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Thermoreversible swelling behaviour of hydrogels based on *N*-isopropylacrylamide with a hydrophobic comonomer

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Abstract

Hydrogels were prepared by free radical polymerisation in aqueous solution of *N*-isopropylacrylamide (NIPA) and of NIPA with di-*n*-propylacrylamide (DPAM), di-*n*-octylacrylamide (DOAM) or di-dodecylacrylamide (DDAM) as hydrophobic comonomer. *N*,*N*-methylene bisacrylamide (BIS) and glyoxal bis(diallyacetal) (GLY) were used as crosslinkers. A series of copolymers with three different comonomer contents was synthesised and for some polymers three different crosslinker concentrations were employed. The swelling equilibrium of these hydrogels was studied as a function of temperature, hydrophobic comonomer species and content in aqueous solutions of the anionic surfactant sodium dodecyl sulfate (SDS). In pure water the gels showed a discontinuous volume phase transition at 33 and 30 °C for PNIPA and hydrophobically modified PNIPA copolymeric hydrogels, respectively. The swelling ratio *r* and the transition temperature (LCST) increased at low temperatures with the addition of SDS, this is ascribed to the conversion of non-ionic PNIPA gels into polyelectrolyte gels through the binding of SDS. At SDS concentration below 0.5 wt%, gels exhibited a single discontinuous volume transition at 36–38 °C. However, for SDS concentration above 0.5 wt%, two discontinuous volume transitions at 36–40 and 70 °C were observed. Additionally, the replacement of BIS by the novel octafunctional crosslinker glyoxal bis(diallylacetal) (GLY) yielded an increase in the swelling ratio. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-isopropylacrylamide); Hydrophobically modified polymers; Hydrogel

1. Introduction

Poly(*N*-isopropyl acrylamide) (PNIPA) forms swollen hydrogels of crosslinked species due to the presence of both hydrophilic amide groups and hydrophobic isopropyl groups in its sidechains. The hydrogels are temperature-sensitive, and a dramatic swelling transition occurs at the lower critical solution temperature (LCST) of PNIPA, 32–33 °C in water [1–3]. Below this temperature the gel is swollen, hydrated and hydrophilic, whereas above the LCST, the gel shrinks and forms a collapsed, dehydrated and hydrophobic state due to the breakdown of the delicate hydrophilic/hydrophobic balance in the network structure. The temperature sensitivity of PNIPA gels has received increasing attention in recent years, this is due not only to industrial applications but also in fundamental research [4–8]. Such materials are useful as immunoassays [9], drug delivery systems [4,10], in separation processes [11,12], and for the immobilisation of enzymes [13].

Many studies have been reported in the past decade on thermosensitive hydrogels based on the monomer NIPA [1] and its copolymers with the most widely studied comonomers, such as acrylic acid (AA) [14–17], methacrylic acid (MAA) [16,17], 2-methyl-2-acrylamidopropane sulphonic acid (AMPS) [16,17], trimethyl-acrylamidopropyl ammonium (TMAAI) [18], 3-methyl-1-vinylimidazolium iodide (MVI) [19], sodium acrylate (SA) [20], sodium methacrylate (SMA) [20], and 1-(3-sulphopropyl)-2-vinyl-pyridinum-betaine (SPV) [21]. Very recently, Mashelkar et al. [22] investigated the swelling behaviour of hydrophobically modified NIPA copolymer gels in aqueous sodium dodecyl sulfate (SDS). The swelling ratios and LCST were found to be remarkably enhanced, which was interpreted on the basis of electrostatic repulsion due to binding of SDS to the polymer chains. The change in the transition temperature was found to be influenced strongly by the addition of small amounts of ionic surfactants and the nature of the hydrophobic group.

The focus of this study is the synthesis of novel copolymeric thermosensitive hydrogels of NIPA with the double alkyl chain acrylamide monomers di-*n*-propylacrylamide (DPAM), di-*n*-octylacrylamide (DOAM) and di-*n*-dodecylacrylamide (DDAM), respectively. These comonomers

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were chosen because (1) it has been reported for hydrophobically modified polyacrylamide [23] that for a similar hydrophobe level, double-chain hydrophobes considerably enhance the thickening efficiency with respect to single-chain hydrophobes. This indicates that there is a much stronger hydrophobic interaction between acrylamide derivatives containing two alkyl chains than those containing only one alkyl chain. We supposed that the use of double chains comonomers would enhance hydrophobic interactions with surfactants such as SDS and thus enhance swelling. (2) Introduction of a hydrophobic component also improves the mechanical strength of hydrogels [24]. In this paper, we have studied the effects of SDS content, initial crosslinker concentration, hydrophobic content and crosslinker type on the swelling behaviour and phase transition temperature of PNIPA-based hydrogels. To our knowledge the swelling behaviour of NIPA/DPAM, NIPA/DOAM and NIPA/DDAM hydrogels has not been investigated before.

2. Experimental

2.1. Materials

NIPA, the crosslinkers *N*,*N*-methylene bisacrylamide (BIS) and glyoxal bis(diallylacetal) (GLY), the initiator ammonium persulphate (APS), the activator *N*,*N*,*N*′*N*′-tetramethyl ethylene diamine (TEMED), acryloyl chloride (AC) (96% purity) and dioxane (HPLC grade) were purchased from Aldrich Chemical Co. Sodium *n*-dodecyl sulphate (SDS) (99% purity), di-*n*-propylamine (99% purity), triethylamine (TEA) (99% purity) and di-*n*-octylamine (95% purity) were purchased from Lancaster synthesis Ltd. Di-*n*-dodecylamine (≥97% purity) was purchased from Fluka Chemical. Tetrahydrofuran (THF) (HPLC grade) was purchased from Riedel-de Haën. AC, GLY and di-*n*-octylamine were distilled at either the normal pressure or under vacuum, SDS was twice recrystallised from ethanol and NIPA was recrystallised from toluene/*n*-hexane (27:73, v/v) prior to use, other chemicals were used without further purification. All aqueous solutions were prepared using deionised water.

2.2. Synthesis of hydrophobic monomers

The hydrophobic comonomers DPAM, DOAM and DDAM were prepared following the preparation technique for *N*-alkylacrylamides [25]. An example of the experimental procedure used for DPAM synthesis is as follows. A 500 ml, four-necked flask was equipped with a thermometer, mechanical stirrer, nitrogen inlet and addition funnel. After purging with nitrogen, the di-*n*-propylamine (0.11 mol, 11.1309 g) and triethylamine (0.12 mol, 12.143 g) were dissolved in 100 ml tetrahydrofuran (THF) and placed in the flask. The solution was then cooled to ~2 °C using a thermostated water bath with a cooling unit. Acryloyl chloride (0.11 mol, 8.94 ml) was dissolved in 100 ml THF and then very slowly added to the reaction flask over a period of at least 2.5 h at such a rate that the temperature remained at 2–5 °C (a white precipitate, triethylamine hydrochloride formed as the acryloyl chloride was added). Then the resulting mixture was stirred at a constant temperature (10 °C) for 2 h. Then, Triethylamine hydrochloride was removed by filtration and THF was evaporated off using a rotary evaporator at 40 °C under vacuum. Finally the crude product (yellow liquid) was purified by distillation with CuCl as a polymerisation inhibitor under vacuum (at ≈ 0.2 mm Hg, boiling point: 82–83 °C). The gravimetric conversion was 51%. The purity of this monomer was checked by NMR, mass spectroscopy and elemental analyses for carbon, hydrogen and nitrogen. The results of the elemental analyses were in good agreement with their theoretical values (i.e. C 68%; H 10.7%; N 8.7% for DPAM). A typical ^{1}H NMR spectrum in $CDCl_3$ for DPAM is shown in Fig. 1.

The preparation of DOAM and DDAM used the same technique as DPAM, but the purification procedures were different. The crude DOAM solution was purified by silica gel chromatography using acetonitrile, which was removed using a rotary evaporator. Finally an amber coloured oil-like liquid was obtained. Attempts to distil this liquid under vacuum were not successful due to decomposition, this result being in good agreement with Maier's report [26]. The gravimetric conversion was 48%. The purification procedure for DDAM was the same as for DOAM, and the conversion was 48.4%. The structures of the three monomers, as well as that of NIPA, are shown in Fig. 2.

2.3. Synthesis of hydrogels

The gels were prepared by free radical crosslinking

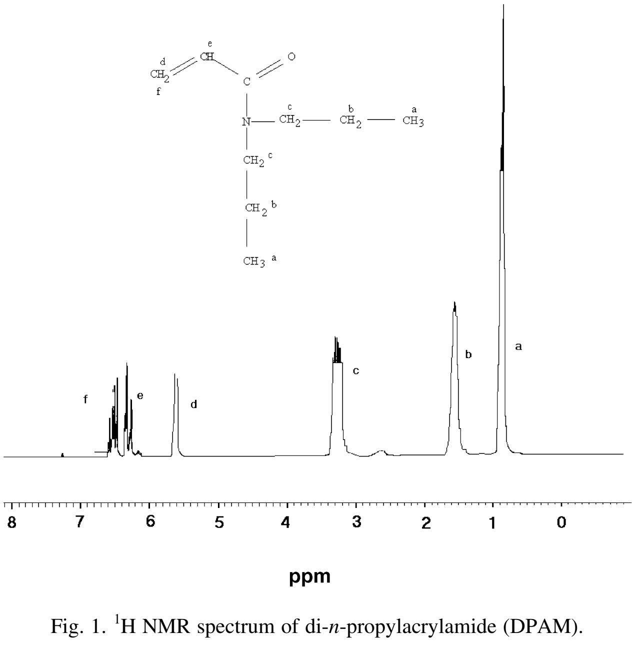

Fig. 1. ^{1}H NMR spectrum of di-*n*-propylacrylamide (DPAM).

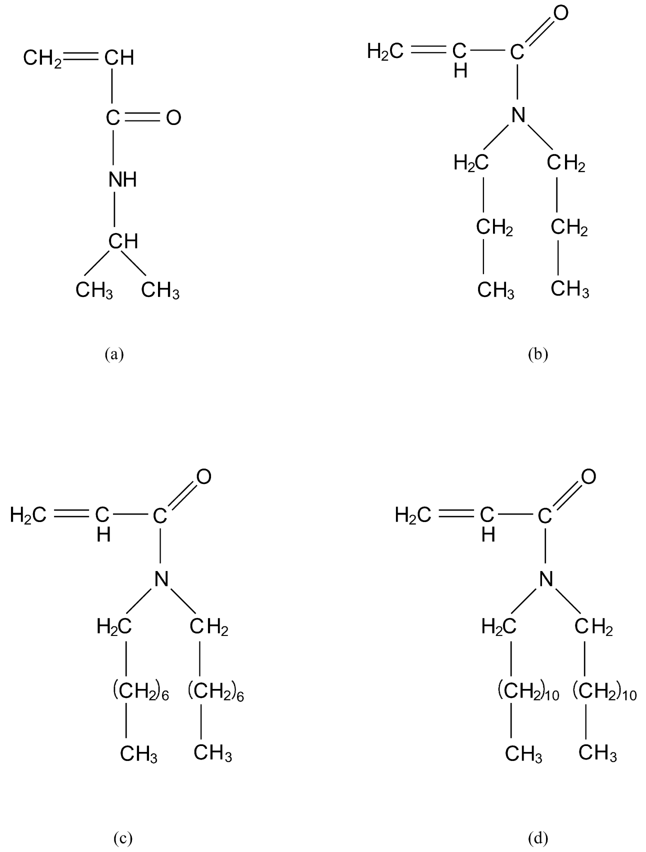
(a) (b) (c) (d)

Fig. 2. Structures of the monomers (a) NIPA; (b) DPAM; (c) DOAM; (d) DDAM.

copolymerisation in a water–dioxane (1:1, w/w) mixture. After preliminary experiments it was found that this composition of the solvent used for the monomer feed was critical for obtaining both a homogeneous feed and high conversion. Water alone could not be used as solvent due to the sparing solubility of hydrophobic monomers and GLY.

The ratio NIPA/mixed solvent was always 15/85 (w/w) and the concentrations of APS and TEMED were each fixed at 1 mol% with respect to total monomers. Polymerisation and post-polymerisation procedures for P(NIPA-*co*-DPAM), etc. are identical to those given previously for P(NIPA-*co*-AA) by Huglin and coworkers [15]. However, the conditions of polymerisation employed in this study were slightly different from those used previously [15]. Because of problems of reduced conversion and low rate of reaction, due to the presence of dioxane in the solvent system, it was necessary to increase both the temperature of polymerisation to 30 °C and the length of the polymerisation period to three days from 25 °C and 24 h, respectively. To assess consistency for each of the different xerogel compositions with regard to their properties, syntheses were conducted in at least three separate cylindrical glass bottles of ~15 mm diameter and 100 mm height. Thin disks of the xerogels (diameter ~10 mm and thickness ~2 mm) were shaped by cutting. In addition, the discs and pellets were washed not only with distilled water, but also using acetone to remove any possible unreacted monomers and/or linear homopolymers.

2.4. Conversion

The weight of dry xerogel, m_x, was determined after removal of unreacted monomers and linear polymers by alternately swelling the hydrogels in deionised water/acetone for one week (the swelling medium being changed daily) in a refrigerator with temperature ~8 °C, drying the hydrogels in an oven at 47 °C for 48 h and then to constant weight, m_x, in a vacuum oven at 45 °C for ~24 h. The ratio, θ, of m_x to total mass of monomers, m_t, in the feed mixture represents the fractional conversion to crosslinked polymer. It is not possible to distinguish between monomers and linear polymers within the total quantity ($m_t - m_x$). Hence θ represents the minimum conversion. In these experiments, we found that the average value of θ was ~0.98. Due to the high conversion, therefore, the sol fraction removed cannot exceed 0.02 and the overall average copolymer composition can be approximated to the initial feed composition.

2.5. Nomenclature

The samples are denoted according to the composition of xerogels on the assumption of high conversion. The content of hydrophobic monomers such as DPAM, DOAM and DDAM is in mol%. For example NIPA/DPAM5/BIS0.1 denotes that (number of moles of DPAM/number of moles NIPA) = 5% and that [(number of moles of BIS)/(number of moles of NIPA + number of moles of DPAM)] = 0.1%.

2.6. Swelling and deswelling measurements

Temperature dependent measurements were carried out in either a thermostated water bath or a refrigerator. The dried xerogel disc was swollen to equilibrium for a minimum period of 48 h over a range of temperatures (8–80 °C) on both heating and cooling. The swelling media used were deionised water and aqueous solutions of SDS, and the concentrations of aqueous SDS were 0.1, 0.5 and 1.0 wt%, respectively. After swelling equilibrium was reached (~48 h), the hydrogels were removed from the swelling media, the excess surface solvent was lightly surface dried with filter paper, then weighed, the corresponding weight being m_h. The swelling ratio r was obtained from Eq. (1), in which m_h and m_x are the weights of hydrogel and xerogel, respectively.

$$r = m_h/m_x. \tag{1}$$

At least three samples of each hydrogel were used to yield three values of m_h, the average of which was used to calculate r; the results indicate that the gel is stable and the response is repeatable.

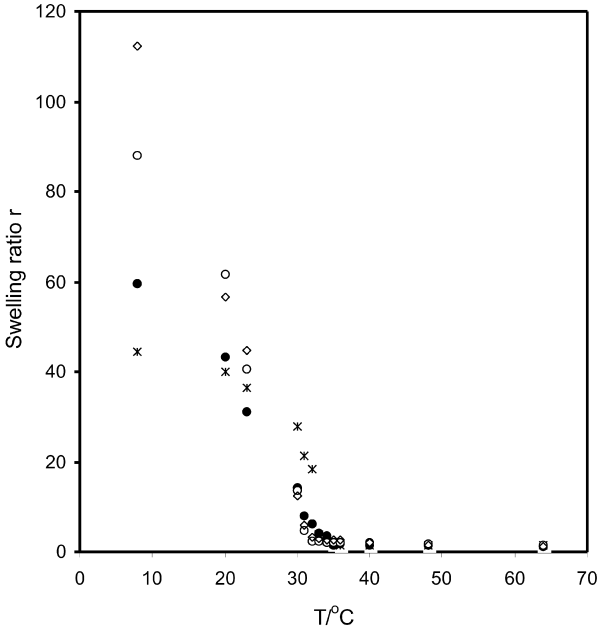

Fig. 3. Dependence of swelling ratio *r* on temperature in pure water for hydrogels with different contents of DPAM: (*) NIPA/BIS0.1; (●) NIPA/DPAM1/BIS0.1; (○) NIPA/DPAM5/BIS0.1; (◇) NIPA/DPAM10/BIS0.1.

3. Results and discussion

3.1. Swelling in water

A brief resume on the reasons for the volume phase transition in PNIPA hydrogel will be useful for the following discussion. Most researchers have noted the hydrophilic nature of –C=O and –N–H groups, the H-bonding ability of these groups being instrumental in stabilising a coil conformation below the LCST, which means that polymer–water interactions predominate over polymer–polymer interactions. On the other hand, the pendent isopropyl group and the hydrocarbon backbone are hydrophobic in nature, the hydrophobic groups being exposed to form aggregates above the LCST. This forces the polymer chain into a globule conformation in which polymer–polymer interactions are dominant. In a word, the volume phase transition results from a change in the balance between various types of interaction, especially hydrogen bonding and hydrophobic interactions.

The contents of hydrophobic comonomers (DPAM, DOAM and DDAM) in this study were 0 (i.e. pure PNIPA), 0.5, 1.0, 3.0, 5.0 and 10 mol% with the content of crosslinker BIS fixed at 0.1 wt%. In addition, for the purpose of comparison, a second system was investigated with varying crosslinker contents of BIS with the same hydrophobic comonomer content (5 wt%). Fig. 3 shows the temperature dependence of the swelling obtained on heating hydrogels with contents of DPAM of 0, 1, 5 and 10 mol%, respectively, all with the same content of BIS. The four curves display the same tendency, viz. a fall in *r* with *T*, which becomes sharper in the vicinity of the critical temperature. Finally, in the high temperature regime there is almost complete deswelling for all gels, and *r* attains a value close to unity.

The main difference among the four systems lies in the lowest temperature region, the value of *r* for PNIPA being increased dramatically upon incorporation of 1–10 mol% of DPAM comonomer. It can also be noted that the value of *r* increases with increasing content of DPAM as well. Generally, the swelling ratio of a hydrogel is decreased by incorporating a hydrophobic chain. For example, when a highly hydrophobic acrylate, 2-ethylhexyl acrylate was incorporated into 2-hydroxyethyl methacrylate, the swelling ratio decreased [27]. However, our results show that the swelling ratio increases with increasing DPAM content. This result was obtained not only for DPAM hydrogels, but also those containing DOAM and DDAM, although the values of *r* are different. For brevity, swelling curves are not reproduced here for hydrogels with DOAM and DDAM as comonomers. In copolymeric systems the swelling process is controlled by the introduction of a second monomer with hydrophobic character. The maximum hydration degree and diffusion of swelling agent into a gel, as well as the organisation of water molecules in the gel, will change depending on the chemical composition and the distribution of the hydrophobic monomeric units along the macromolecular chains [27]. Indeed, our copolymeric hydrogels containing DPAM units should tend to favour the adoption of a compact or globular conformation, due to hydrophobic interactions between isopropyl and methyl groups, for example. Thus a decrease in the capacity for water absorption is expected and our contrary results are thus difficult to understand in this respect.

At a particular content of crosslinker BIS, the swelling ratio at lower temperature increases upon incorporating hydrophobic comonomers such as DPAM, DOAM and DDAM, which has been mentioned above. The swelling ratio increases in the order DPAM $>$ DOAM $>$ DDAM (see Fig. 4), this can simply be attributed to increasing hydrophobic character with increasing length of the hydrophobic monomer chains. The increased hydrophobicity leads to decreased water uptake and a lower swelling ratio. For all the hydrogels, the cooling process was also carried out, and almost all the swelling ratios were the same as those obtained on heating (data not distinguished in the plots presented here). Thus the reversible nature of swelling and deswelling was confirmed.

Fig. 3 shows that all four hydrogels exhibit an LCST, the value of LCST being defined according to methods described elsewhere [16] as the minimum in plots of $\mathrm{d}r/\mathrm{d}T$ vs. T (not shown here). LCST values thus obtained are listed in Table 1. Our results indicate that the LCST of PNIPA hydrogels is about 33 °C, this is in good agreement with the literature [1–3]. However, the LCST decreases upon incorporation of hydrophobic comonomer, a finding also in accord with the literature [28–30]. It is apparent that

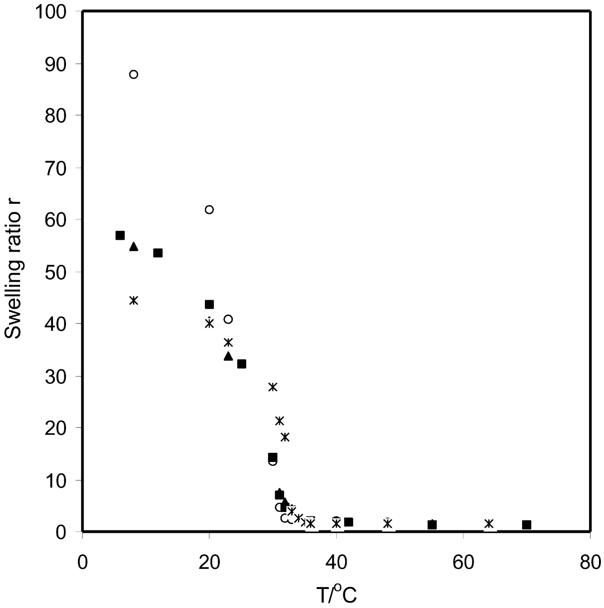

Fig. 4. Dependence of swelling ratio r on temperature in pure water for hydrogels with different hydrophobic comonomers: (○) NIPA/DPAM5/BIS0.1; (■) NIPA/DOAM5/BIS0.1; (▲) NIPA/DDAM5/BIS0.1; (∗) NIPA/BIS0.1.

(1) the phase transition behaviour can be controlled by incorporating more hydrophilic or hydrophobic monomer in the gel. (2) The LCST of PNIPA copolymer gel decreases upon incorporation of hydrophobic comonomers.

Table 1 also shows that the effect of hydrophobic comonomer type/chain length on the value of the LCST is extremely slight, and the LCST values are almost independent of hydrophobic comonomer content, especially for low contents. The slight decrease of LCST is presumed to be due to increased hydrophobicity; hence, the balance between hydrogen bonding and hydrophobic interactions is shifted. In particular, the decrease in the coil-to-globule transition can be ascribed to reduce hydrogen bonding due to the incorporation of hydrophobic comonomer.

Table 1
Values of LCST (°C) for homopolymer and copolymer hydrogels swollen in water

Sample	LCST (±1 °C)
NIPA/BIS0.1	33
NIPA/DPAM1/BIS0.1	30
NIPA/DPAM5/BIS0.1	30
NIPA/DPAM10/BIS0.1	30
NIPA/DOAM3/BIS0.1	31
NIPA/DOAM5/BIS0.1	30
NIPA/DOAM10/BIS0.1	30
NIPA/DDAM3/BIS0.1	30
NIPA/DDAM5/BIS0.1	30
NIPA/DDAM10/BIS0.1	30
NIPA/DPAM5/BIS0.1	30
NIPA/DPAM5/BIS0.25	30
NIPA/DPAM5/BIS0.5	30
NIPA/DPAM5/BIS1	30

The effect of crosslinker concentration on swelling ratio and LCST are summarised in Fig. 5 and Table 1. At low-to-medium temperatures, the value of r for these hydrogels increases with decreasing BIS concentration. This is presumably due to the increasing mesh size of the network with decreasing crosslinker concentration, which enhances the diffusion of water molecules into the hydrogel network. Table 1 shows that the LCST values for these hydrogels are unaffected by the crosslinker concentration. This result is in accord with those reported by Huglin et al. [16] for hydrogels of NIPA/AMPS10/BIS.

3.2. Swelling in aqueous SDS solutions

We investigated the influence of SDS concentration on the value of the LCST and swelling ratio of PNIPA and P(NIPA-*co*-DPAM/DOAM/DDAM) hydrogels over a concentration range 0–1 wt% SDS. It is known that the binding of surfactant micelles to hydrogels cause an elevation of the LCST as a result of electrostatic repulsion between the charges of polymer-bound micelles. The concentration at which such surfactant binding takes place has been referred to as the critical aggregation concentration (CAC), but concur with Kokufuta et al. [31], who noted that it is rather difficult to judge whether the CAC in the uncrosslinked polymer is the same as that in the gel system or not. In addition, it is questionable whether the CAC can be defined for the gel system, because the surfactant binding mechanism is presently unclear. In the present study,

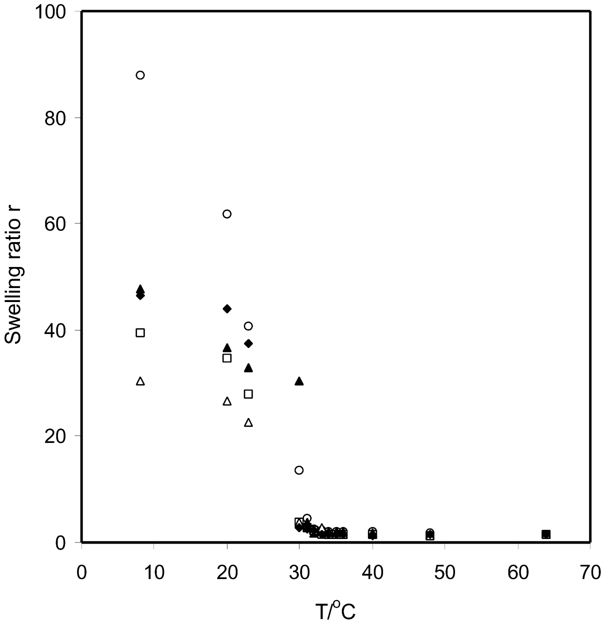

Fig. 5. Dependence of swelling ratio r on temperature in pure water for hydrogels with different crosslinker contents or type: (○) NIPA/DPAM5/BIS0.1; (▲) NIPA/DPAM5/BIS0.25; (□) NIPA/DPAM5/BIS0.5; (△) NIPA/DPAM5/BIS1; (◆) NIPA/DPAM5/GLY1.

although the effect of SDS concentration on the LCST and swelling ratio has been examined for PNIPA and P(NIPA-*co*-DPAM/DOAM/DDAM) hydrogels over a range 0–1.0 wt% of SDS concentration, the results are interpreted without discussing a CAC.

3.3. Different hydrophobic content and SDS concentration

The hydrophobic comonomers contents were 1, 3 and 5 mol% and for each of the systems the content of BIS was fixed at 0.1 mol%. For all of these nine copolymers *r* was measured at a minimum of 12 different temperatures and 3 different aqueous SDS concentrations.

As an example, the temperature dependences of *r* for hydrogels with 1, 3 and 5 mol% DPAM as hydrophobic comonomer for aqueous SDS solutions are presented for Figs. 6–8. These graphs show *r* vs. temperature for P(NIPA-*co*-DPAM) hydrogels as a function of DPAM content (from 0 to 5 mol%) for 0.1, 0.5 and 1.0 wt% SDS solutions, respectively. Very similar plots were obtained for hydrogels with DOAM or DDAM as hydrophobic comonomer, except for the rather lower value of *r* at the same SDS concentration, temperature and hydrophobic content.

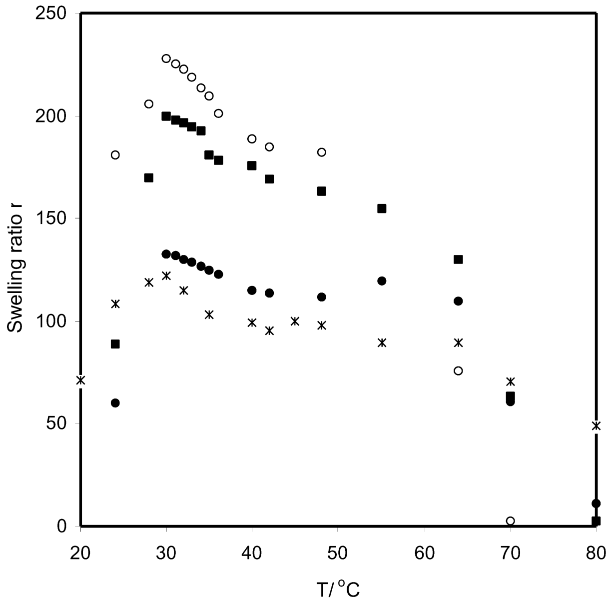

Fig. 7. Dependence of swelling ratio *r* on temperature in 0.5 wt% aqueous SDS solution for hydrogels with different contents of DPAM: (○) NIPA/DPAM5/BIS0.1; (■) NIPA/DPAM3/BIS0.1; (●) NIPA/DPAM1/BIS0.1; (∗) NIPA/BIS0.1.

The following conclusions may be drawn. First, addition of SDS at concentration up to 0.5 wt% causes a significant increase in the value of *r* relative to its value in water, at 20 °C (Figs. 3, 6 and 7). The values *r* of hydrogels of NIPA/BIS0.1 and NIPA/DPAM5/BIS0.1 are 40.1 and 61.7 in water at 20 °C (Fig. 3), whereas in aqueous 0.1 wt% SDS solution, the value of *r* is much larger: 48.9 and 174, respectively (Fig. 6). Upon further increase in SDS concentration to 0.5 wt%, the maximum value of *r* attained is 71.4 and 188, respectively, at 20 °C. But it should be noted that upon further increasing SDS concentration to 1 wt% (Fig. 8), the value of *r* only increases slightly to 78.4 and 196.3, respectively. Second, at a particular concentration of SDS, for example 0.5 wt% SDS (Fig. 6), the values of *r* increase with increasing DPAM content. Third, the value of LCST not only increases in aqueous SDS solution, but also a single LCST is not displayed for SDS concentrations above

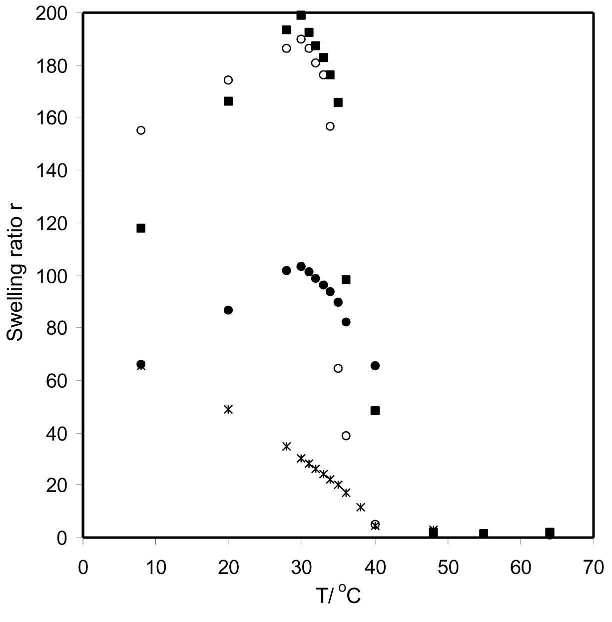

Fig. 6. Dependence of swelling ratio *r* on temperature in 0.1 wt% aqueous SDS solution for hydrogels with different contents of DPAM: (○) NIPA/DPAM5/BIS0.1; (■) NIPA/DPAM3/BIS0.1; (●) NIPA/DPAM1/BIS0.1; (∗) NIPA/BIS0.1.

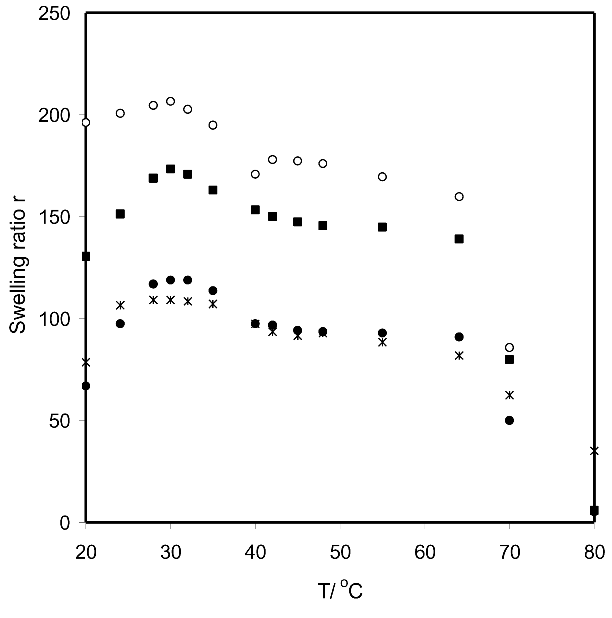

Fig. 8. Dependence of swelling ratio *r* on temperature in 1.0 wt% aqueous SDS solution for hydrogels with different contents of DPAM: (○) NIPA/DPAM5/BIS0.1; (■) NIPA/DPAM3/BIS0.1; (●) NIPA/DPAM1/BIS0.1; (∗) NIPA/BIS0.1.

Table 2
Values of LCST (°C) for homopolymeric and copolymeric hydrogels swollen in aqueous SDS solutions. The uncertainty is ±1 °C for the 0.1 wt% samples, and ±2 °C for the other two

Sample	0.1 wt%	0.5 wt%	1.0 wt%
NIPA/BIS0.1	37	35, 70	38, 70
NIPA/DPAM1/BIS0.1	38	36, 70	36, 70
NIPA/DPAM3/BIS0.1	37	36, 70	36, 70
NIPA/DPAM5/BIS0.1	36	37, 70	37, 70
NIPA/DPAM10/BIS0.1	36		
NIPA/DOAM1/BIS0.1			38, 70
NIPA/DOAM3/BIS0.1	35	36, 68	40, 70
NIPA/DOAM5/BIS0.1	36	36, 68	40, 70
NIPA/DOAM10/BIS0.1	37		
NIPA/DDAM3/BIS0.1	36	36, 68	40, 70
NIPA/DDAM5/BIS0.1	37	37, 70	39, 70
NIPA/DDAM10/BIS0.1	35	39, 70	40, 70
NIPA/DPAM5/BIS0.1		37, 70	
NIPA/DPAM5/BIS0.25		37, 70	
NIPA/DPAM5/BIS0.5		36, 70	
NIPA/DPAM5/BIS1		36, 70	

0.5 wt%; instead there are two LCST regions. In the absence of SDS, the LCST of PNIPA hydrogels is at 33 °C (see Table 1). However, in the presence of 0.1 wt% SDS, the LCST increases. For the copolymer hydrogels, the value of LCST is around 30 °C in water and 35–38 °C in 0.1 wt% aqueous SDS solutions (see Table 2). For SDS concentrations above 0.5 wt%, two discontinuous volume transitions are observed, one at around 35–40 °C and another one at 70 °C. Table 2 shows that the LCST does not depend strongly on SDS concentration, however, the high temperature transition is essentially independent of hydrophobic comonomer and BIS content. Finally, for all the hydrogels, reversibility of the swelling was confirmed by the identical shape of the swelling curve obtained on heating or cooling (data not distinguished in the plots presented here).

Because the mechanism of surfactant binding onto hydrophobically modified hydrogels is unknown and the complexity introduced by multiple interaction parameters (polymer–polymer; polymer–water; polymer–SDS; water–water; water–SDS; and SDS–SDS) in these multicomponent systems, the explanation for the high temperature volume transition is at present tentative. However we can note firstly that the swelling of these gels in aqueous SDS solution was observed to be uniform throughout the bulk, which implies a homogeneous interaction between the SDS and the hydrogel. It is also evident that the hydrogels do not contain ionisable groups in their chemical structure; hence, there should not be any electrostatic repulsion forces between the polymer chains. The observed effects of the anionic surfactant SDS on NIPA and NIPA-*co*-DPAM gels can thus be readily understood by assuming that the gel is ionised upon binding of SDS molecules to the polymer network: It is reasonable to suppose that the SDS binds to the polymer network within the gel phase through hydrophobic interactions. The SDS molecule consists of a long aliphatic hydrocarbon chain and NIPA has hydrophobic isopropyl moeities, $CH_2(CH_3)_2$, as side groups and CH_2CHR in its backbone. Hydrophobically modified NIPA copolymers contain not only NIPA but also have double-alkyl chains in the hydrophobic group (Fig. 2). When SDS molecules diffuse into the gel network of NIPA or NIPA/DPAM, strong association should take place through the hydrophobic interaction between the isopropyl groups of NIPA, alkyl groups of hydrophobic comonomer and long chain alkyl groups of the SDS, thus increasing the surface charge density of hydrogels as the neutral polymers chains become polyelectrolytes. These acquired network charges and the counterions associated to the charges exert an extra osmotic pressure on the network. As a result, the polymer conformation will become more like an expanded coil than a globule, and both the transition temperature and volume change at the transition will be increased.

The increase in swelling ratio with increasing DPAM content at a particular concentration of SDS can be attributed to the incorporation of more hydrophobic comonomer into PNIPA gel. Thus the copolymer gel network will contain more hydrophobic groups, the interactions between SDS and polymer chains through hydrophobic interactions will be stronger, and more SDS will bind onto polymer chains. Increased binding of charged surfactants would increase the charge density of polyelectrolyte chains and thus led to an enhanced swelling ratio. The binding of SDS to PNIPA has been studied by many groups [32–36]. The interaction of SDS with hydrophobically modified polymers has attracted less attention, however Biggs et al. [37] have presented evidence for selective binding at hydrophobic sites in hydrophobically modified polyacrylamide. Iliopoulos et al. [38] have suggested, on the basis of experiments on hydrophobically modified poly(sodium acrylate) in solutions of non-ionic surfactants, that the hydrophobic groups are present in mixed micelles, leading to enhanced crosslinking of the polymer network compared to simple inter-chain association of unmodified polymer. Shinde et al. [22] observed non-uniform swelling of hydrophobically modified PNIPA in SDS solutions, but did not analyse surfactant binding or its relation to micellisation or aggregation. Further work will need to be carried out to investigate SDS binding in our hydrophobically modified PNIPA hydrogels.

The presence of SDS in the swelling medium at a concentration above 0.5 wt% leads to two discontinuous volume transitions (Figs. 7 and 8). A similar observation has been reported recently by Mashelkar et al. [22] for their hydrophobically modified PNIPA hydrogels. They have attributed this to the presence of heterogeneous phases as a result of uneven binding of surfactant molecules. But in the present study, our gels are always transparent and swelling is uniform throughout the bulk, so there is homogeneous interaction of SDS with our gels. Therefore, we are unable to attribute two volume transitions to heterogeneous swelling.

Due to the values of the multiple unknown interaction parameters in these multi-component systems, it is only possible to make qualitative postulates to account for the two discontinuous volume transitions in aqueous SDS.

SDS concentrations above 0.5 wt% exceed the critical micelle concentration (CMC) ~0.24 wt%, so that micelles of SDS must be associated with polymer chains (this is also likely to occur below the CMC for the surfactant solution). The binding of SDS onto polymer chains is the dominant interaction between SDS and polymer chain before binding saturation occurs. At this stage the polymer chains have a maximal negative charge and the electrostatic repulsion force is dominant. This interaction favours an expanded conformation, which enhances the water diffusion into the polymer network, and the balance between various types of interaction such as hydrogen bonding and hydrophobic interaction is destroyed, the consequence being an increase in both the transition temperature and swelling ratio.

It is evident that only a low concentration of SDS is necessary to achieve saturated binding of SDS to these polymers, because the value of r did not change dramatically with SDS concentration up to 1.0 wt% (see Fig. 8). Two transition temperature were only found for SDS concentrations of 0.5 wt% and above. We suggest the following explanation for the second transition, and the more continuous decrease in swelling ratio. At a sufficiently high SDS concentration, saturation of binding of SDS micelles to polymer chains occurs. At higher concentration additional SDS forms unbound micelles. Due to the charges present on the anionic surfactant and its associated counter ions, screening of inter-chain repulsions could occur, leading to a steady decrease in swelling ratio. This scenario has previously been proposed for neutral polymer/SDS complexes [39] where the concentration at which saturated binding and/or the formation of free micelles occurs is denoted C_2 (as opposed to C_1, the critical aggregation concentration). Here, we suppose that saturated binding also occurs in hydrogel/SDS solution, although the critical aggregation transition may be suppressed, as mentioned earlier. An increase in temperature may favour the unbinding of SDS molecules from the PNIPA chains, and the formation of more free micelles and thus increased charge screening and a decrease in swelling ratio. Why a discontinuity in swelling ratio as a function of temperature occurs specifically at 70 °C is at present unclear though.

At a particular concentration of SDS (0.5 wt%) the influence of crosslinker content was examined, the effect on swelling ratio and transition temperature being shown in Fig. 9 and Table 2. Fig. 9 shows that the swelling ratio increases with decreasing BIS content and the LCST is independent of the BIS content, as for the hydrogel in water.

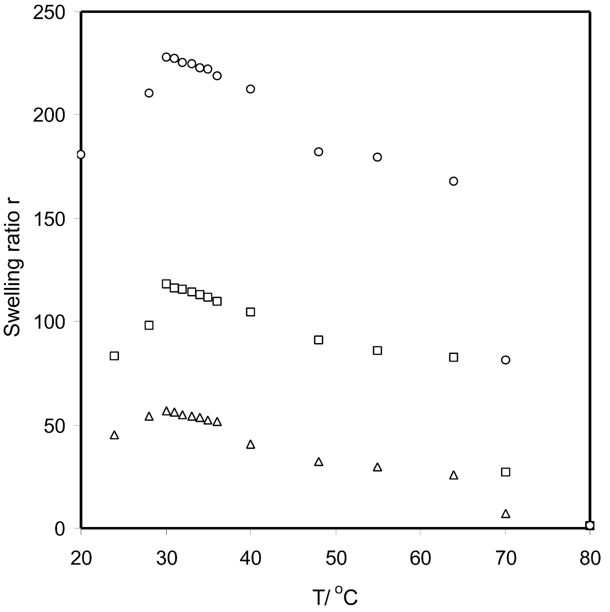

Fig. 9. Dependence of swelling ratio r on temperature in 0.5 wt% aqueous SDS solution for hydrogels with different crosslinker contents: (○) NIPA/DPAM5/BIS0.1; (□) NIPA/DPAM5/BIS0.5; (△) NIPA/DPAM5/BIS1.

3.4. Enhancement of swelling

Due to the low swelling ratio of PNIPA hydrogels, various comonomers have been incorporated [14]. However, the role and nature of chemical crosslinker have received much less attention. BIS is used most frequently as crosslinker because of its water solubility, water being normally used as reaction medium. Huglin and coworkers [14,15,21] developed a novel octafunctional crosslinker glyoxal bis(diallyacetal) GLY, used in several copolymeric PNIPA hydrogel systems, and the results indicated that the swelling increases dramatically using GLY instead of BIS as crosslinker. This may be because GLY is an inefficient crosslinker (low reactivity ratio) leading to a low crosslink density and therefore enhanced swelling [14]. In the present, a sample of composition NIPA/DPAM5 crosslinked with the novel crosslinker GLY was prepared. Fig. 5 shows the values of r at 20 °C in water for NIPA/DPAM5/GLY1 and NIPA/DPAM5/BIS1 are 44 and 27, respectively. The swellability of the P(NIPA-*co*-DPAM) hydrogels is clearly enhanced by the use of GLY, at comparable molar contents of crosslinker. As the functionality of GLY and BIS are eight and four, respectively, a gel of say, 1 mol% BIS should be compared with one of $(4/8)1 = 0.5$ mol% GLY, but nonetheless the influence of GLY in enhancing swelling remains evident.

4. Conclusions

P(NIPA-*co*-DPAM or DOAM or DDAM) hydrogels were prepared by free-radical crosslinking copolymerisation in a water/dioxane mixture solvent at 30 °C with BIS or GLY as a crosslinker. The content of hydrophobic comonomer in the PNIPA network was varied and the effect of two different crosslinkers and their concentration on the swelling ratio and LCST was investigated. The following conclusions were drawn:

1. For P(NIPA-*co*-DPAM/DOAM/DDAM) hydrogels in water at low temperature, the swelling ratio increases with the hydrophobic comonomer content, and the sequence of increasing swelling is DPAM > DOAM > DDAM. The swelling transition has a thermoreversible character.
2. The swelling ratio increases with decreasing crosslinker BIS content, although the values of LCST are not affected by the crosslinker concentration.
3. The LCST decreases when hydrophobic comonomers are incorporated into PNIPA. However, the type of hydrophobic comonomer does not have dramatic influence on the LCST.
4. The effects of surfactant on the swelling equilibrium and phase transition temperature of NIPA and NIPA/DPAM or DOAM or DDAM hydrogels were studied in aqueous solution for several surfactant concentrations. An increase in the phase transition temperature is accompanied by an increase in the swelling ratio when using the anionic surfactant SDS. When the SDS concentration exceeds 0.5 wt%, there appear to be two volume phase transitions, the lower transition becoming increasingly broad as concentration is increased.
5. There are indications that the swelling can be enhanced by using GLY to replace BIS as crosslinker.

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References

[1] Schild HG. Prog Polym Sci 1992;17:163.
[2] Hirokawa Y, Tanaka T. J Chem Phys 1984;81:6379.
[3] Bar YH, Okano T, Sakurai Y, Kim SW. Pharm Res 1991;8:624.
[4] Bae YH, Okano T, Hsu R, Kim SW. Macromol Chem Rapid Commun 1987;8:481.
[5] Dong LC, Hoffman AS. J Control Release 1986;4:223.
[6] Freitas RFS, Cussler EL. Chem Engng Sci 1987;42:97.
[7] Okano T. Adv Polym Sci 1993;110:180.
[8] Sayil C, Okay O. Polymer 2001;42:7637.
[9] Monji N, Hoffman AS. Appl Biochem Biotechnol 1987;14:107.
[10] Hoffman AS, Afrassiabi A, Dong LC. J Control Release 1986;4:213.
[11] Freitas RFS, Cussler EL. Chem Engng Sci 1987;42(1):97.
[12] Champ S, Xue W, Huglin MB. Polymer 2001;42:6439.
[13] Dong LC, Hoffman AS. J Control Release 1986;4:223.
[14] Xue W, Champ S, Huglin MB. Polymer 2001;42:2247.
[15] Xue W, Champ S, Huglin MB. Polymer 2001;42:3665.
[16] Huglin MB, Liu Y, Velada JL. Polymer 1997;38:5785.
[17] Velada JL, Liu Y, Huglin MB. Macromol Chem Phys 1998;199:1127.
[18] Lee WF, Hsu CH. Polymer 1998;39:5393.
[19] Lee WF, Hsu CH. J Appl Polym Sci 1999;74:3242.
[20] Liu Y, Velada JL, Huglin MB. Polymer 1999;40:4299.
[21] Xue W, Champ S, Huglin MB. Eur Polym J 2001;37:869.
[22] Shinde VS, Badiger MV, Lele AK, Mashelkar RA. Langmuir 2001;17:2585.
[23] Volpert E, Selb J, Candau F. Macromolecules 1996;29:1452.
[24] Etsuo K, Zhang YQ, Toyoichi T, Mamada A. Macromolecules 1993;26:1053.
[25] McCormick CL, Nonaka T, Johnson CB. Polymer 1988;29:731.
[26] Maier L. Helv Chim Acta 1973;56:1252.
[27] Vázquez B, Roman JS, Peniche C, Cohen ME. Macromolecules 1997;30:8440.
[28] Park TG, Hoffman AS. J Biomed Mater Res 1990;24:21.
[29] Park TG, Hoffman AS. Biotechnol Bioengng 1990;35:152.
[30] Badiger MV, Lele AK, Bhalerao VS, Varghese S, Mashelkar RA. J Chem Phys 1998;109:1175.
[31] Kokufuta E, Suzuki H, Sakamoto D. Langmuir 1997;13:2627.
[32] Winnik FM, Ringsdorf H, Venzmer J. Langmuir 1991;7:905.
[33] Meewes M, Rička J, de Silva M, Nyffenegger R, Binkert T. Macromolecules 1991;24:5811.
[34] Kokufuta E, Zhang Y-Q, Tanaka T, Mamada A. Macromolecules 1993;26:1053.
[35] Wu XY, Pelton RH, Tam KC, Woods DR, Hamielec AEJ. Polym Sci 1993;31:957.
[36] Tam KC, Wu XY, Peltion RHJ. Polym Sci 1993;31:963.
[37] Biggs S, Selb J, Candau F. Langmuir 1992;8:838.
[38] Sarrazin-Cartalas A, Iliopoulos I, Audebert R, Olsson U. Langmuir 1994;10:1421.
[39] Mears SJ, Deng Y, Cosgrove T, Pelton R. Langmuir 1997;13:1901.