

# Thermoreversible swelling behaviour of hydrogels based on N-isopropylacrylamide with acidic comonomers

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Hydrogels have been prepared by free radical polymerization in aqueous solution of N-isopropylacrylamide (NIPA) and of NIPA with acrylic acid (AA), methacrylic acid (MAA) and 2-methyl-2-acrylamido-propanesulfonic acid (AMPS) as comonomers. For each copolymerization three different compositions were used, and for all systems three concentrations of a tetrafunctional crosslinker were employed. Swelling ratios,  $r = (\text{mass hydrogel}/\text{mass dry polymer})$ , were measured on heating from 20°C and then on cooling back to 20°C, and the swelling/deswelling was shown to be thermoreversible. Lower critical swelling temperatures ( $T_c$ ) were exhibited except for copolymers of medium–high content of AMPS. The influences of composition and crosslinker concentration on  $r$  and  $T_c$  are discussed. The unusual behaviour of hydrogels containing MAA as comonomer is explained on the basis of attractive hydrophobic interactions. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

Certain polymers and copolymers, generally crosslinked chemically, swell in water to form environmentally sensitive hydrogels<sup>1</sup>. This response can be to a variety of factors such as photoirradiation, components additional to water in the swelling medium, pH, pressure and temperature. The last of these has received considerable attraction and potential applications of thermally reversible hydrogels have been reviewed<sup>1</sup>. Among such applications, one of the most attractive is that of affording a means of separation which constitutes, in principle, a viable alternative to ultrafiltration.

Many useful and valuable materials, especially macromolecules, exist or are produced in dilute aqueous solution and a clear need exists for an efficient means of separation via removal of water<sup>2,3</sup>. Examples include concentration of antibiotics in fermentation liquors, recovery of protein products of genetically engineered micro-organisms, rejection of albumins from cheese whey and rapid absorption of fluids from wounds at ambient temperature. Absorption can be effected simply by silica gel, but this has a limited capacity and necessitates high temperature drying prior to re-use. Ultrafiltration requires high pressure and suffers from shear-induced concentration polarization near the membrane. The procedure involving thermoresponsive gels is based on an entirely different principle. Operation at atmospheric pressure and ambient temperature, necessity for only slight warming for re-use and capacity of a very small mass of dry gel to concentrate a large volume of solution all constitute attractive features regarding production and operating costs.

The volume change in these gels is due to a thermodynamic characteristic of the linear polymer: a lower critical solution temperature (LCST)<sup>4,5</sup>. The relevant theory involves a subtle interplay of several parameters. However, in essence, certain polymers of appropriate composition and crosslinking density can swell enormously in water at ambient temperature and shrink at an elevated consolute point, the lower critical swelling temperature (LCSWT). The same process applied to an aqueous solution leads to selective absorption of water into the gel, thereby concentrating the required solute in the remaining solution. Warming the isolated swollen hydrogel to the LCSWT releases absorbed water, which is discarded, allowing the shrunken gel to be reused at ambient temperature for the same or a different operation.

There is evidence<sup>6</sup> that the LCST and LCSWT do not differ greatly. Here this critical temperature will be denoted by  $T_c$ . The efficiency of gels in excluding macromolecules during swelling is an important factor and will depend on the crosslinking density.

Hydrogels comprising or containing units of N-isopropylacrylamide (NIPA) are among the most widely studied of materials of this type. In fact, reports have been made of their use not only to imbibe water and exclude macromolecules but also<sup>7</sup> to absorb and subsequently release heavy metal and other ions from aqueous solution. The coil-to-globule transition in aqueous poly-(NIPA) solutions and gels occurs at  $T_c$  and results from changes in balance between various types of interaction, but especially hydrogen bonding and hydrophobic interaction<sup>8</sup>.

Studies involving copolymers containing NIPA have been made, including the use of acidic comonomers<sup>9–11</sup>. Here, however, we wish to make a more systematic and

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comparative examination of the role of the nature and content of comonomer as well as the content of crosslinker. The acidic comonomers selected are acrylic acid (AA), methacrylic acid (MAA) and 2-methyl-2-acrylamido propane sulfonic acid (AMPS). At this stage no studies have been made on separations, attention being focused on swellability and  $T_c$ .

## EXPERIMENTAL

### Materials

AA, MAA, NIPA, the crosslinker N,N-methylene bisacrylamide (BIS) and the activator N,N,N',N'-tetramethylene diamine (TEMED) were purchased from Aldrich Chemical Co. AMPS and the initiator ammonium persulfate (APS) were obtained from Sigma Chemical Co. and Wilkinson-Vickers Ltd, respectively. AA and MAA were purified by distillation under reduced pressure and NIPA was recrystallized from toluene/*n*-hexane (27/73 v/v). Deionized water from a Millipore Milli-U10 water purification system was used in the preparation of hydrogels and in the swelling experiments. All other chemicals were used as received.

### Synthesis of hydrogels

The gels were prepared by radical crosslinking copolymerization in aqueous solution. In all cases the ratio NIPA/water was 15/85 (wt/wt). Preliminary tests showed the need to use equimolar proportions of APS and TEMED. To obtain a reasonable rate of reaction at the selected polymerization temperature, 25°C, the concentration of initiator and activator was fixed at 1 mol% with respect to monomer or total monomers. The acidic comonomer and BIS were added according to the desired concentration. All materials except for NIPA were added as aqueous solutions to the flask containing solid NIPA. The aqueous mixture, not yet containing TEMED, was bubbled with nitrogen for 10 min in an ice/water bath, after which the activator was added. The feed mixtures were introduced into moulds formed by two glass microscope slides separated by a 50 × 10 mm poly(tetrafluoroethylene) gasket of 2 mm thickness. The moulds were put into sealed plastic bags and the systems were allowed to polymerize in a water bath at 25°C (±0.1°C). Different polymerization times were checked and it was found that 6 h was sufficient to obtain very high conversions. After that period of time the gels were removed, weighed and washed thoroughly with water. Finally, the gels were dried to constant weight in a vacuum oven at 45°C. Polymerizations were carried out to very high fractional conversions on a weight basis,  $C$  ( $C \geq 0.98$ ), as indicated by the ratio of weight of extracted dry gel to that of total monomer(s) initially. Since the extracted dry gel is crosslinked polymer, the value of  $C$  is, in principle, only an apparent one that does not allow for possible conversion of monomer(s) to soluble linear polymer. Allowance for the latter would give an actual fractional conversion greater than the apparent one, i.e. > 0.98. Consequently the sol fraction removed cannot exceed 0.02 and the overall average copolymer composition can be approximated very well to the initial feed composition.

### Swelling measurements

Each dried sample was swollen in water at room

temperature until equilibrium was confirmed (24 h). The samples were brought to each of several increasing temperatures and held there for 6 h to attain swelling equilibrium. It should be stressed that determination of the water content expressed as a swelling ratio,  $r$ , via equation (1) in which  $w_h$  and  $w_x$  are the weights of swollen and dry samples, is a demanding procedure requiring great care and attention.

$$r = \frac{w_h}{w_x} \quad (1)$$

The swollen strip of hydrogel at a fixed swelling temperature was removed from its container and surface-dried lightly and rapidly with filter paper; it was then weighed in a stoppered tared vial. The sample was then replaced in the water for a minimum of 30 min and  $w_h$  was determined again as before. This procedure was generally repeated at least three times and an average value of  $w_h$  was used to obtain  $r$ . Uncertainty or error in  $r$  is taken to arise solely from uncertainty or error in  $w_h$ , which was overall ca. ±0.5% with respect to the average value of  $w_h$  used to calculate  $r$ . For swelling at each of several decreasing temperatures exactly the same procedure was adopted. The absence of any sol fraction in the extracted samples used for swelling was confirmed by deliberately drying to completeness and weighing the samples after swelling/deswelling over a range of temperature. The final weight was identical to the initial weight of the dry sample prior to the swelling/deswelling.

## NOMENCLATURE

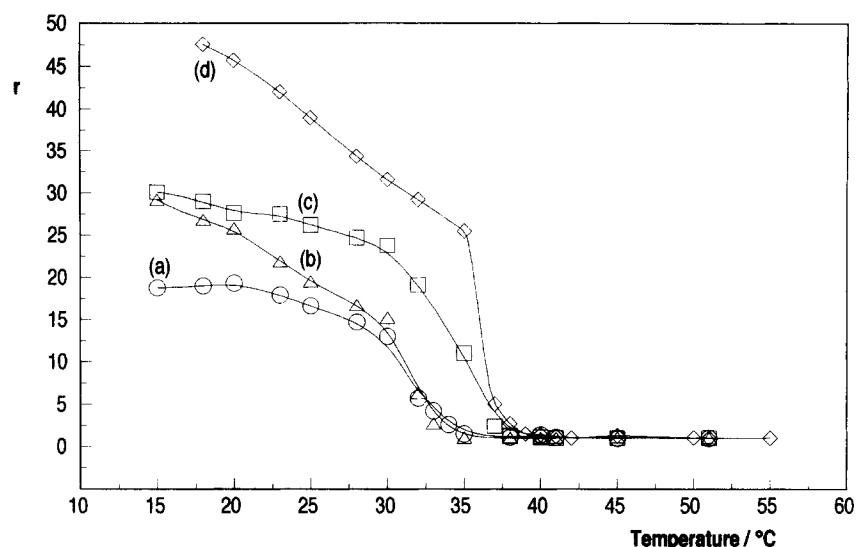
The samples are denoted by the previously given abbreviations for components together with their compositions. The composition of an acidic comonomer is its mol% with respect to NIPA and the content of BIS is its mol% with respect to monomer or total monomers. For example a hydrogel, NIPA/MAA5/BIS0.5, is synthesized from 85 g water + 15 g NIPA ( $\equiv 15/113.16$  mol NIPA). The content of MAA is  $(5/100)(15/113.16)$  mol, and the content of BIS is  $(0.5/100)[(15/113.16) + (5/100)(15/113.16)]$ . Note also that (see 'Experimental') the contents of APS and TEMED in the hydrogel synthesis are each  $(1/100)[(15/113.16) + (5/100)(15/113.16)]$  mol.

## RESULTS AND DISCUSSION

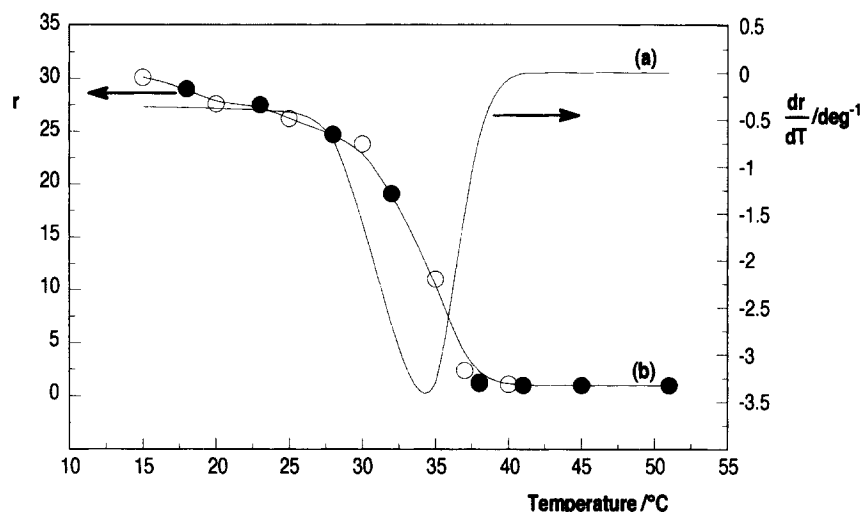
The swelling capacity in hydrogels is commonly denoted by the equilibrium water constant (EWC), which is the mass of imbibed water relative to the total mass of swollen hydrogel. Here we are adopting the gravimetric swelling ratio  $r$  (equation (1)). It is readily shown that  $EWC = (r - 1)/r$ .

The contents of acidic comonomers were 0 (i.e. pure poly(NIPA)), 1, 5 and 10 mol%, and for each of the systems the contents of BIS were 0.25, 0.5 and 1 mol%. Since three different acidic comonomers were used, the total number of hydrogels investigated was 30.

For all these polymers  $r$  was measured at several (at least 10) temperatures starting from 15°C. The selected temperatures ( $T$ ) were separated by ca. 5°C except in the vicinity of  $T_c$  where they were separated by ca. 1°C. Examples of plots of  $r$  vs  $T$  are given in Figure 1, which relates to poly(NIPA) and three copolymers, all having the same content of crosslinker and the same content of acidic comonomer for the copolymeric gels. The same



**Figure 1** Variation of swelling ratio  $r$  with temperature for hydrogels of (a) NIPA/BIS0.5, (b) NIPA/MAA1/BIS0.5, (c) NIPA/AA1/BIS0.5 and (d) NIPA/AMPS1/BIS0.5. For clarity, no distinction is made between data points obtained in heating and cooling cycles



**Figure 2** Influence of temperature on swelling ratio  $r$  for hydrogel of NIPA/AA1/BIS0.5. (a) Differential plot of  $dr/dT$  vs  $T$ . (b) Data obtained on heating ( $\circ$ ) and on cooling ( $\bullet$ )

general form of curves is displayed by the four systems, viz. a fall in  $r$  with  $T$ , which becomes sharper in the vicinity of the critical temperature. Finally, at higher temperature there is complete deswelling and  $r$  attains a value of unity. The main difference among the systems lies in the low temperature region ( $T < T_c$ ) where the swelling of poly(NIPA) is only moderate but increases in value with MAA as comonomer, increasing further with AA as acidic compound and attaining its highest values in poly(NIPA-co-AMPS).

Because the deswelling is not discontinuous, it is not easy to assign an exact value to  $T_c$  and cognizance of this difficulty is rarely taken in the literature. Hence we have used a computer program to afford the derivative  $dr/dT$  at each temperature. In an example of the relevant plot (Figure 2a) it is seen that, although  $dr/dT$  must be zero at high temperature where  $r$  has a constant value of unity, at low temperature  $r$  decreases with  $T$  and hence  $dr/dT < 0$ . The critical temperature is indicated clearly at the minimum of the curve. Figure 2b is the normal plot of  $r$  vs  $T$  not only for data obtained on heating but also

for the cooling process. As all the points fall on a common curve, the reversible nature of swelling and deswelling is confirmed.

For brevity, swelling curves are not reproduced here for all the systems. Instead, the main features are extracted and summarized in Table 1 for poly(NIPA) and in Tables 2, 3 and 4 for copolymers containing AA, MAA and AMPS, respectively. Specific features and comments on them are now considered.

#### Poly(NIPA)

At ambient temperature, linear poly(NIPA) dissolves in water to adopt an extended chain conformation (coil), which changes to a more compact configuration (globule) on heating to the LCST. The transition at this temperature results from changes in the balance between hydrogen bonding interactions, that are disrupted, and hydrophobic interactions between water and the N-isopropyl groups.

With regard to the crosslinked poly(NIPA), Table 1 indicates that the polymer has a critical temperature

**Table 1** Swelling ratio at, below and above the critical temperature for NIPA hydrogels of different crosslinker content

NIPA/BIS1		NIPA/BIS0.5		NIPA/BIS0.25	
<i>T</i> (°C)	<i>r</i>	<i>T</i> (°C)	<i>r</i>	<i>T</i> (°C)	<i>r</i>
20	12.8	20	19.3	20	22.9
34 <sup>a</sup>	5.4	32 <sup>a</sup>	7.2	32 <sup>a</sup>	8.6
40	1.0	40	1.0	40	1.1

<sup>a</sup> Critical temperature**Table 2** Swelling ratio at, below and above the critical temperature for poly(NIPA-co-AA) hydrogels of various crosslinker content

NIPA/AA1/BIS1		NIPA/AA1/BIS0.5		NIPA/AA1/BIS0.25	
<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>
20	23.7	20	27.6	20	50.2
34 <sup>a</sup>	12.2	34 <sup>a</sup>	14.1	34 <sup>a</sup>	18.1
40	1.0	40	1.1	40	1.1
NIPA/AA5/BIS1		NIPA/AA5/BIS0.5		NIPA/AA5/BIS0.25	
<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>
20	24.9	20	36.6	20	79.0
34 <sup>a</sup>	11.1	35 <sup>a</sup>	15.2	35 <sup>a</sup>	54.1
40	1.0	40	1.1	40	1.1
NIPA/AA10/BIS1		NIPA/AA10/BIS0.5		NIPA/AA10/BIS0.25	
<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>
20	62.2	20	85.5	20	131
47 <sup>a</sup>	18.4	47 <sup>a</sup>	27.6	47 <sup>a</sup>	44.5
51	1.2	51	1.1	51	1.2

<sup>a</sup> Critical temperature**Table 3** Swelling ratio at, below and above the critical temperature for poly(NIPA-co-MAA) hydrogels of various crosslinker content

NIPA/MAA1/BIS1		NIPA/MAA1/BIS0.5		NIPA/MAA1/BIS0.25	
<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>
20	17.3	20	25.8	20	36.3
32 <sup>a</sup>	5.7	32 <sup>a</sup>	7.2	32 <sup>a</sup>	8.9
35	1.0	35	1.0	37	1.0
NIPA/MAA5/BIS1		NIPA/MAA5/BIS0.5		NIPA/MAA5/BIS0.25	
<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>
20	17.0	20	22.7	20	35.6
32 <sup>a</sup>	6.7	32 <sup>a</sup>	8.4	32 <sup>a</sup>	11.3
37	1.0	37	1.0	37	1.0
NIPA/MAA10/BIS1		NIPA/MAA10/BIS0.5		NIPA/MAA10/BIS0.25	
<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>
20	18.4	20	25.3	20	33.5
32 <sup>a</sup>	8.2	32 <sup>a</sup>	10.4	32 <sup>a</sup>	16.2
40	1.0	40	1.0	40	1.0

<sup>a</sup> Critical temperature

essentially independent of crosslinker content and undergoes complete deswelling at ca. 6°C above  $T_c$ . The ability to imbibe water at ambient temperature, however, is only moderate at high crosslinker content and, although this capacity is enhanced on reducing the content of BIS to 0.25 mol%, the resultant value of  $r = 22.9$  is not exceptionally high in this neutral polymer.

#### Nature of the comonomer

At comparable concentration of BIS and comonomer, the swelling ratio at ambient temperature is enhanced

with respect to the value of  $r$  for PNIPA, the effect increasing in the order  $r$  (PNIPA) <  $r$  (with MAA) <  $r$  (with AA) <  $r$  (with AMPS). One exception is evident in Table 4 for NIPA/AMPS1/BIS1, for which  $r = 16.2$ . In comparison with all other relevant tabulated data this magnitude of  $r$  would be expected to be >  $r$  (with AA), viz. > 24.9. We have considered several possibilities but are unable to provide a satisfactory explanation of this single oddity among all the entries in Tables 1–4.

Enhancement of water absorption by introduction of hydrophilic groups into PNIPA is, of course, to be expected<sup>12,13</sup>. Perhaps less expected is the significantly lower swelling induced by MAA groups compared with that by AA units, even though both moieties display weak anionic polyelectrolyte characteristics. This point will be discussed in the next section. With the exception of gels of the highest content (10 mol%) of AA, it is seen that the critical temperature is essentially unchanged among the PNIPA, P(NIPA-co-MAA) and P(NIPA-co-AA) systems and also for P(NIPA-co-AMPS) of low content of AMPS. At moderate or high AMPS content,  $T_c$  is either high or is not exhibited at all, viz. there is a smooth, continuous fall in  $r$  with temperature and  $dr/dT$  vs  $T$  does not have a minimum, the variation being linear.

#### Concentration of comonomer

With AA and AMPS as comonomer, there is a strong tendency for  $T_c$  to increase with content of comonomer. The linear homopolymers of AA and AMPS in water do not exhibit a lower critical solution temperature. Hence, the balance between hydrogen bonding and hydrophobic

interactions that result in coil-to-globule transition at 34°C in PNIPA must be disturbed towards enhanced hydrogen bonding, leading to a wider span of solubility or, in the case of a gel, a higher span of temperatures before  $T_c$  is attained. This effect will increase with increasing content of AA or AMPS units.

However, the linear homopolymer of MAA is exceptional in the respect that in aqueous solution it does exhibit inverse solubility-temperature behaviour, the reported<sup>14,15</sup> lower critical solution temperature being ~ 56°C. Consequently, the PMAA chains in the copolymers do not

**Table 4** Swelling ratio at, below and above the critical temperature for poly(NIPA-co-AMPS) hydrogels of various crosslinker content

NIPA/AMPS1/BIS1		NIPA/AMPS1/BIS0.5		NIPA/AMPS1/BIS0.25	
<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>	<i>T</i> °C	<i>r</i>
20	16.2	20	45.7	20	76.7
33 <sup>a</sup>	5.4	36 <sup>a</sup>	15.1	37 <sup>a</sup>	14.5
37	1.0	42	1.0	65	1.1
NIPA/AMPS5/BIS1		NIPA/AMPS5/BIS0.5		NIPA/AMPS5/BIS0.25	
20	49.6	20	117	20	326
55 <sup>a</sup>	12.2	55	49.4	55	200
60	1.0	65	17.8	65	138
NIPA/AMPS10/BIS1		NIPA/AMPS10/BIS0.5		NIPA/AMPS10/BIS0.25	
20	68.6	20	206	20	444
40	61.3	40	171	40	402
60	31.4	60	122	60	367

<sup>a</sup> Critical temperature

elevate the  $T_c$ , the value of which is similar to that of PNIPA, at least at concentrations of MAA used here (Table 3).

With regard to swelling ratios themselves, there is a general trend for  $r$  to increase with increase in content of acidic comonomer, when the latter is AA or AMPS. One instance where this increase is less than would be expected is NIPA/AA5/BIS1 ( $r = 24.9$ ) compared with NIPA/AA1/BIS1 ( $r = 23.7$ ). Here the enhanced swelling induced by additional AA is clearly balanced by the high crosslinking density (1 mol% BIS).

Poly(NIPA-co-MAA) gels have entirely different characteristics in the respect that, at a particular content of crosslinker, the swelling ratio is essentially independent of content of MAA. There are significant differences among the linear polyelectrolytes PAMPS, PAA and PMAA. The first of these is an extremely strong acid, and indeed incorporation of a very high concentration of NaCl is needed to suppress its polyelectrolyte behaviour in water<sup>16</sup>. PAA is a rather stronger acid than PMAA. Thus, at pH = 5.7, the degrees of dissociation for the former and the latter are 0.3 and 0.1 respectively, the  $pK_a$  values under these conditions being 6.4 for PAA<sup>17</sup> and 6.9 for PMAA<sup>18</sup>. However, this difference is not a dramatic one and is unlikely to be the dominant factor in resolving the issue in question.

There is experimental evidence that linear PMAA in aqueous solution adopts a relatively compact conformation<sup>19,20</sup> emanating from hydrophobic interactions between methyl groups. In the corresponding copolymeric hydrogels containing MAA units this effect will be maintained and indeed should increase with MAA content, with the result that enhanced formation of a compact or globular conformation may actually decrease the level of swelling. Acting against this effect is the increasing content of weakly ionized carboxyl groups which (cf. findings for copolymers containing AA, Table 2) increase the swelling. The net balance for the MAA containing gels is for the values of  $r$  to become sensibly independent of content of MAA.

Some measure of support for this postulate is afforded by the findings on swelling in aqueous media of different

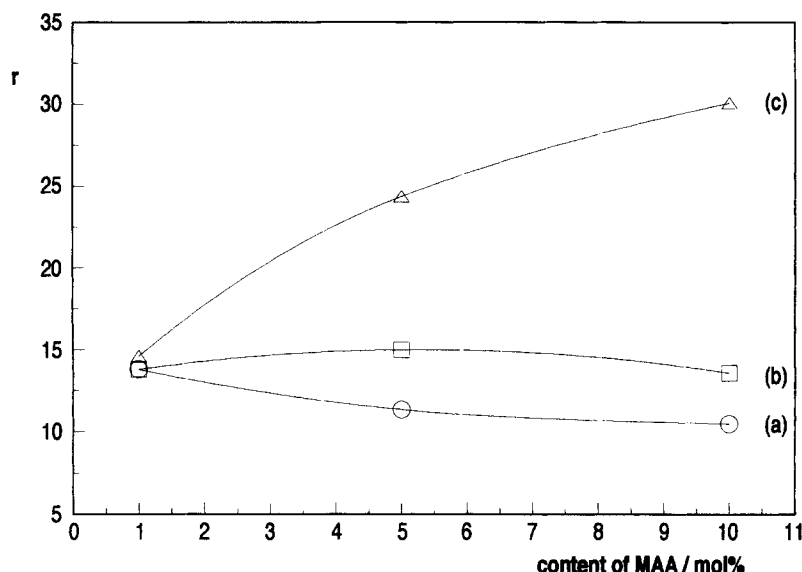
pH, viz. pH = 1 (HCl solution), pH = 5.7 (water) and pH = 12 (NaOH solution). Figure 3 shows that at low pH, although the change of swelling ratio is not large, the sequence is for  $r$  to decrease with increasing content of MAA. Here the lowest level of swelling occurs at the highest MAA content, protonation of the carboxylic groups inducing a compact conformation. At pH = 5.7 the value of  $r$  is sensibly independent of copolymer composition. At high pH the behaviour is the opposite of that at low pH. Very large swelling occurs for the gel of highest MAA content, where the MAA units are predominantly in the ionized state<sup>21,22</sup>. Under these conditions, development of a compact conformation is prevented and electrostatic repulsions between anionic groups lead to enhanced swelling.

#### Concentration of crosslinker

Neither the true (or effective) crosslinking densities nor the molecular mass between junction points has been measured. However, for purposes of comparison it will suffice to consider instead the concentration of BIS (in mol%).

When there is finite swelling, i.e. when  $r > 1$ , all systems exhibit the customary decrease in  $r$  with increasing content of BIS. For poly(NIPA) and most of the copolymers, the value of  $T_c$  is unaffected by the crosslinker concentration. It is to be noted that this independence holds for poly(NIPA-co-AA) of the highest content of AA (10 mol%), even though the actual constant value of  $T_c$  is elevated to 47°C (Table 2). In the other highly swellable systems, i.e. those including AMPS, there is only a slight decrease in  $T_c$ , measurable when the content of AMPS is 1 mol% (Table 4). When the content of AMPS is 5 mol%,  $T_c$  attains the largest value measured for all the hydrogels, i.e. 55°C at the highest content of BIS used. At lower content of BIS and for all the copolymers containing 10 mol% of AMPS, no  $T_c$  could be detected.

Among the most detailed theoretical treatments of phase behaviour and, in particular, influence of crosslinking density is that of Cussler and co-workers<sup>23</sup>. It requires a knowledge of several pure component parameters and an



**Figure 3** Influence of MAA concentration on swelling ratio at 25°C, for hydrogels of poly(NIPA-co-MAA) all containing 1 mol% of BIS. The pH values of the swelling media are (a) 1, (b) 5.7 and (c) 12

adjustable correction parameter. Comparison with experimental results for poly(NIPA) and poly(diethylacrylamide) afforded good grounds for the validity of the theory for these two non-ionic gels<sup>24</sup>. To the unavailability of the relevant parameters at present is compounded the problem that in the present case each of the polymeric pure components is different with respect to nature and/or composition. Consequently, the present findings have been given only qualitatively. It is, nonetheless, of interest to note that the treatment of Cussler *et al.* does refer to the possibility of obscuring the consolute region with increasing crosslinking density for systems wherein the solvent has a much larger cohesive density than is exhibited by the gel (which is invariably so in hydrogels).

## CONCLUSIONS

The relatively simple synthesis has produced crosslinked polymers to high conversion. At ambient temperature the swelling ratios range from moderate up to those characteristic of superabsorbent polymers<sup>25</sup>. For many of the gels, deswelling to the dry state is complete at a temperature not too displaced from  $T_c$ , the latter lying generally at ca. 32–37°C. With specific reference to the potential of these materials as separation devices, the higher the initial value of  $r$  the better, in order that the initial aqueous test solution may thereby become more concentrated. With regard to swelling, completeness of deswelling, and avoidance of very high temperatures, sample NIPA/AA5/BIS0.25 appears promising. On the other hand, selectivity in excluding polymers below a certain size from the gel pores is also an important requirement and the nominal crosslinking density (0.25 mol% BIS) of this polymer could well be too low for this purpose. Hence, a more suitable sample may be NIPA/AA10/BIS1 in view of its high degree of crosslinking. In comparison with the other material suggested, it has a somewhat smaller swellability at ambient temperature ( $r = 62.2$ , cf.  $r = 79.0$ ), a higher value of  $T_c$  and a higher temperature (51°C, cf. 40°C) needed to regenerate the gel for re-use by swelling.

Further work is planned to measure the actual crosslinking densities of these materials by compression-strain analysis and to investigate further the effect of pH of the swelling medium.

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