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SHORT COMMUNICATION

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# Swelling of hydrophobically modified poly(acrylamide) and poly(acrylamide)-*co*-(acrylic acid) gels in surfactant solutions

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**Abstract** A series of hydrophobically modified polyacrylamide and polyacrylamide-*co*-poly(acrylic acid) gels with systematically varying hydrophobicity were prepared by free-radical polymerization of acrylamide, *n*-alkylacrylamides ($n = 10$, 12, and 14), and acrylic acid. The swelling of these gels was examined in water and in both anionic and cationic surfactant solutions. It was found that the gels which incorporated acrylic acid showed extremely high swelling in water. Maximum swelling was observed in gels which incorporated 10 mol% acrylic acid. The swelling of these gels was much less in solutions of both anionic and cationic surfactants than in water. The gels which did not incorporate acrylic acid demonstrated little swelling in water, but showed increased swelling in both anionic and cationic surfactant solutions with increased hydrophobicity of the gel.

**Key words** Hydrophobically modified polymers · Gels · Surfactants · Polyacrylamide · poly(acrylic acid)

## Introduction

Polymer gels are capable of undergoing dramatic volume changes in aqueous systems, at times swelling up to several hundred times their original size. The magnitude of this swelling has been shown to be affected by numerous factors including surfactant concentration, pH, and the presence of hydrophobic side chains [1–8]. The effect of such factors on the swelling of nonionic poly(*N*-isopropylacrylamide) (NIPA) gels has probably received the most attention, although research on NIPA gels has primarily focused on how these factors affect the temperature at which the gel undergoes the volume phase transition. The swelling of NIPA gels has been shown to increase in solutions of the anionic surfactant sodium dodecyl sulfate (SDS). The swelling of NIPA gels in SDS increases with surfactant concentration up to a specific concentration. This is explained by the electrostatic repulsion between the charged head groups of the SDS molecules bound within the gel [2, 9, 10], giving the polymer chains an ionic character.

Polyelectrolyte gels such as poly(acrylic acid) (pAA) or copolymer gels which contain fractions of an ionizable group such as AA have been shown to undergo increases in swelling which are dependent upon the solution pH [6, 11–13]. This increase in swelling has been attributed to the increased ionization of the AA groups at higher pH which creates significant electrostatic repulsion within the gel. Importantly, the swelling of these polyelectrolyte gels has been shown to further increase at high pH when the gel contains a small number of hydrophobic side chains [6]. The swelling of such hydrophobically modified (HM) polyelectrolyte gels has also been examined in surfactant solutions, and it has been found that at a constant pH the swelling of the gels increases with increased surfactant concentration [5]. This increase in swelling with surfactant concentration has also been observed in a HM nonionic gel, polyacrylamide (pAM) [7]. Non-modified pAM gels do not exhibit appreciable swelling, and the swelling of the modified pAM gel can be explained to result from the increased interaction of the surfactant with the hydrophobic side chains. The more surfactant bound within the gel, the stronger the electrostatic repulsion between the charged head groups of the surfactant molecules, and the greater the overall swelling of the gel.

In this note we report the swelling behavior of pAM gels of systematically varied hydrophobicity, in particular the remarkable swelling behavior of HMpAM gels which in addition incorporate some AA into the polymer backbone. The swelling of these gels was determined in water and in the presence of both anionic and cationic surfactants. The gels which incorporated AA demonstrated extremely large swelling in water, but only in the presence of hydrophobic side chains. For these gels, the swelling was substantially less in the presence of very small amounts of either anionic or cationic surfactants. On the other hand, the HM gels which did not incorporate AA exhibited low swelling in water which increased upon the addition of either anionic or cationic surfactants, with the degree of swelling depending upon the amount and the hydrophobicity of the side chain in the gel.

## Experimental

### Materials

Triethylamine (BDH) was purified by refluxing for several hours over KOH, while AM (Aldrich) was recrystallized twice from $CHCl_3$. AA (Aldrich) was distilled prior to use. The initiator 2,2′-azobis(isobutyronitrile) (AIBN) (Aldrich) was recrystallized twice from ethanol. Electrophoresis grade *N*,*N*′-methylenebisacrylamide (BIS) (BDH), (SDS) (Aldrich), dodecylamine (Sigma), and acryloyl chloride (Aldrich) were used as received without further purification. Water was purified using a Milli-Q system (Millipore).

### Methods

#### *Monomer preparation*

*N*-*n*-alkylacrylamide monomers were prepared by addition of 8.35 ml (0.06 mol) triethylamine and 8.0 ml (0.067 mol) acryloyl chloride to a cold solution of 0.05 mol *N*-*n*-decylamine (C10), *N*-*n*-dodecylamine (C12), or *N*-*n*-tetradecylamine (C14) in $CHCl_3$. This mixture was allowed to react overnight and was then washed several times with a concentrated NaCl solution containing a small amount of concentrated HCl. The $CHCl_3$ phase was then extracted several times with a $NaCl/K_2CO_3$ solution and was dried with $MgSO_4$. The mixture was then filtered and the solvent was removed by rotary evaporation. The monomer was recrystallized twice from acetone and recovered as white crystals with a yield of 61%.

#### *Gel preparation*

AM copolymer and terpolymer gels were prepared by free-radical polymerization of AM, *N*-*n*-alkylacrylamides, and, in the case of the terpolymer gels, AA, in dimethyl sulfoxide. The fraction of the *N*-*n*-alkylacrylamides was varied from 1.0 to 2.5 mol% (relative to AM), while the fraction of AA remained constant at 10 mol% (relative to AM). In all cases, 2.0 g (0.028 mol) AM was used, with 0.023 g (0.001 mol, 0.5 mol%) AIBN as initiator, and 0.022 g (0.001 mol, 0.5 mol%) BIS as crosslinker in the case of the copolymer gels, or 0.043 g (0.002 mol, 1.0 mol%) BIS in the case of the terpolymer gels. Gelation was carried out in a petri dish at approximately 70 °C overnight. The gelled samples were washed with large amounts of water for 1 week to remove residual solvent and unreacted monomer.

#### *Swelling studies*

Small pieces of gel were cut using a no. 4 cork borer and dried overnight at 70 °C. The dry samples were then weighed and placed into 20-ml screw-top vials with the appropriate equilibrating solution (water or surfactant). The gel samples remained in the surfactant solution at room temperature until equilibrium was attained (2 weeks), after which the gels were removed from the vials, blotted dry with filter paper, and weighed. The degree of swelling of the gel samples at various surfactant concentrations was determined as the ratio $(m_s - m_d)/m_d$, where $m_s$ is the mass of the swollen gel and $m_d$ is the mass of the dry gel. All reported swell ratios are averages of at least three trials. The error bars represent the standard deviation between the trials.

## Results

### HMpAM-AA gels

The HMpAM gels which incorporate AA into the backbone of the polymer chains (HMpAM-AA) exhibit large swelling ratios in water (Fig. 1), up to almost 500 times the original dry mass of the gel, while still retaining their physical shape. Without incorporation of hydrophobe (C10, C12, or C14), the swelling ratio is quite small, but increases significantly with the incorporation of even a small amount of hydrophobe. At all but the highest

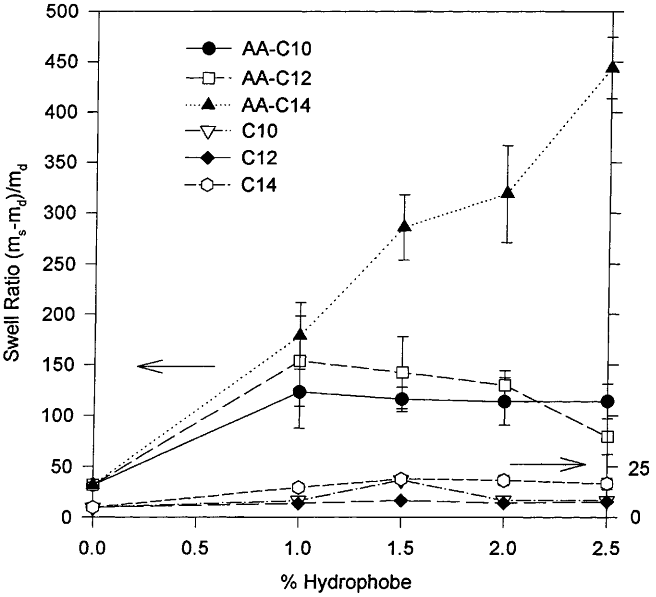

**Fig. 1** Swelling of hydrophobically modified polyacrylamide-acrylic acid (*HMpAM-AA*) (10% AA) and HMpAM gels in water. HMpAM-AA gels (*upper three curves*) scale to *left*, HMpAM gels (*lower three curves*) scale to *right*

degree of hydrophobe incorporation, swelling in water is dependent on the length of the hydrophobic side chain and increases as *n* increases from 10 to 12 to 14. As the amount of the particular hydrophobe incorporated within the gel increases to 2.5%, however, different trends are observed. For the gels which incorporate the C14 hydrophobe, the swelling continues to increase significantly as the hydrophobe content in the gel increases, while swelling ratios for the gels with the shorter hydrophobes (C12 and C10) stay about the same or even decrease slightly. In all cases, however, the observed swelling for the HMpAM-AA gels is much greater than for the HMpAM gels which do not incorporate AA (Fig. 1). As the amount of AA in the gel varies from 5 to 40% while the amount of hydrophobe is kept constant (C14, 2.5%), maximum swelling in water occurs at 10% AA (Fig. 2). HMpAM-AA gels in both anionic and cationic surfactant solutions exhibit much lower swelling than the same gels in water, even at surfactant concentrations as low as 2 mM (Figs. 3, 4). This trend is observed in all the gels, regardless of the amount of hydrophobe, the length of the hydrophobe, or the amount of AA incorporated into the gel.

### HMpAM gels

The swelling of HMpAM gels is strongly dependent upon the nature and amount of hydrophobe incorporated into the polymer gel. In all cases, the swelling of the gels increases with the hydrophobicity of the side chain and with the amount of hydrophobe in the gel (Figs. 5, 6). The swelling of all gels also increases with increasing surfactant concentration (both anionic and cationic), although the pAM-C14 gels undergo an initial decrease in swelling (with respect to swelling in water) at low concentrations of surfactant (up to 7 mM). At concentrations of surfactant above 7 mM the swelling ratios again increase with increasing surfactant concentration.

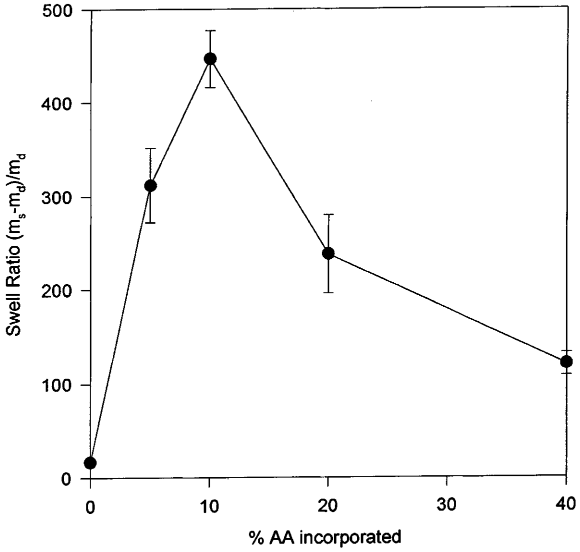

**Fig. 2** Swelling of HMpAM-AA gels with various AA content in water. All gels contain 2.5% *N-n*-tetradecylamine (*C14*) hydrophobe

## Discussion

### HMpAM-AA gels

The large swelling of the HMpAM-AA gels compared to the HMpAM gels which do not incorporate AA (Fig. 1)

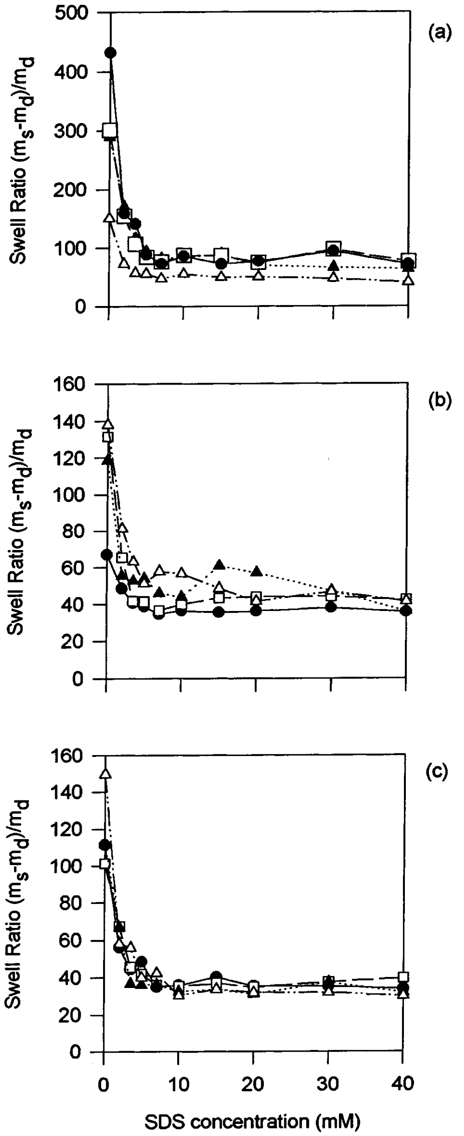

**Fig. 3a–c** Swelling of HMpAM-AA gels in sodium dodecyl sulfate (*SDS*) (10% AA). **a** C14 hydrophobe, **b** C12 hydrophobe, and **c** C10 hydrophobe. ● 2.5% hydrophobe, □ 2.0% hydrophobe, ▲ 1.5% hydrophobe, ∇ 1.0% hydrophobe

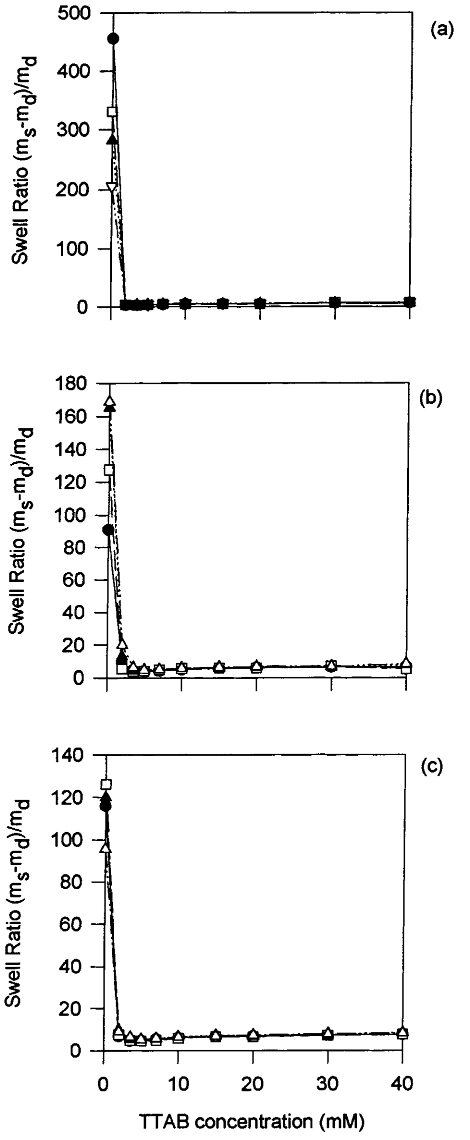

**Fig. 4a–c** Swelling of HMpAM-AA gels in, TTAB (10% AA). **a** C14 hydrophobe, **b** C12 hydrophobe, and **c** C10 hydrophobe. ● 2.5% hydrophobe, □ 2.0% hydrophobe, ▲ 1.5% hydrophobe, ▽ 1.0% hydrophobe

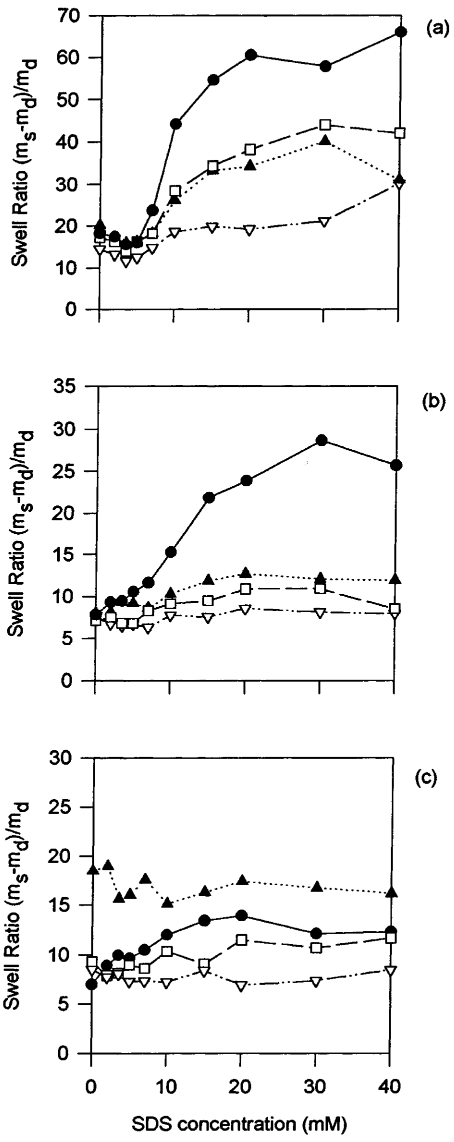

**Fig. 5a–c** Swelling of HMpAM gels in SDS. **a** C14 hydrophobe, **b** C12 hydrophobe, and **c** C10 hydrophobe, ● 2.5% hydrophobe, □ 2.0% hydrophobe, ▲ 1.5% hydrophobe, ▽ 1.0% hydrophobe

can be partially attributed to the presence of the AA groups, specifically the osmotic pressure exerted by the counterions when AA becomes ionized, together with the repulsive Coulombic forces. Large swelling ratios similar to those reported here have been reported by Philippova et al. [5] for hydrophobically modified pAA gels in water, and were also attributed to the ionic nature of the AA groups as described previously. The presence of AA alone can explain the increase in swelling observed here between the pAM and pAM-AA gels which do not incorporate hydrophobe, but cannot solely account for the extreme increases in swelling which are observed when even a small amount of hydrophobe is incorporated into the gel. In this study we have found that pAM-AA gels which incorporate hydrophobe swell significantly more in water than those which do not incorporate hydrophobe and also swell significantly more than those which incorporate hydrophobe but not AA (Fig. 1). This behavior of the pAM gels was not observed for the pAA gels studied by Philippova and coworkers [5, 6], who found that pAA gels which are not HM swell to a similar extent as those which are HM. The lower swelling observed by us for the pAM-AA gels which do not incorporate hydrophobe compared to those for pAA gels without hydrophobe observed by Philippova and coworkers can be attributed to the fact

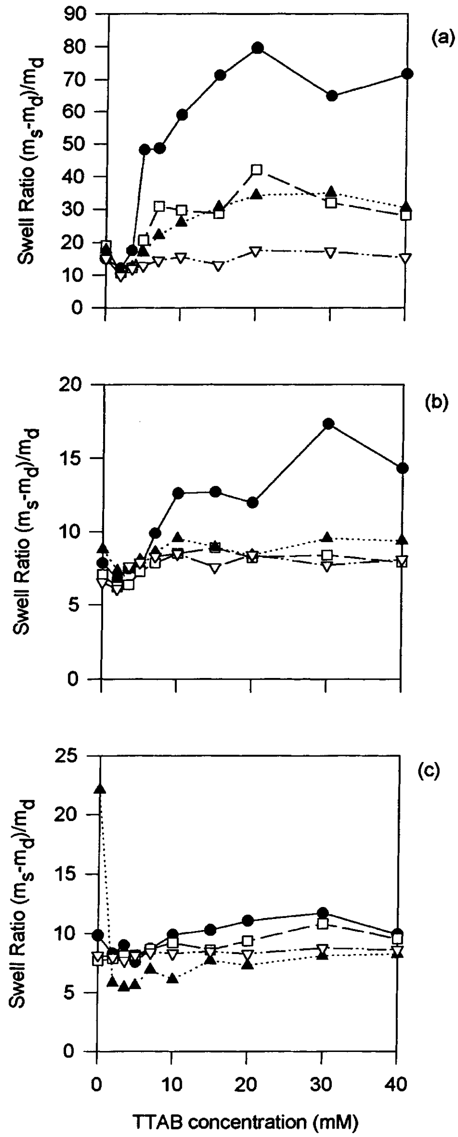

**Fig. 6a–c** Swelling of HMpAM gels in TTAB. **a** C14 hydrophobe, **b** C12 hydrophobe, and **c** C10 hydrophobe. ● 2.5% hydrophobe, □ 2.0% hydrophobe, ▲ 1.5% hydrophobe, ▽ 1.0% hydrophobe

that the fraction of AA in the pAM-AA gels reported here is fairly low (10%) as opposed to the pure pAA gels studied by Philippova and coworkers. Because the fraction of AA in the pAM-AA gel is much lower, the repulsive forces arising from the ionization of the AA groups in this gel sample are much weaker than those which arise from the ionization of the pure pAA gel. However, the fact that the HMpAM-AA gels swell significantly with a small incorporation of hydrophobe while maintaining the AA content of the gel indicates that the hydrophobe, and the interaction of the hydrophobe with AA groups, plays an extremely important role in the swelling of the HMpAM-AA gels. A discussion of the possible roles the hydrophobe may play in the swelling behavior is presented below.

In general, as the hydrophobe increases in length, the swelling of HMpAM-AA gels in water also increases (Fig. 1). This behavior is especially apparent in the swelling of the gels which incorporate the C14 hydrophobe. The increase in swelling may be envisioned as a separation of individual polymer chains within the gel, which may increase with hydrophobe length simply due to the nature of the hydrophobes, i.e. as bulky groups (getting bulkier as the hydrophobe chain length is increased) they occupy a great deal of space between the chains, facilitating an overall increase in the swelling of the gel. As the content of hydrophobe is increased, the chains are further prevented from coming together and the overall swelling of the gel is observed to increase. This works together with the AA groups, which, when ionized, cause the polymer chains to adopt an extended conformation due to electrostatic repulsion; thus, the extended polymer chains are further separated due to the presence of bulky groups which prevent the chains from interacting.

The swelling increase with hydrophobicity may also arise from chain–chain repulsion between the hydrophilic backbone and the hydrophobic side chain, which again increases with hydrophobe length. Rosén et al. [7] recently observed similar hydrophobe-dependent swelling in water for pAM gels which incorporated up to 2.6% poly(ethylene oxide) (PEO) side chains. They attributed the hydrophobe-dependent swelling to the pendant chain architecture and/or the additional chain–chain repulsions between the pAM backbone and the PEO side chains, which can also explain the observations seen here. However, we have to conclude that the exact mechanism which causes the remarkable, hydrophobe-dependent swelling of the HMpAM-AA gels is unclear at this time and needs further elucidation.

At the highest incorporation of hydrophobe (2.5%), we see a slightly different trend. At this degree of incorporation, the gels with the C12 hydrophobe actually undergo a slight decrease in swelling. Philippova et al. [5] observed that the swelling of HMpAA gels decreased as the amount and the length of the hydrophobic side chain in the gel was increased. This decrease in swelling with increased hydrophobicity was explained to result from the attractive hydrophobic interactions between the hydrophobic side chains in the gel. This same explanation of hydrophobic interactions can explain the decrease in swelling of the pAM-AA-C12 gels with the increase in the amount of hydrophobe in the gel that is observed here (Fig. 1). At low concentrations of hydrophobe, the hydrophobic attraction of the side chains is not strong enough to overcome the repulsive osmotic pressure created by the counterions of the ionized AA groups. As the amount of hydrophobe in the gel is increased, however, the strength of the hydrophobic interactions increases, and a decrease in gel swelling is observed. It is expected that as the hydrophobe content increases beyond 2.5%, this decrease in swelling will continue and that a decrease in swelling for the C14-modified gels will also be observed beyond 2.5%. It was not possible, however, to prepare gels with hydrophobe contents greater than 2.5% due to the insolubility of the monomers in the solvent used for polymerization.

As the AA content within the HM gels reported here is increased from 5 to 10%, a significant increase in swelling is observed (Fig. 2), which can be attributed to the presence of more ionized AA groups within the gel; however, as the amount of AA is further increased to 20% and then to 40%, swelling decreases significantly. However, the swelling observed at 40% AA incorporation is still much higher than that observed for HMpAM gels which do not incorporate AA, indicating that the AA groups and the hydrophobes continue to interact to produce an increase in swelling that is greater than that which can be attributed to either the AA or the hydrophobe alone, or to a simple additive effect of the two. The detailed reason for this complex swelling behavior in the terpolymer gels remains to be investigated.

The decrease in swelling of the HMpAM-AA gels in surfactant solutions (Figs. 3, 4) can be attributed to the well-known surfactant–hydrophobe interaction. Even at low concentrations the surfactant–hydrophobe interaction is strong enough to overcome the repulsive osmotic pressure created by the ionized AA groups. The surfactants form mixed aggregates with the hydrophobes on different chains, pulling the chains together and resulting in a decrease in the swelling of the gel. This reduced swelling is observed even with the anionic surfactant SDS, indicating that the hydrophobic interaction is strong enough to overcome the electrostatic repulsion between the polymer chain and surfactant ions. The decrease in swelling is much more dramatic with the cationic surfactant tetradecyl trimethyl ammonium bromide (TTAB), a result of the oppositely charged surfactant masking the charge of the ionized AA groups within the gel.

### HMpAM gels

In the presence of surfactants, the swelling ratios of HMpAM gels increase both with increasing hydrophobicity of the gel and with increasing surfactant concentration. This effect is directly related to surfactant binding by the gel hydrophobe, and is observed for both SDS and TTAB (Figs. 5, 6). There is a small initial decrease in swelling upon surfactant addition, observed most strongly in the C14-modified gels. This is attributed to the formation of mixed surfactant–hydrophobe aggregates involving hydrophobes from different chains, which brings the individual polymer chains in the gel closer together, resulting in an overall decrease in swelling. As the concentration of surfactant increases, however, there is no longer a need to incorporate hydrophobes from different chains, as there are enough surfactant molecules present to completely surround each hydrophobe, and an increase in swelling is subsequently observed due to charge repulsion of the surfactant ions. This swelling reaches a maximum when the hydrophobes are completely surrounded by surfactant molecules and hence no more surfactant can be incorporated into the gel. In the C10- and C12-modified gels the hydrophobic interaction between the side chains is not strong enough to form mixed surfactant–hydrophobe aggregates with hydrophobes from different chains, and therefore the initial decrease in swelling is not as pronounced as in the C14-modified gels.

This trend of increased swelling with increasing hydrophobicity of the gel can be directly correlated to what is observed in HM linear polymers in surfactant solutions. Binding studies of TTAB to C10-, C12-, and C14-modified linear polymers demonstrate clearly that as the length of the hydrophobe or the amount of hydrophobe in the polymer is increased, there is a corresponding increase in TTAB bound to the polymer [14]. In the case of the HM gels, the same increase in binding of surfactant with hydrophobicity manifests itself in an increase in swelling as a result of the increased repulsion of the surfactant ions bound within the gel.

Clearly, this study shows that there is a strong synergistic effect of hydrophobic moieties and ionic charge on the swelling behavior of HMpAM-AA gels. Also, this effect is different for the low-charge networks and low incorporations of hydrophobe studied here compared to the high-charge acrylate networks and higher incorporation of hydrophobes studied by others [5, 6]. Further investigations on the origin of this synergistic effect are required.

## References

1. Tanaka T, Fillmore D, Sun S-T, Nishio I, Swislow G, Shah A (1980) Phys Rev Lett 45:1636
2. Kokufuta E, Zhang Y-Q, Tanaka T, Mamada A (1993) Macromolecules 26:1053
3. Sakai M, Satoh N, Tsujii K, Zhang Y-Q, Tanaka T (1995) Langmuir 11:2493
4. Kokufuta E, Nakaizumi S, Ito S, Tanaka T (1995) Macromolecules 28:1704
5. Philippova OE, Hourdet D, Audebert R, Khokhlov AR (1996) Macromolecules 29:2822
6. Philippova OE, Hourdet D, Audebert R, Khokhlov AR (1997) Macromolecules 30:8278
7. Rosen O, Piculell L, Hourdet D (1998) Langmuir 14:777
8. Sasaki S, Yamazoe Y, Maeda H (1997) Langmuir 13:6135
9. Kokufuta E, Suzuki H, Sakamoto D (1997) Langmuir 13:2627
10. Inomata H, Goto S, Saito S (1992) Langmuir 8:130
11. Beltran S, Baker JP, Hooper HH, Blanch HW, Prausnitz JM (1991) Macromolecules 25:549
12. Kawasaki H, Sasaki S, Maeda H (1997) J Phys Chem B 101:4184
13. Hirotsu S, Hirokawa Y, Tanaka T (1987) J Chem Phys 87:1392
14. Howley C, Marangoni DG, Kwak JCT (1997) Colloid Polym Sci 275:760