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Network and swelling parameters of chemically crosslinked thermoreversible hydrogels

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Abstract

Two series of hydrogels of poly(*N*-isopropylacrylamide-*co*-acrylic acid) have been prepared by copolymerisation in solution using tetrafunctional *N*,*N*′-methylene bis-acrylamide and a novel octafunctional crosslinker glyoxal bis(dially acetal) (GLY) as crosslinker. These thermoreversible hydrogels were swollen to equilibrium in water at 301 K and examined by gravimetric, dimensional and compression–strain measurements. The influence of nature and content of crosslinker on swelling ratio, polymer–water interaction parameter, elastic moduli and effective crosslinking density (ν_e) is reported and discussed. Both series exhibit low crosslinking efficiencies expressed as ν_e/(theoretical crosslinking density calculated from feed composition). The extremely low efficiencies for the GLY-crosslinked gels is responsible, at least in part, for the ultra-high swellability of these hydrogels.

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

1. Introduction

1.1. Abbreviations

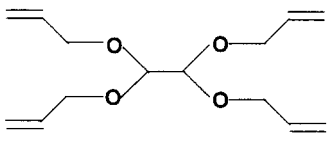
The following abbreviations, are adopted in the text: AA acrylic acid, APS ammonium persulphate, BIS *N*,*N*′-methylene bisacrylamide, DB Dextran blue, GLY glyoxal bis(diallyl acetal), NIPA *N*-isopropylacrylamide, PEG poly(ethylene glycol), PP polypropylene and TEMED tetramethylethylene diamine.

1.2. Nomenclature

The samples are denoted according to the composition of xerogels on the verified assumption of high conversion. The content of AA is its mole% with respect to NIPA and that of crosslinker is its mole% with respect to total principal monomers. For example, NIPA/AA10/BIS0.5 denotes that 100(number of moles of AA/number of moles of NIPA) = 10 and that 100[(number of moles of BIS)/(number of moles of NIPA + number of moles of AA)] = 0.5.

1.3. Background

Useful thermoreversible hydrogels have the ability to afford high values of the swelling ratio r (= mass hydrogel/mass dry xerogel) at ambient or sub-ambient temperature coupled with deswelling at an accessible lower critical swelling temperature T_c. Swelling and deswelling on cooling and heating, respectively, are reversible. The use of such materials to concentrate aqueous solutions of linear macromolecules also requires size selectivity i.e. the dissolved macromolecules should not be absorbed together with water into the gel. Phase diagrams of r vs. temperature have been established for hydrogels of P(NIPA-*co*-AA) crosslinked with BIS [1] and these materials have been employed to concentrate aqueous solutions of PEG and DB [2]. Subsequently it has been shown that thermoreversibility is retained when BIS is replaced by a novel octafunctional crosslinker GLY [3], which has the following structural formula.



With the use of this crosslinker the hydrogels fall into the category of superabsorbent materials. In order to assess size selectivity in relation to dissolved solutes of various sizes, the dimensions of the gel itself should be known. These can be expressed as mesh size or correlation length (measured by neutron scattering [4] or quasielastic light scattering [5]). However, the average molecular weight between crosslinks

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M_c and the effective (as opposed to nominal) crosslinking density ν_e can serve as an alternative rough guide. Evaluation of these parameters on an individual and comparative basis for BIS-crosslinked and GLY-crosslinked hydrogels forms for focus of this communication.

2. Experimental

2.1. Materials

The source of water, NIPA, AA, the initiator APS, the crosslinker BIS and the activator TEMED were as given before, as was also the mode of purification of water, NIPA and AA [1]. The source and purification of GLY were as described previously [3].

2.2. Synthesis of hydrogels

Hydrogels were prepared by crosslinking copolymerisation in solution. Small differences in conditions between reactions using BIS and GLY as crosslinker were necessary due to the insolubility of GLY in water and the need to optimise rate and conversion when using GLY.

With BIS as crosslinker the ratio NIPA/water was 15/85 (wt/wt), concentrations of initiator and activator were each 1 mol% with respect to total principal monomer. AA 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 mixture was introduced into 25 mm diameter glass vials (25 ml capacity with PP snap-fit cap). The vials were placed vertically in a large PP bottle that was then filled with oxygen-free nitrogen, sealed tightly and placed in a thermostat at 298 K for 24 h. The vials were broken and the hydrogels removed and slightly deswollen by immersion in water at 323 K for a short time. The hydrogel rods were inserted in metal tubes of appropriate thickness and diameter. The rods were maintained at 323 K, whilst their protruding ends were cut with a scalpel into thin discs (diameter ~25 mm, thickness 2–3 mm) and pellets (diameter ~25 mm and length ~25 mm). The discs and pellets were washed with distilled water at or below room temperature to remove any possible unreacted monomer and/or linear homopolymers. A separate rod was removed from its vial, washed thoroughly with cold water and dried to constant weight in a vacuum oven at 318 K. The fractional conversion was thereby obtained as described before [2] and found to be 0.92.

With GLY as crosslinker the following differences obtained: Reaction medium was water/1,4-dioxan (1:1 v/v), NIPA/mixed solvent was 8.6/91.4 (wt/wt), concentrations of APS and TEMED were each 2.0 mol% based on total principal monomers, copolymerisation was conducted for three days at 301 K followed by three days at 303 K. The resultant hydrogel was washed with water at room temperature.

2.3. Water content of hydrogels

Gravimetric swelling at 301 K was obtained as a swelling ratio r measured according to the simple procedure adopted previously [1]. Note that water content can also be expressed as fraction of water in hydrogel, W, where $W = (r - 1)/r$.

Discs already used for determination of the gravimetric water content were also employed to obtain the volumetric composition of the hydrogels. At a particular temperature, the volume fraction ϕ_2 of polymer within a hydrogel at swelling equilibrium is given by Eq. (1), in which D_0 and D are the diameters of dry and swollen to equilibrium disc, respectively.

$$\phi_2 = (D_0/D)^3 \quad (1)$$

Dried discs were individually weighed and their diameters measured using a micrometer; the densities (ρ) of xerogel were also obtained from the mass and measured dimensions. A particular problem encountered in drying of the discs was their propensity to curl. This was overcome by drying the hydrogels between perforated sheets of aluminium foil, which inhibited curling by acting a physical barrier rather than by imposing pressure on to the hydrogel. Values of D were measured at 301 K, using a binocular microscope positioned directly above the swollen disc to allow direct reading of the diameter and a magnification of 2–3 times. Full details have been given elsewhere [6].

2.4. Compression–strain measurements

Elastic moduli of the hydrogels were determined by stress (compression)–strain measurements. A full description of the compression rig and experimental details for its use have been given previously [7]. No barrelling effects were noted during compression.

3. Results and discussion

3.1. Swelling properties

Table 1 summarises the swelling properties of the copolymers prepared in the presence of five different concentrations of BIS within the range 0.50–2.5 mol%. The

Table 1
Volume fraction of polymer (ϕ_2), swelling ratio (r) and polymer–water interaction parameter (χ) at swelling equilibrium at 301 K for poly(NIPA-*co*-AA) hydrogels prepared in the presence of different contents of BIS

Sample	r	ϕ_2	χ
NIPA/AA10/BIS0.5	8.5	0.12	0.56
NIPA/AA10/BIS1.0	7.1	0.13	0.56
NIPA/AA10/BIS1.5	6.7	0.13	0.56
NIPA/AA10/BIS2.0	6.5	0.14	0.56
NIPA/AA10/BIS2.5	6.2	0.15	0.57

Table 2
Volume fraction of polymer (ϕ_2), swelling ratio (r) and polymer–water interaction parameter (χ) at swelling equilibrium at 301 K for poly-(NIPA-*co*-AA) hydrogels prepared in the presence of different contents of GLY

Sample	r	ϕ_2	χ
NIPA/AA10/GLY1.5	94	0.04	0.50
NIPA/AA10/GLY2.0	86	0.07	0.52
NIPA/AA10/GLY2.5	51	0.18	0.57
NIPA/AA10/GLY3.0	41	0.23	0.59
NIPA/AA10/GLY3.5	23	0.25	0.60
NIPA/AA10/GLY4.0	12	0.41	0.70

corresponding data for hydrogels prepared in the presence of six different concentrations of GLY within the range 1.5–4.0 mol% are listed in Table 2. The very high swellability in the GLY-crosslinked gels, cf. that in the gels crosslinked by BIS, is evident. Moreover, the effect of increasing crosslinker content in reducing the swelling is much more pronounced for the former than for the latter. Because of the two-fold factor between the respective functionalities, the listed BIS-crosslinked samples should be compared with corresponding GLY-crosslinked gels of contents that are one half of those listed in Table 1, i.e. 0.25–1.25 mol% GLY. As seen in Table 2, the actual contents of GLY were all above this range (because otherwise the ultrahigh swelling would have induced fragility and rendered it almost impossible to cut pellets for compression–strain measurements). GLY-crosslinked gels thus come into the category of superabsorbent materials and, as reported previously by us [3], the values of r for them are 1000–2000 at temperatures much below 301 K, i.e. at 278 K. This high swellability appears to be an inherent characteristic of GLY-crosslinked gels, because the relevant temperature used here, 301 K, is not dramatically lower than the T_c for BIS-crosslinked and GLY-crosslinked gels.

The polymer–water interaction parameter χ (obtained as described in the following section) has values that increase only slightly with increasing content of BIS (Table 1), whereas the increase with increasing content of GLY is more pronounced (Table 2). However, the significant factor is probably the dependence of interaction parameter on polymer concentration in gel, expressed as ϕ_2. Inclusion of the data in Tables 1 and 2, i.e. for BIS-crosslinked and GLY-crosslinked hydrogels shows a reasonable fit of χ vs. ϕ_2 on a single curve (not reproduced here), which extrapolates to $\chi = 0.46$ at infinite dilution.

3.2. Network parameters

Young's moduli E were obtained as the slopes in plots of stress (τ) vs. strain ($\lambda - 1$), where τ is the applied force per unit area of hydrogel and λ is the ratio of deformed length to undeformed length of hydrogel. Over the range of strain covered, 0 to -0.07, the plots were linear.

The theoretical crosslinking density ν_t is given as follows in terms of concentration C (mol dm^{-3}) of crosslinking agent of functionality f

$$\nu_t = Cf/2 \tag{2}$$

In Eq. (2) values of $f = 4$ and $f = 8$ are taken for BIS and GLY, respectively. The values of C were calculated from the mole% of crosslinker in the feed and by taking the density ρ of all the xerogels as 1.1 kg dm^{-3}. This latter value is the average of densities obtained from direct weights and micrometrically measured dimensions of all the dried discs and pellets used (the value of ρ was virtually independent of the concentration of crosslinker over the range used here).

The effective crosslinking density ν_e was obtained from the results of compression strain measurements using Eqs. (3) and (4). At low strains, i.e. 0 to -0.07, plots of τ vs. $(\lambda - \lambda^2)$ were linear, thereby yielding the compression moduli G as the slope from which values of ν_e were obtained via Eq. (4) where RT has its normal meaning. For the present systems, a solvent was included within the reaction medium and hence the correction factor [8] V_u/V_f is required in Eq. (4). V_u and V_f are the volumes of the dry unstrained xerogel and the network at its formation, respectively.

$$\tau = G(\lambda - \lambda^{-2}) \tag{3}$$

$$G = \mathrm{R}T\nu_e\phi^{1/3}\left[\frac{V_u}{V_f}\right]^{2/3} \tag{4}$$

From the values of ν_e and ρ the molar mass per crosslink (M_c) was calculated via Eq. (5).

$$M_c = \frac{\rho}{\nu_e} \tag{5}$$

Finally, values of the polymer–water interaction parameter χ were calculated from the following expression valid at swelling equilibrium, in which V_1 is the molar volume of water at 301 K

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \nu_e V_1(\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \tag{6}$$

Before considering the network parameters it will be useful at this juncture to supplement on the basis of Eq. (6) the previous discussion on the values of χ. Isolation of χ depends mainly on the mixing contribution, i.e. the first three terms on the LHS of Eq. (6). Numerically, it is found that the elastic contribution, i.e. remaining terms, have only a slight effect on the derived value of χ. Because in the present system wherein ϕ_2 and ν_e are small, this is especially true and Eq. (6) can be reduced as follows to an excellent approximation

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 \sim 0 \tag{7}$$

Expansion of the logarithmic series, followed by truncation of terms in ϕ_2^4, ϕ_2^5, ϕ_2^6 etc. and rearrangement yields

$$\chi \sim 1/2 + \phi_2/3 \tag{8}$$

Table 3
Network parameters at 301 K for poly(NIPA-*co*-AA) hydrogels prepared in the presence of different contents of BIS

Sample	E (kPa)	G (kPa)	ν_t (mol dm^{-3})	ν_e ($10^{-3}\times$ mol dm^{-3})	M_c (kg mol^{-1})
NIPA/AA10/BIS0.5	5.89	1.81	0.102	5.13	216
NIPA/AA10/BIS1.0	9.64	2.95	0.203	8.27	134
NIPA/AA10/BIS1.5	14.9	4.35	0.305	12.7	87.4
NIPA/AA10/BIS2.0	16.8	5.12	0.406	14.3	78.0
NIPA/AA10/BIS2.5	22.0	6.68	0.508	18.4	60.4

Table 4
Network parameters at 301 K for poly(NIPA-*co*-AA) hydrogels prepared in the presence of different contents of GLY

Sample	E (kPa)	G (kPa)	ν_t (mol dm^{-3})	ν_e ($10^{-3}\times$ mol dm^{-3})	M_c (kg mol^{-1})
NIPA/AA10/GLY1.5	0.845	0.271	0.420	1.78	656
NIPA/AA10/GLY2.0	1.32	0.419	0.839	2.26	517
NIPA/AA10/GLY2.5	4.54	1.44	1.05	5.71	204
NIPA/AA10/GLY3.0	5.29	1.68	1.26	6.16	189
NIPA/AA10/GLY3.5	6.52	2.07	1.47	7.31	159
NIPA/AA10/GLY4.0	9.28	2.93	1.68	8.85	132

Of course full implementation of Eq. (6) does allow in principle the values of χ to be <0.50. However, Eq. (8) indicates that $\chi \geq 0.50$. In fact use of Eq. (8) in conjunction with the values of ϕ_2 affords values of χ that lie in close accord with those listed in Tables 1 and 2.

The values of E, G, ν_t, ν_e and M_c are listed in Tables 3 and 4 for the BIS-hydrogels and GLY-hydrogels, respectively. For an elastic hydrogel the ratio E/G should equal 3.0 in the limit of vanishingly small strain. For finite strain the value of E/G should be slightly <3.0 in extension and slightly >3.0 when using compression [6]. For the eleven sets of data in Tables 3 and 4 the values of E/G do not deviate significantly from the average value of 3.20. In all cases an increase in nominal content of crosslinker leads to an increase in elastic moduli and effective crosslinking density and to a decrease in M_c. At comparable molar contents the elastic moduli of the GLY-hydrogels are much smaller than those of the BIS hydrogels. In general ν_e varies with ν_t according to Eq. (9) in which α is the value of effective crosslinking in the absence of any included chemical crosslinker; it may arise from physical crosslinking or crosslinking induced when γ-irradiation is used in the synthesis. The parameter β is a measure of crosslinking efficiency ($\beta = \nu_e/\nu_t$ when $\alpha = 0$) and its magnitude is usually [9–12] ≤ 1.0, although one unusual case has been reported [9] where $\beta > 1.0$.

$$\nu_e = \alpha + \beta\nu_t \tag{9}$$

Plots (not reproduced here) according to Eq. (9) display linearity for the BIS-hydrogels with $\alpha = 0.6\times 10^{-3}$ mol dm^{-3} and $\beta = 0.037$. For the GLY-hydrogels linearity is also displayed, but the value of ν_e for NIPA/AA10/GLY2.0 seems to be too low in relation to the overall fit of the other points. Using the remaining five points the plot yields $\alpha = 0$ mol dm^{-3} and $\beta = 0.005$. Consequently the crosslinking efficiency is low for BIS and extremely low for GLY. This finding must be responsible, at least in part, for the ultra-high swelling of the GLY-crosslinked gels. In principle the content of crosslinker in the terpolymer can be calculated at each stage of fractional conversion for a specified feed composition. If such contents of crosslinker in terpolymer are very low, this would account for the observed low crosslinking efficiency. However, the relevant reactivity ratios are not available and, unfortunately, the same applies to the relevant Q, e values that have been shown previously [11,13] to be an acceptable alternative. Finally, in connection with crosslinking efficiency, it has been pointed out by Mark [14] that gel formation in solution is often characterised by low crosslinking efficiency due to formation of a large number of elastically ineffective dangling ends in the network. It is not possible to make meaningful comparison of the present network parameters with literature values because such values are scant [15] for thermally reversible gels and, as far as we are aware, non-existent for the particular hydrogels considered here.

Acknowledgements

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