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New superabsorbent thermoreversible hydrogels

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Abstract

The novel octafunctional crosslinker glyoxal bis(diallylacetal) (GLY) was employed in the synthesis of thermosensitive hydrogels of (*N*-isopropylacrylamide-*co*-acrylic acid). The resultant chemically crosslinked networks show levels of swellability in water significantly higher than those previously reported for such copolymers crosslinked by *N,N'*-methylene bisacrylamide (BIS) whilst retaining the ability to deswell at temperatures above the lower critical temperature (T_c). Additionally, the replacement of BIS by GLY yielded a decrease in the T_c of the hydrogels, indicating that incorporation of GLY into the polymer network increases the hydrophobicity of the network; this is consistent with the structure of GLY and its sparing solubility in water. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-isopropylacrylamide-*co*-acrylic acid); Thermosensitive hydrogel; Superabsorbent

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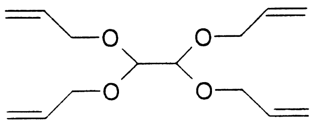
1. Introduction

Abbreviations

The following abbreviations, either alone or prefixed by P for the polymeric form, are adopted in the text: AA acrylic acid, AMPS 2-methyl-2-acrylamidopropane sulphonic acid, APS ammonium persulphate, BIS *N,N'*-methylene bisacrylamide, EDMA ethylene dimethacrylate, GLY glyoxal bis(diallylacetal), NIPA *N*-isopropylacrylamide and TEMED tetramethylethylene diamine. The structural formula of GLY [also known as (tetra-allyloxy)ethane] is as follows.



Nomenclature

The samples are denoted according to the composition of xerogels on the (verified) assumption of high conversion. The content of AA is its mol% with respect to NIPA and that of crosslinker (BIS or GLY) is its mol% with respect to total principal monomers. For example NIPA/AA10/GLY0.5 denotes that 100(number of moles of AA/number of moles of NIPA) = 10 and that 100[(number of moles of GLY)/(number of moles of NIPA + number of moles of AA)] = 0.5.

Background

Much of the published work on thermoreversible swelling is focused on chemically crosslinked hydrogels of PNIPA [1], which has a lower critical swelling temperature (T_c) of ca. 32–34°C in which region there is a coil-to-globule transition. However, the swelling ratio r (= mass of hydrogel/mass of xerogel) is rather low and for this reason co-monomers have been incorporated [2–5]. At too high a content of polar co-monomer there is no T_c and r merely decreases in value without attaining the value of unity for complete deswelling [2,4]. The role and nature of chemical crosslinker have received much less attention than the corresponding aspects of the co-monomer. BIS is used most frequently as crosslinker because of its water solubility coupled with the normal use of water as reaction medium [2–4]. In certain circumstances xerogels can be synthesised in bulk [6]. When the crosslinker and co-monomer are non-polar, a non-polar solvent can be used in place of water as synthesis medium [5].

Our present interest is the use of thermoreversible gels to concentrate aqueous solutions of linear macromolecules [7] and bacteria [8]. Since the concentrating effect arises from transfer of water alone from solution to xerogel, a prime requirement of the xerogel is its ability to afford a very high value of r at ambient temperature. Superabsorbent polymers are, of course, characterised by high swellability. However, their swelling is not, and does not need to be, thermoreversible. Our earlier studies on hydrogels containing

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NIPA with acidic and salt co-monomers and BIS as crosslinker [2,4] showed that very high swelling is afforded by the presence of the strongly acidic AMPS [2], but a value of T_c is exhibited only when the content of AMPS is low. Apart from insufficiently high swellability the system comprising NIPA with a moderate content of AA and a low content of BIS afforded most promise [2]. Accordingly, the present work deals with the possible enhancement of r and the retention of a convenient value of T_c that might be afforded by a different crosslinker. Crosslinkers containing allylic groups are often incorporated more uniformly into a crosslinking terpolymerisation than vinyl groups and, because of their low-moderate reactivity relative to acrylic acid monomers, have been proposed as components of supersorbers [9,10]. An example of such a crosslinker is GLY. As far as the authors are aware, the use of GLY, an octafunctional crosslinker, in the synthesis of highly swellable thermoreversible hydrogels has hitherto not been reported and this constitutes the theme of the present communication.

2. Experimental

2.1. Materials

The source of water, NIPA, AA, the initiator APS, the crosslinker BIS and the activator TEMED was as given before [2], as was also the mode of purification of water, NIPA and AA [2]. Dioxan (HPLC grade) and GLY were purchased from Aldrich Chemical Co. Dioxan was used without further purification and GLY was purified via distillation under reduced pressure (118.5–22°C/2 mmHg). Heat sealable fabric was obtained from Dexter Non-Wovens (Churnside, Scotland).

2.2. The physical properties of GLY

No physical properties of GLY could be located in the literature. Accordingly values of density and refractive index were measured over a range of temperature using a Paar DMA 55 digital densimeter and a Bellingham and Stanley Abbé refractometer, respectively.

2.3. Synthesis of hydrogels

The gels were prepared by free radical crosslinking copolymerization in a water–dioxan solution (1:1 (v/v)). 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 GLY in it, and the use of pure dioxan gave rise to problems of low conversions.

The ratio NIPA/mixed solvent was always 8.6/91.4 (wt/wt) and the concentrations of initiator and activator were each fixed at 1 mol% with respect to total monomers. The hydrogels were prepared in a mould following the polymerisation and post-polymerisation procedures given in detail elsewhere [7]. However, the conditions of polymerisation employed in this study were slightly different from those used previously [7]. Because of problems of reduced conversion and low rate of reaction, due to the presence of dioxan in the solvent system, it was necessary to increase both the temperature of polymerisation to 28–30°C and the length of the polymerisation period to six days from previous 25°C and 24 h, respectively.

2.4. Conversion

The value of the fractional conversion θ, calculated as given previously [7], was ca. 0.90. Allowance for the possible conversion of monomers to soluble linear polymer would give an actual fractional conversion greater than the apparent one, i.e. >0.90. Therefore, the sol fraction removed cannot exceed 0.1 and the overall average copolymer composition can be approximated to the initial feed composition.

2.5. Swelling measurements

The fragility of the swollen GLY hydrogels rendered it impossible to handle them directly. Consequently, it was necessary to place the dry xerogels in a fabric sachet prepared with dimensions sufficient to accommodate the swollen volume of the hydrogels. These sachets were prepared as follows: a perforated non-woven fabric was cut to the appropriate size (150 mm × 300 mm). This strip of material was then folded to form a square (150 mm × 150 mm). Two of the three open sides were then heat sealed with a domestic iron. The dried weighed xerogel (ca. 0.5 g) was then placed in the open sachet. Initial experiments indicated swelling ratios of ca. 10^2–10^3 for GLY-crosslinked P(NIPA-*co*-AA) hydrogels, and hence a mass of 0.5 g was calculated to be sufficient to yield hydrogels of maximum volumes consistent with the volume available within the sachets. The open side of the sachet was heat sealed and the (sachet + xerogel) was dried in a vacuum oven at 45°C to constant weight.

Prior to the swelling measurements, the swelling ratios of the sachet material were determined in water over the temperature range of the experiments. The value of the swelling ratio for the sachet material was 1.85 ± 0.10 and independent of the temperature. Hence the mass of a swollen sachet is 1.85 m_{sd}, where m_{sd} is the measured mass of dry sachet.

To a dry sachet (m_{sd}) was added a portion of dry xerogel to give a total mass m_0. A sachet plus its contents was swollen in water at 65°C until swelling equilibrium was confirmed (72 h). At each of several decreasing temperatures the sachet containing the swollen hydrogel was removed from its container and surface dried lightly and rapidly with filter paper; it was then weighed (m) in a stoppered tared container. The sample was then replaced in the water for a minimum of 30 min. and the value of m

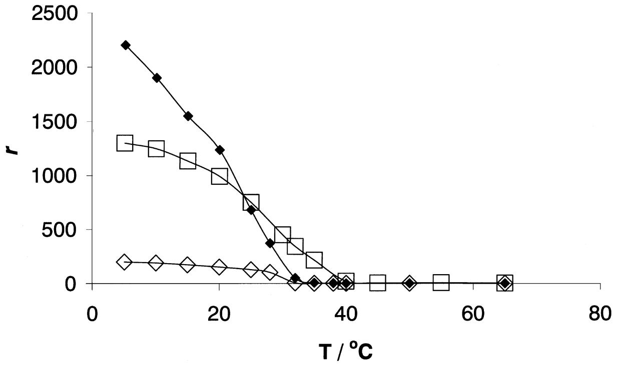

Fig. 1. Variation of swelling ratio *r* with temperature for hydrogels of: (◆) NIPA/AA10/GLY0.25, (□) NIPA/AA10/GLY0.5, (◇) NIPA/AA10/GLY1.0, swollen in pure water. Data points are for cooling cycle.

determined again as before. Allowance for the mass of swollen sachet gives the mass of hydrogel as ($m - 1.85m_{\mathrm{sd}}$). The mass of initial dry xerogel is ($m_0 - m_{\mathrm{sd}}$). Hence the swelling ratio *r* is given as

$$r = \frac{m - 1.85m_{\mathrm{sd}}}{m_0 - m_{\mathrm{sd}}} \qquad (1)$$

This procedure was repeated at least three times and an average value of *m* was used to obtain *r*. Uncertainty or error in *r* is taken to arise solely from uncertainty or error in *m*, which was overall ca. ±1% with respect to the average value of *m* used to calculate *r*. For swelling at each of several increasing temperatures exactly the same procedure was adopted. The absence of any sol fraction and the absence of hydrogel loss during the swelling process were confirmed by deliberately drying to completeness and weighing of samples after swelling/deswelling over a range of temperature. The final weight was identical with the initial weight of dry sample prior to the swelling/deswelling.

3. Results and discussion

3.1. Physical properties of GLY

The density (ρ) at 25°C of GLY is 0.9653 g cm^{-3} and its dependence on temperature (T) is given by ($\mathrm{d}\rho/\mathrm{d}T$) = -9×10^{-4} g cm^{-3}°C^{-1}. The refractive index (n) at 25°C and 589 nm is 1.4519 and its variation with temperature (T) is given by ($\mathrm{d}n/\mathrm{d}T$) = -4×10^{-4}°C^{-1}. It was found that GLY was miscible with the following monomers: AA, styrene, 2-methyoxyethylacrylate, *N*,*N*-dimethylacrylamide, 2-hydroxyethylmethacrylate and *N*-vinyl-2-pyrrolidone, methyl methacrylate and the solvents: acetone, chloroform, ethanol, dioxan, hexane, methanol, and toluene. It should be noted that GLY is only sparingly soluble in water and the aqueous monomer feed containing NIPA and AA (i.e. NIPA/AA10).

Table 1
Values of T_c and swelling ratio *r* at 20°C in water for hydrogels of NIPA/AA10/GLY and NIPA/AA10/BIS

	T_c (°C)	*r* at 20°C
NIPA/AA10/BIS0.25	38	70
NIPA/AA10/GLY0.25	27	1237
NIPA/AA10/BIS0.50	37	30
NIPA/AA10/GLY0.50	27	993
NIPA/AA10/BIS1.00	35	15
NIPA/AA10/GLY1.00	27	153

3.2. Swelling experiments

3.2.1. Swelling ratio

The variation of *r* with temperature (T) within the range 5–65°C is shown in Fig. 1. Practically complete deswelling occurs at $T \geq 45$°C. In the swollen state the value of *r* increases at any particular temperature with decreasing content of GLY. The highest values of *r* were obtained at the lowest temperature (5°C). Since the percentage water in a hydrogel (W) is given by $W = 100(r - 1)/r$, these values of *r* correspond to $W = 99.8$–99.9%, which are typical of superabsorbent materials [11]. Even at $T \sim$ ambient temperature, the reduced swelling still remains high. The values of *r* at 20°C are listed in Table 1, where the corresponding values obtained previously [7] for the gels crosslinked with BIS are also given for comparison. The swellability is clearly enhanced dramatically by the use of GLY, at comparable molar contents of crosslinker. In fact because 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 even on this basis the influence of GLY on enhancing swelling remains evident.

This is believed to be due to the lower crosslinking density of the GLY-hydrogels. The crosslinking efficiency of a polymer network is given by ν_e/ν_t, where ν_t is the theoretical crosslinker concentration calculated from the content of crosslinker in the feed mixture and ν_e the effective crosslinking concentration obtained, after appropriate correction for the presence of water in the feed mixture [12], from compression–strain measurements on the hydrogel in water. Values of ν_e/ν_t obtained previously at 28°C for hydrogels crosslinked with both BIS and GLY [13], were ca. 0.033 and 0.006, respectively. The difference in the effective crosslinking density of GLY and BIS hydrogels was indicated also by the weak and fluid nature of the GLY hydrogels compared to the rigidity of the BIS hydrogels.

3.2.2. Thermoreversibility

The curves in Fig. 1 are of identical form for both heating and cooling cycles. The hydrogels thus exhibit thermosensivity and thermoreversibility. Despite the lower values of *r* for the BIS-crosslinked hydrogels, the swelling/deswelling curves of the BIS and GLY systems are of the same overall form. However, differences occur between the values of T_c.

It is evident from Fig. 1 that it is difficult to assign a fixed value to this temperature, since deswelling is not a sharp discontinuous phenomenon. Instead, T_c has been regarded as the temperature or temperature region where the rate of change of swelling ratio with temperature is a maximum. By means of a computer programme plots (not reproduced here) of dr/dT vs. T were constructed. The values of T_c thereby afforded by the minima are listed in Table 1 together with the values obtained by the same procedure for the corresponding hydrogels crosslinked with BIS [7].

The reduction of T_c from 35–38°C in the BIS-crosslinked gels to ca. 27°C for the present systems is significant enough to lie outside the bounds of experimental uncertainty. In general hydrophobicity lowers T_c. As in copolymerisation involving EDMA [14], for example, full crosslinking capability may be reduced by non-participation of functional moieties (pendent groups) and/or cyclisation. Indeed the low crosslinking efficiency in the present systems is suggestive of the existence of such effects. The precise mechanism must be quantifiable on the basis of relevant reactivity ratios, which are not known. Certainly the low crosslinking efficiency can account for the ultra-high swelling and the strongly hydrophobic nature of GLY must be responsible at least in part for the low value of T_c.

Finally, it was found during these experiments that the problem of heterogeneity in P(NIPA-*co*-AA) hydrogels synthesised from aqueous feeds at temperatures close to T_c [15] did not occur, when feeds prepared with a mixed water/dioxan solvent system were utilised. The homogeneity of the hydrogels prepared in this mixed solvent system can be explained by the fact that the copolymers do not exhibit a T_c in this solvent system.

4. Conclusions

1. The novel crosslinker GLY has been employed to prepare superabsorbent thermosensitive P(NIPA-*co*-AA) hydrogels.
2. The difference in the swelling ratios of hydrogels crosslinked with BIS or GLY is due to the low crosslinking efficiency of GLY relative to that of BIS.
3. The lower value of T_c for hydrogels crosslinked with GLY, cf. that of hydrogels crosslinked with BIS, is suggested as being due in part to the hydrophobic character of GLY.

Acknowledgements

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