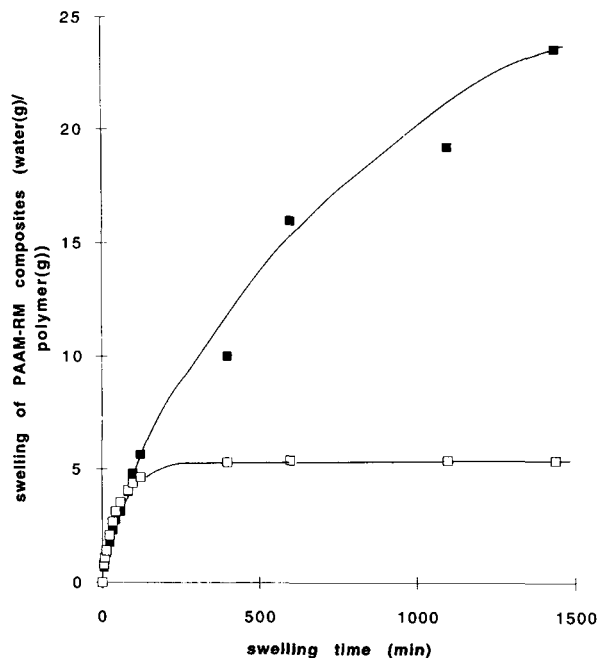


**Figure 2** FTIR spectra of different polymers: (a) PAAM; (b) RM (St/UP = 20/80, weight ratio); (c) PAAM-RM composite prepared at  $70^\circ\text{C}$  (AAM/RM = 1/1, weight ratio); (d) PAAM-RM SIRPN composite prepared at  $130^\circ\text{C}$  (AAM/RM = 1/1, weight ratio).

transformed into acidic groups. After cooling to room temperature, the UP was twice dissolved in acetone and precipitated in water to remove the low molecular weight constituents; then, UP was again dissolved in acetone and water was added in steps in order to precipitate an increasingly smaller molec-

**Table II** FTIR Fingerprints of Different Polymers

Polymer	Infrared Characteristics: Absorption Bands ( $\text{cm}^{-1}$ )
PAAM	3500 ( $\text{NH}_2$ ); 1650 ( $\text{CONH}_2$ )
RM	1728 ( $\text{C}=\text{O}$ ); 1642 ( $\text{C}=\text{C}$ ); 817 (benzene ring)
PAAM-RM composite	3500 ( $\text{NH}_2$ ); 1650 ( $\text{CO}=\text{NH}_2$ ); 1720 ( $\text{C}=\text{O}$ ); 810 (benzene ring)



**Figure 3** Weight absorbed per gram of PAAM-RM composite from water as a function of time, at room temperature: (■) PAAM-RM composite prepared at 70°C (AAM/RM = 1/1, weight ratio); (□) PAAM-RM SIRPN composite prepared at 130°C (AAM/RM = 1/1, weight ratio).

ular weight of UP. The obtained fractions of UP were dried for 24 h in vacuum.

The molecular weight of each fraction was determined by titration with a 0.1M NaOH solution using phenolphthalein as an indicator. The number-average molecular weight,  $\bar{M}_n$ , was calculated with the expression  $\bar{M}_n = 2/N_{\text{COOH}}$ ,  $N_{\text{COOH}}$  being the moles of NaOH used in the titration. In this study, the fraction with  $\bar{M}_n = 1100$  g/mol of UP was used.

#### Preparation of the Reactive Microgels (RM)<sup>8</sup>

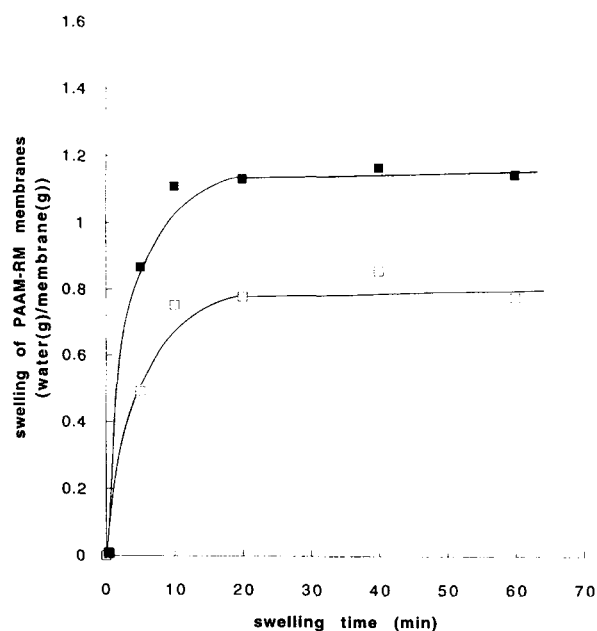
The RM were prepared starting from an emulsion in water of an unsaturated polyester and St containing AIBN as the initiator. The polymerization took place by heating at 70°C for 3 h. In this case, the UP acts as a multifunctional component which is a crosslinking agent for the linearly polymerizing St, an emulsifying agent because of its carboxyl endgroups, and a source of active carboxyl groups and double bonds on the surface of RM and in the interior. The copolymerization was carried out in a reaction vessel with magnetic stirring in a N<sub>2</sub> atmosphere. The total amount of monomer (St + UP) was 4 g. For a given weight ratio of St to UP, the calculated amount of UP was dispersed in water (0.1 L) at 70°C and neutralized with NaOH (0.4N). Af-

ter 15 min, the required amount of St was added and solubilized in UP during 3 h. Then, the copolymerization was started by the addition of AIBN at 70°C { [AIBN] = 0.1 g/4 g (St + UP) }. After 3 h, the copolymerization was terminated by cooling the vessel in an ice bath and adding 100 mg of hydroquinone as the polymerization inhibitor.

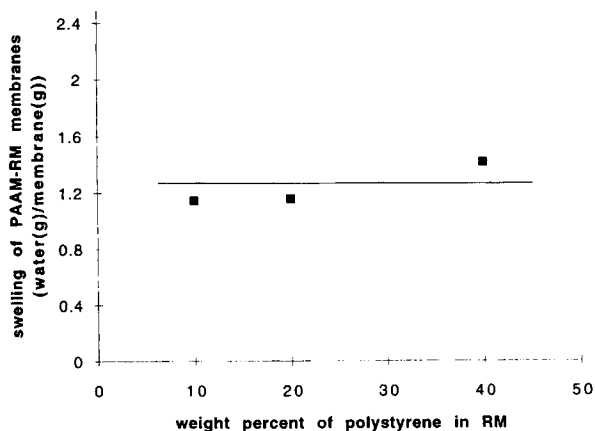
The RM particles were precipitated by adding 5 mL of 2N HCl, separated by filtering and washed with enough water to become free of chloride anions. The RM were deposited in a cone bottle with stirring, by adding water to the solution of RM in dioxane at 30°C until it became turbid and keeping the system overnight at room temperature.

#### Preparation of PAAM-RM Composites

The PAAM-RM composites were prepared by free-radical solution polymerization. The polymerization was performed in a two-neck 100 mL round-bottom flask, with magnetic stirring, in a N<sub>2</sub> atmosphere. To a suspension of microgels (1.75 g) in 15 mL water, AAM (1.75 g) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.02 g) were added. The mixture of AAM and RM was heated at about 70°C for 60 min to generate a crosslinked material. Another crosslinked material, denoted for reasons to be explained later by PAAM-RM SIRPN, was



**Figure 4** Weight absorbed per gram of PAAM-RM membranes from water as a function of time, at room temperature: (■) PAAM-RM composite prepared at 70°C (AAM/RM = 1/1, weight ratio); (□) PAAM-RM SIRPN composite prepared at 130°C (AAM/RM = 1/1, weight ratio). The membranes were prepared by hot pressing at 200°C for 10 min.



**Figure 5** The effect of composition of RM on the amount of water absorbed by PAAM–RM membranes at room temperature. PAAM–RM membrane composite: AAM/RM = 1/1, weight ratio, prepared by hot pressing at 200°C for 10 min; swelling time: 48 h; room temperature.

also prepared by heating at 130°C for 60 min. The obtained materials were dried in air for 48 h, then transferred to a vacuum oven.

#### Extraction Experiments of the PAAM–RM Composites

Soxhlet extractions were performed on ca. 0.5 g of dried samples. A two-solvent process involving, first, dioxane, which dissolves RM, and then water, which dissolves PAAM, was employed.

#### Measurement of the Reduced Viscosity

The reduced viscosity of a dilute solution of RM in dioxane was determined with an Ubbelohde viscometer at the temperature of  $20 \pm 0.2^\circ\text{C}$ .

#### Infrared Spectra

The infrared spectra of different polymer samples were recorded with KBr pellets on a Mattson Alpha Centauri instrument.

#### Preparation of PAAM–RM Membranes

Thin membranes were prepared from the powder composites by hot pressing at 200°C for 10 min in a Carver Laboratory Press at a pressure of 120 kg/cm<sup>2</sup>.

#### Swelling of PAAM–RM Composites

The swelling of PAAM–RM composites was performed by immersing dry samples of PAAM–RM

composites in glass tubes containing the respective liquid. The swollen samples were removed from the mixtures after various times, the liquid on their surface was wiped with tissue paper, and then they were quickly weighed. The swelling of the samples was calculated using the expression  $S = (W_s - W_0)/W_0$ , where  $W_0$  and  $W_s$  are the weights of the dried and swollen samples, respectively.

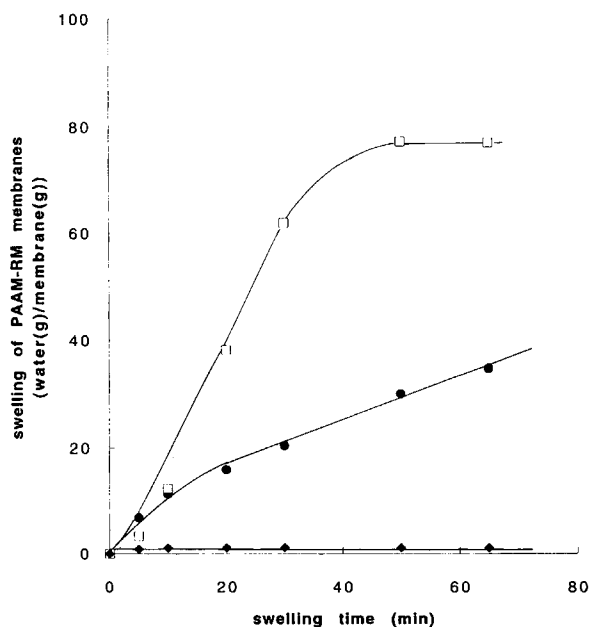
## RESULTS AND DISCUSSION

### Intrinsic Viscosity and Molecular Weight of RM

Three different RM were prepared by changing the weight ratio of St to UP. Reduced viscosities of RM were measured with an Ubbelohde viscometer. The molecular weight of RM was calculated from the intrinsic viscosity  $[\eta]$  using the following equation<sup>9</sup>:

$$[\eta] = K\bar{M}^a$$

where  $\bar{M}$  is the average molecular weight, and  $K = 0.223 \text{ mL/g}$  and  $a = 0.226$  are the Mark–Houwink constants.<sup>10</sup> The intrinsic viscosities ( $[\eta]$ ) and the molecular weights ( $\bar{M}$ ) of different RM are listed in Table I, which shows that  $[\eta]$  depends upon the weight ratio of St to UP.



**Figure 6** Swelling of the PAAM–RM membranes for different PAAM to RM weight ratios in water, at room temperature: (□) PAAM–RM membrane (AAM/RM = 10/1, weight ratio); (●) PAAM–RM membrane (AAM/RM = 5/1, weight ratio); (◆) PAAM–RM membrane (AAM/RM = 1/1, weight ratio).

**Table III Solubility/Swelling Behavior of Different Polymers**

Solvent	PAAM	RM	PAAM-RM Membrane
Decane	×	×	×
THF	×	○	×
Benzene	×	×	×
Chloroform	×	×	×
Acetone	×	×	×
Dioxane	×	○	×
Acrylic acid	△	△	△
Alcohol	×	×	×
Water	○	×	△

○: soluble; ×: nonsoluble; △: swollen. PAAM-RM membrane: AAM/RM = 1/1 (weight ratio), prepared by hot pressing at 200°C for 10 min.

### Weight Loss of PAAM-RM Composites During Extraction with Dioxane and Water

Because RM is soluble in dioxane, while PAAM is soluble in water, the weight losses in these solvents provide indications about the fractions of RM and PAAM involved in the crosslinking. The results are plotted in Figure 1, which shows that, with an increasing amount of RM, the weight loss due to the extraction with water decreased. The weight loss due to the extraction with dioxane was nearly negligible.

Figure 1 shows that the weight loss of the PAAM-RM composite extracted with dioxane is much less than that extracted with water; hence, that the RM particles enter more easily into the crosslinked network. This is because the RM particles contain many reactive groups on their surface. There are three possible mechanisms by which RM can enter into the crosslinked network: (1) The polyacrylamide radical is attached to a double bond of the RM; (2) the  $-\text{CONH}_2$  groups of PAAM react with the  $-\text{COOH}$  groups present on the surface of RM, to form diacrylamines;<sup>11</sup> and (3) the particles react with each other.

### FTIR Spectra

The FTIR spectra of PAAM, RM, and the PAAM-RM composite are presented in Figure 2. The major vibration bands of the chemical groups contained in the respective polymers are listed in Table II.

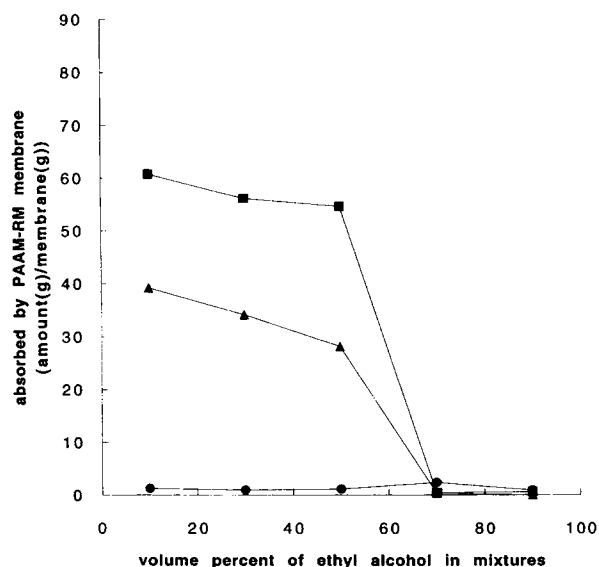
The spectrum of PAAM [Fig. 2(a)] exhibits a strong absorption at  $3500\text{ cm}^{-1}$ , which can be assigned to the stretching vibration of  $\text{NH}_2$  groups of PAAM. The peak at  $1650\text{ cm}^{-1}$  is due to the combined motion of  $\text{NH}_2$  and CO stretching in the  $-\text{CONH}_2$  group.<sup>12</sup> The major vibration bands ob-

served in the spectrum of RM are at  $1728$ ,  $1642$ , and  $817\text{ cm}^{-1}$  [Fig. 2(b)]. The strong absorption at  $1728\text{ cm}^{-1}$  is assigned to the stretching vibrations of the C=O groups in the UP chain. The peaks at  $1641$  and  $817\text{ cm}^{-1}$  are assigned to the stretching vibrations of the double bonds in the UP chain and to the carbon skeleton signals of the benzene rings in the polystyrene chain, respectively.<sup>13</sup> It is clear that all the major vibration bands of PAAM and RM appear also in the FTIR spectrum of the PAAM-RM composite [Fig. 2(c)].

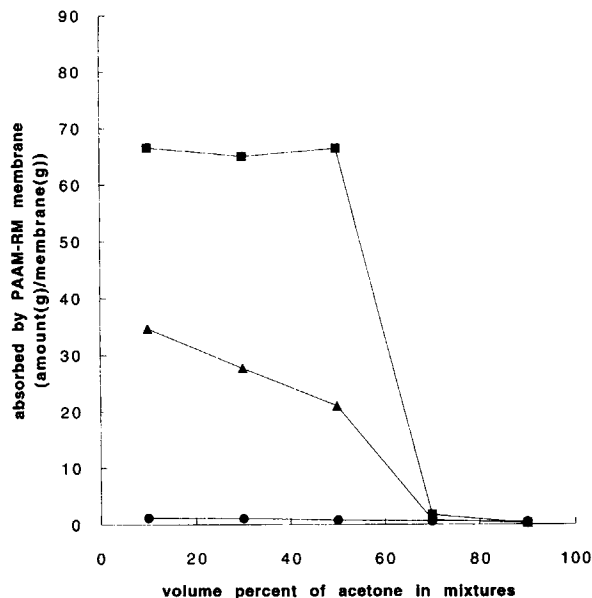
The FTIR spectrum of the PAAM-RM SIRPN composite prepared at  $130^\circ\text{C}$  is also given in Figure 2 [Fig. 2(d)]. The same FTIR spectrum as that of the PAAM-RM composite prepared at  $70^\circ\text{C}$  can be observed. This means that even though the crosslinked density increases with increasing reaction temperature the differences in the microstructure cannot be detected in the FTIR spectra. In contrast to the FTIR spectra, the experimental results regarding the extractions by dioxane and water clearly indicate the presence of crosslinking.

### The Swelling of PAAM-RM and of PAAM-RM SIRPN in Water as a Function of Time, for a PAAM/RM Weight Ratio of 1

RM crosslinked PAAMs were prepared both at  $70^\circ\text{C}$  and at  $130^\circ\text{C}$ . In the latter conditions, a crosslinked material was obtained, which does not dissolve at



**Figure 7** The swelling of PAAM-RM membrane in ethyl alcohol-water mixtures, at room temperature: (■) PAAM-RM membrane (AAM/RM = 10/1, weight ratio); (▲) PAAM-RM membrane (AAM/RM = 5/1, weight ratio); (●) PAAM-RM membrane (AAM/RM = 1/1, weight ratio); swelling time: 48 h.

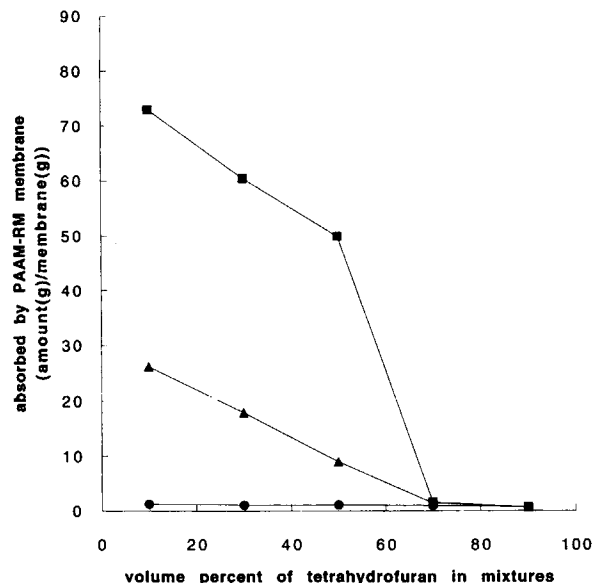


**Figure 8** The swelling of PAAM-RM membrane in acetone-water mixtures at room temperature: swelling time: 48 h. The symbols are as in Figure 7.

all in water. It is likely that the RM particles interacted not only with PAAM but also among themselves, forming an RM network that trapped the PAAM chains within. A semi-interpenetrating reactive polymer network (SIRPN) was thus obtained containing polyacrylamide chains in an RM network.

Figure 3, which presents the results of swelling experiments carried out with composites prepared at 70 and 130°C, shows that the amount of water absorbed by the PAAM-RM composite obtained at 70°C increases with time and has the tendency to saturate after 1400 min. However, the amount of water absorbed by the PAAM-RM SIRPN composite obtained at 130°C is much lower and saturates after about 3 h. The lower swelling can be attributed to the SIRPN structure at the higher temperature.

Furthermore, membranes from both kinds of crosslinked materials have been prepared by hot pressing at 120 kg/cm<sup>2</sup> and 200°C for about 10 min. The results of the swelling experiments for both kinds of membranes are presented in Figure 4, which shows that the difference in their swellings is small. The amount of water absorbed by both membranes reached equilibrium at the same time (about 20 min). This is probably because, at the higher temperature of 200°C, the RM particles can crosslink among themselves thermally; a similar crosslinking probably also occurs among the PAAM chains. Consequently, the swelling of the membranes should, indeed, decrease. The differences generated by the dif-

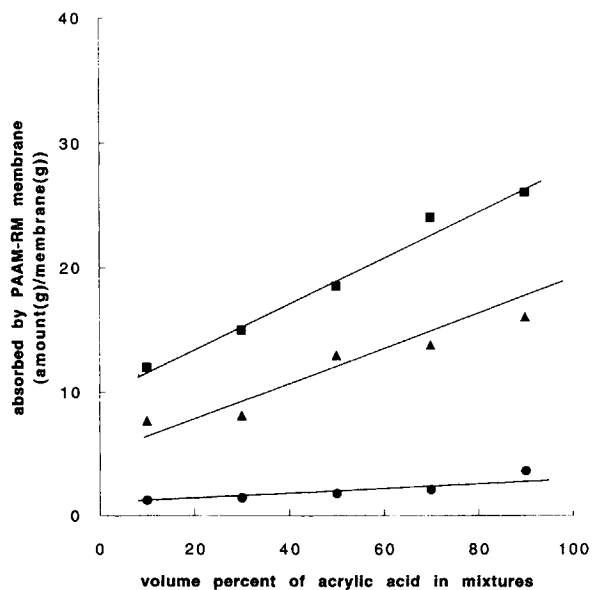


**Figure 9** The swelling of PAAM-RM membrane in tetrahydrofuran-water mixtures at room temperature: swelling time: 48 h. The symbols are as in Figure 7.

ferent crosslinking temperatures of 70 and 130°C are almost eliminated by the hot pressing.

#### Effect of the Composition of the RM on the Swelling in Water of Membranes

Three kinds of RM were synthesized by changing the weight ratio of St to UP (St/UP = 10/90, 20/



**Figure 10** The swelling of PAAM-RM membrane in acrylic acid-water mixtures at room temperature: swelling time: 48 h. The symbols are as in Figure 7.

80, 40/60) (see Table I). Using the different RM, membranes, hot-pressed at 200°C for 10 min, were prepared for a weight ratio of AAM to RM of unity. Figure 5 shows that the amount of water absorbed by these membranes is independent of the weight percent of St in RM.

#### Effect of the Composition of the Composite on the Swelling in Water

Figure 6 presents the amount of water absorbed at room temperature by the membranes (prepared at 130°C and subsequently hot pressed at 200°C for 10 min) for various weight ratios of AAM/RM as a function of time. As expected, the amount of water absorbed by the membranes decreases with increasing content of RM. Two factors affect the swelling of the membranes: the crosslinking density and the ratio between the hydrophobic and the hydrophilic components of the membranes.

#### Behavior of PAAM, RM, and PAAM-RM Membranes in Different Pure Solvents

Table III presents the solubility/swelling behavior of PAAM, RM, and PAAM-RM membranes in different solvents. PAAM is soluble in water, but does not dissolve in the other solvents listed in Table III. RM is soluble in tetrahydrofuran and dioxane, but is only swollen by acrylic acid. PAAM-RM membranes (prepared at 130°C and subsequently hot-pressed at 200°C for 10 min) can be swollen only in water and in acrylic acid.

#### Swelling of PAAM-RM Membranes in Different Mixtures of Organic Solvent and Water

To explore the possibility of using the membranes for pervaporation, swelling experiments were carried out in the mixtures: ethyl alcohol-water, acetone-water, tetrahydrofuran-water, and acrylic acid-water. The results are presented in Figures 7-10. As expected, Figures 7-9 show that the amount absorbed decreases with a decreasing amount of water in the mixture. Very little swelling occurs for a weight ratio of AAM/RM of unity. It is also important to emphasize that the membranes do not dissolve at all in water, dioxane, acetone, tetrahydrofuran, and acrylic acid. In contrast, Figure 11 shows that the amount absorbed in the mixture of acrylic acid and water increases with a decreasing amount

of water. This result can be attributed to the high swelling of the PAAM-RM composites in both acrylic acid and water.

#### CONCLUSION

Reactive microgels (RM), prepared from St and unsaturated polyester via a self-emulsification method, introduced in an aqueous acrylamide (AAM) solution can generate PAAM-RM composites. Such composites have been prepared at 70 and 130°C. Only those prepared at 70°C are partially soluble in water. Membranes were also obtained by hot pressing at 200°C the composites prepared at 130°C. These membranes were insoluble in water, dioxane, acetone, tetrahydrofuran, and acrylic acid. The swelling of the composites prepared at 130°C and of the membranes in water, dioxane, acetone, tetrahydrofuran, acrylic acid, and their mixtures: acetone-water, tetrahydrofuran-water, ethyl alcohol-water, and acrylic acid-water, was investigated.

#### REFERENCES

1. K. Meinel, U.S. Pat. 2,901,468 (Aug. 25, 1959).
2. J. Uliver, *Prod. Finish (Cincinnati)*, **34**, 66 (1970).
3. A. H. Steinhauer and H. J. Revoir, U.S. Pat. 2,926,105 (Feb. 23, 1960).
4. M. John and Z. Hussain, *J. Microbiol. Methods*, **19**, 307 (1994).
5. L. Desnoyers, I. Therien, and P. Manjunath, *Mol. Reprod. Dev.* **37**, 425 (1994).
6. A. Gramthy Latha, B. K. George, K. G. Kannan, and K. N. Ninan, *J. Appl. Polym. Sci.*, **43**, 1159 (1991).
7. W. Funke, H. Bauer, B. Joos, J. Kaczum, B. Kleiner, and O. Okey, *Polym. Int.*, **30**, 591 (1993).
8. U. Flammer, M. Hirsch, and W. Funke, *Macromol. Rapid. Commun.*, **15**, 343 (1994).
9. E. A. Collins, J. Bares, and F. W. Billmery, Jr., *Experiments in Polymer Science*, Wiley, New York, 1973.
10. M. Hirsch, PhD Thesis, University of Stuttgart, 1992.
11. A. Jr. Streitwieser and C. H. Heathcock, *Introduction Organic Chemistry*, 3rd ed, Maxwell Macmillan, New York, 1989.
12. G. Socrates, *Infrared Characteristics Group Frequencies*, Wiley, New York, 1980.
13. C. E. Melonan, *Elementary Infrared Spectroscopy*, Macmillan, New York, 1963.

Received December 7, 1994

Accepted February 14, 1995