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Polymer 48 (2007) 7539–7545

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Effect of the incorporation of a low amount of carbohydrate-containing monomer on the swelling properties of polyacrylamide hydrogels

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Received 26 January 2007; received in revised form 8 October 2007; accepted 11 October 2007

Abstract

In this work, the influence of the incorporation of a small amount of carbohydrate-containing monomer *N*-acryloyllactosylamine (LAM) on the swelling behavior of covalently-crosslinked polyacrylamide hydrogels in water has been reported. The incorporation of LAM into the copolymer was assessed by ATR–FTIR and thermogravimetric experiments. The main result is that the equilibrium water uptake was significantly decreased as soon as the hydrogel contained LAM considering a constant amount of crosslinking agent. The greatest difference of water uptakes between carbohydrate-free hydrogel and carbohydrate-containing hydrogel occurred for the lowest crosslinker amount of 1 mol%. In that case, the value of the water uptake reached ∼56-fold for the carbohydrate-free hydrogel and decreased down to 41-fold for the 10 mol% LAM hydrogel. Additional NMR experiments were used to measure the amount of non-crystallizable water which was higher for carbohydrate-free hydrogel than that for lactose-containing hydrogel confirming the water uptake results.

Keywords: Hydrogel; Carbohydrate; Polyacrylamide

1. Introduction

Hydrogels are hydrophilic polymer networks which may absorb from 10 to 20% up to thousand times their dry weight in water [1].

Since the pioneering work of Wichterle and Lim in 1960 [2] on covalently-crosslinked hydroxyethylmethacrylate (HEMA) hydrogels, and because of their hydrophilic character and potential to be biocompatible, hydrogels have been of great interest to biomaterial scientists for many years. Examples of applications which have attracted considerable success can be found in the fields of cell encapsulation [3], artificial burn dressings [4] and more recently tissue engineering as matrices for repairing and regenerating a wide variety of tissues and organs [5,6].

Among the different hydrophilic monomers the more often used are HEMA, (meth)acrylamide, (meth)acrylic acid, etc. But some works have already been done using carbohydrate-containing monomers [7–9].

The potential interest to incorporate carbohydrate as a substituent in a polymer material is based on the structural diversity of carbohydrates and their specific molecular recognition which should allow a wide range of applications in the biotechnological and biomedical fields [10,11].

Dealing with a fundamental approach, it is important to know how a given physical–chemical property of a polymer material is affected by the incorporation of carbohydrates. For this reason, we have chosen to study the swelling capacity of polyacrylamide hydrogels in water with a small amount of covalently linked carbohydrate which is the main difference

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doi:10.1016/j.polymer.2007.10.032

compared to previous works on carbohydrate-containing hydrogels [7–9].

For that purpose, we have copolymerized a carbohydrate monomer, the *N*-acryloyllactosylamine (LAM), with an excess of acrylamide (AM) as comonomer using free radical polymerization (initial mol% ratio of comonomers LAM/AM: 0, 2, 5 and 10) in the presence of different amounts of a crosslinking agent (*N*,*N*′-methylene-bisacrylamide). We studied both the influence of the carbohydrate content and of the crosslinkage on the swelling ratio (SR) of the hydrogel in water. The incorporation of carbohydrate monomer in the hydrogel was assessed by ATR–FTIR and thermogravimetric experiments. Then, we have correlated the SR values with the amount of non-crystallizable water of the hydrogel obtained by NMR experiments.

2. Experimental

2.1. Material

α-D-Lactose monohydrate (99.5% purity) (Acros), acryloyl chloride (98% purity) (Fluka), acrylamide (98% purity) (Fluka), *N*,*N*′-methylene-bisacrylamide (96% purity), ammonium persulphate (98% purity) and *N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine (99% purity) (Acros) were used without further purification.

2.2. *N-Acryloyl-4-O-(β-D-galactopyranosyl)-β-D-glucopyranosylamine (LAM)* **3** *synthesis*

The method used involved the preparation of a functional carbohydrate monomer consisting of two steps reaction (Scheme 1) of (i) the synthesis of lactosylamine **2** by amination of lactose **1** at the anomeric position [12], followed by (ii) the acryloylation of lactosylamine [13] to obtain LAM **3**.

(i) Synthesis of lactosylamine – To an aqueous solution of α-D-lactose (0.4 M, 10 g, 29.23 mmol into 73 mL of water) containing NH_4HCO_3 (0.2 M, 1.155 g, 14.62 mmol), commercial aq. NH_3 (16 M) was added. The reaction was undertaken in a closed thick glass vessel. The solution was heated for 48 h at 42 °C. Ammonia was then removed under vacuum and the remaining solution was freeze-dried to eliminate salts and water. Lactosylamine was obtained quantitatively as a brownish-orange solid. ^1H and ^{13}C NMR (not shown) assessed the purity of the product.

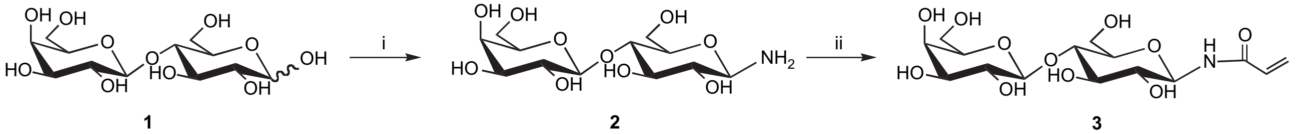
(ii) Synthesis of LAM – Lactosylamine (1 g, 2.93 mmol, 1 eq.) was added to a solution of sodium carbonate (2 g, 18.9 mmol into 42 mL of a mixture $MeOH/H_2O$ 1/1). The mixture was stirred at 0 °C while acryloyl chloride (14.65 mmol, 5 eq.) was added dropwise. The reaction was controlled by TLC in the eluent *i*-PrOH–AcOEt–H_2O (3:3:1). After 60 min, the solution was diluted with water. Acryloyl chloride and the solvents were removed under vacuum. The product was diluted in water and the aqueous solution was then applied onto a C-18 silica gel column. The fractions containing product were pooled and lyophilized. LAM (683 mg, 1.73 mmol) was obtained in 59% yield.

$R_f = 0.23$ (3:1:1 *i*-PrOH–AcOEt–H_2O). ^1H NMR (250 MHz, D_2O): δ (ppm) 4.46 (d, H-1 gal, $J_{1,2} = 7.8$ Hz), 5.1 (d, H-1 glc, $J_{1,2} = 8.7$ Hz), 5.87 (m, $CH{=}CH_2$), 6.31 (m, $CH{=}CH_2$).

^{13}C NMR (62.5 MHz, D_2O): δ (ppm) 60.1 (C-6 glc), 61.3 (C-6 gal), 68.8 (C-4 gal), 71.2 (C-2 gal), 71.8 (C-2 glc), 72.8 (C-3 gal), 75.3 (C-3 glc), 75.6 (C-5 gal), 76.7 (C-5 glc), 78 (C-4 glc), 79.5 (C-1 glc), 103.1 (C-1 gal), 129.6 ($CH{=}CH_2$), 129.9 ($CH{=}CH_2$), 169.6 ($C{=}O$).

2.3. *Hydrogel synthesis*

Monofunctional monomers with molar feed ratios of 0/1, 1/50, 1/20 and 1/10 LAM/AM were mixed and the crosslinking agent, *N*,*N*′-methylene-bisacrylamide $CH_2{=}CH(C{=}O){-}NH{-}CH_2{-}NH{-}(C{=}O){-}CH{=}CH_2$ (BIS), was added in the amount of 1, 1.5, 2 and 3 mol% of AM. Ammonium persulphate $(NH_4)_2S_2O_8$ (APS) and *N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine (TMEDA) were used as initiating systems in aqueous condition. In a classical experiment, three aqueous solutions of equal volume ($V = 1.2$ mL) of AM (2.4 mmol), of LAM (0, 48, 120 or 240 μmol) and of BIS (24, 36, 48 or 72 μmol) were mixed. Nitrogen was bubbled through the mixture for 15 min to remove dissolved oxygen that would act as an inhibitor for the reaction. Then two solutions of equal volume ($V = 0.2$ mL) of APS (48 μmol) and TMEDA (48 μmol) were added. The mixture (total volume of 4 mL) was rapidly casted between glass slides and polymerized within 20 h at room temperature. The resulting hydrogel (thickness of 2 mm) was either cut into disks of 2.9 cm for the swelling ratio measurements or divided into pieces in the case of ATR–FTIR, TGA and NMR experiments. Those pieces were placed in an excess of degased water for 48 h (the water was changed every 12 h to remove any unreacted monomers, linear copolymer, crosslinking agent and initiators). The pieces were then dried for 24 h in an oven at 60 °C.



Scheme 1. Synthesis of *N*-acryloyl-4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranosylamine (LAM) **3**. Conditions: (i) NH_4HCO_3, aq. NH_3, 42 °C, 48 h; (ii) acryloyl chloride $CH_2{=}CHCOCl$, $MeOH/H_2O$, Na_2CO_3, 0 °C, 1 h.

Copolymer hydrogels are hereafter designated as 0% LAM (PAM), 2% LAM, 5% LAM and 10% LAM hydrogel, depending on the LAM/AM molar feed ratio.

2.4. Swelling measurement

The equilibrium weight swelling ratio (SR) is defined as

$$\mathrm{SR} = W_s/W_d$$

where W_s is the weight of the swollen hydrogel after immersion in degassed water for 48 h and W_d is the weight of the dry hydrogel.

W_s is obtained by extrapolating at zero time the linear regression of the $W(t)$ values which are decreasing with time because of solvent evaporation. $W(t)$ values are obtained by weighing during a total time of 10 min at intervals of 2 min the wet hydrogel just after it has been removed from the water-bath.

2.5. ATR–FTIR experiments

ATR–FTIR was performed on a Bruker IFS 66 spectrometer equipped with an attenuated total reflectance accessory (ATR single-reflexion, Diamond, incident angle 45°, Pike Miracle, Pike Technologies, Madison, USA).

2.6. Thermogravimetric experiments

Thermal studies of the dry gel samples were performed using a thermogravimetric analyser (TGA) (TGDTA 92-16.18 Setaram, France) with a sample weight of 5–10 mg introduced in a quartz crucible. The temperature range in these experiments encompassed 25–600 °C at a heating rate of 20 $^\circ\mathrm{C\,min^{-1}}$ using an argon purge at a flow rate of 1 $\mathrm{L\,h^{-1}}$.

In order to avoid the continuous weight loss starting at the beginning of the heating observed previously on linear polyacrylamide [14] the following temperature program was used: heating from 25 to 200 °C with a heating rate of 20 $^\circ\mathrm{C\,min^{-1}}$; isotherm at 200 °C for 120 min and finally heating to 600 °C with a heating rate of 20 $^\circ\mathrm{C\,min^{-1}}$.

2.7. NMR experiments

NMR experiments were performed with a Bruker AM360 spectrometer equipped with a 5 mm broad band probe without field/frequency lock control. ^{2}H NMR spectra were recorded at a frequency of 55.3 MHz. The free induction decay (FID) were recorded using a $\pi/2$ pulse width (15 μs) and a recycle delay of 2 s. To obtain spectra with a good signal to noise (S/N) ratio 800 transients were added. The FID signals were typically sampled with 4096 real data points over a 20 kHz spectra width and an exponential line broadening of 3 Hz was used (which is small compared to the experimental linewidth which is 40 Hz at RT and 2500 Hz at 250 K). Peak areas were measured by numerical integration of the spectra. Temperature was controlled in the range 245–300 K by a Bruker VT100 system (±1 K regulation). Calibration was performed before each set of measurements was carried out using the standard procedure with a reference methanol sample.

3. Results and discussion

We consider that a statistical copolymerization occurs as that was already shown on different comonomer systems consisting of classical monomer and a vinyl sugar derivative: acrylamidolactamine-*co*-*N*-isopropylacrylamide (NIPAM) [15], and 4-vinylphenyl-D-gluco(D-manno)hexitol-*co*-acrylamide [16]. In both cases, the product of the corresponding reactivity ratio is close to 1.

We have also checked that the copolymerization of LAM and AM with similar molar feed ratios LAM/AM but without crosslinking agent led to highly water-soluble chains [17].

3.1. Swelling ratio

Fig. 1 shows the SR values versus the amount of crosslinker BIS/AM mol% in the range 1–3% for different initial mol% ratio of LAM/AM of 0, 2, 5 and 10%.

Equilibrium weight swelling ratio values are in the range 27–57 $\mathrm{g\,g^{-1}}$.

For a constant LAM/AM ratio, SR decreases with the mol% ratio BIS/AM. That is easily explained by the fact that the distance between crosslinking points is smaller as soon as the crosslinker amount increases. So the crosslinking degree of the network restricts its swelling capacity. This is a classical behavior of a neutral polymer hydrogel which has been theoretically demonstrated by Eq. (1) [18]:

$$q \sim [(0.5 - \chi_{12})/r_c]^{3/5} \tag{1}$$

where:

- q is the equilibrium volume swelling ratio;
- χ_{12} is the polymer–solvent interaction parameter;
- $r_c \sim$ [R]/[M]: the crosslinking degree of the network;
- [R] is the crosslinker concentration;
- [M] is the monomer concentration.

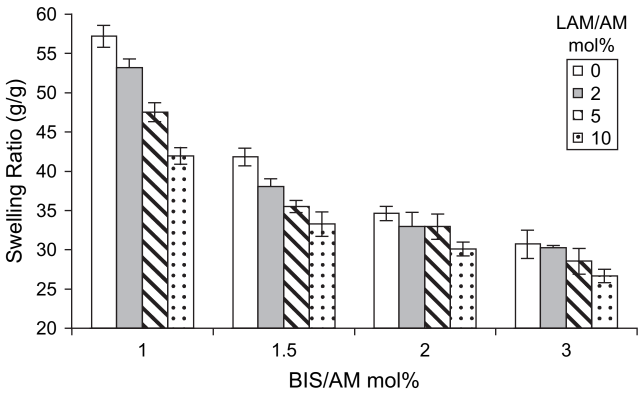


Fig. 1. Swelling ratio results of 0, 2, 5 and 10% LAM hydrogels versus BIS/AM mol%.

In our case $[R]/[M] = [BIS]/([AM] + [LAM]) \sim [BIS]/[AM]$ as $[AM] \gg [LAM]$.

Our experimental results can be roughly analyzed using Eq. (1) even if we measure for convenience the weight swelling ratio and not the volume swelling ratio. Eq. (1) means that a decrease of the swelling ratio is expected with the crosslinker amount.

For $LAM/AM = 0$, i.e. carbohydrate-free polyacrylamide hydrogels, the SR values are decreasing exponentially as expected from Eq. (1). Between 1 and 3% of crosslinking mol%, SR value decreases from 57 down to 31 $g\,g^{-1}$, i.e. 46% loss of the swelling ratio. Then as the LAM/AM mol% increases from 2, 5 and 10%, the difference between the SR values at 1 and 3% of crosslinking mol% decreases to 43, 40 and 36%, respectively.

The other main information of this swelling study is the general decrease of SR with the initial feed ratio of LAM/AM considering the crosslinker amount constant (Fig. 1). We can observe that as soon as LAM is incorporated in the hydrogel, the weight swelling ratio value decreases. For a fixed crosslinker amount, the greatest difference between 0% LAM hydrogel and a 10% LAM hydrogel is obtained when the gel is the loosest, i.e. for the smallest BIS/AM mol% of 1%. In that case, the weight swelling ratio value decreases from 57 down to 42 $g\,g^{-1}$, i.e. 23% of reduction in swelling ratio. Then, the loss is only 20, 13 and 13%, for BIS/AM mol% of 1.5, 2 and 3%, respectively.

Considering the crosslinking mol% ratio of 1 and 1.5%, there is a pronounced and significant decrease of the swelling ratio with the carbohydrate content. This behavior could be explained by the replacement of carbohydrate groups which have less affinity for water than the amide groups. It could also be explained by a higher steric hindrance due to the higher size of the carbohydrate moieties as compared to amide function. Another tentative explanation of gel shrinkage behavior when the carbohydrate level increases could be explained by the formation of physical crosslinking points due to the interaction between the carbohydrate moiety of LAM and acrylamide constitutional repeating units of the copolymers. Livney et al. [19] indeed suggest that the experimental increase of the swelling of PAM hydrogels with rising concentrations of glucose solutions may be explained by the enthalpic favorable interaction between glucose and PAM.

The decrease of the swelling ratio with the carbohydrate content is less pronounced for crosslinking mol% ratio of 2 and 3%. For example, considering the highest crosslinking degree, SR value decreases not significantly from 29 ± 2 to 27 ± 1 $g\,g^{-1}$ for 5% LAM hydrogel and 10% LAM hydrogel, respectively. To resume, for the higher amount of crosslinking the SR value decreases with the carbohydrate content but there the difference is not significant. The relatively high bars of errors in SR values could be explained by a low incorporation of the carbohydrate monomer. We tried to perform carbohydrate analysis which is a quantitative method that we commonly used [20–22] to confirm the level of incorporation of LAM in the hydrogel but without success probably due to the entrapment of the carbohydrate into the three dimensional structure of the hydrogel. Finally we succeeded in the carbohydrate analysis of AM-*co*-LAM linear copolymers obtained by a similar free radical copolymerization process of AM and LAM without BIS. The result was a level of incorporation of LAM below 50 mol% with discrepancies between the values. That could be an explanation of the relatively high bars of errors obtained in the case of SR values of carbohydrate-containing hydrogels.

What we observed is the water-solubility of the corresponding linear LAM copolymers. Water appears to be a thermodynamically good solvent for LAM copolymers. However, water is perhaps not as good a solvent for our carbohydrate copolymers as for PAM. It is well documented that water is a thermodynamically good solvent for PAM (A_2 of the order of 10^{-4} $mol\,cm^3\,g^{-2}$ at 25 °C in water [23]) but Klein and Herzog [24] have concluded that lower values of intrinsic viscosities and second virial coefficient A_2 are an indication of a lower degree of polymer–water interaction of poly(vinylsaccharide)s compared to PAM.

Following this analysis, we have performed curve fitting of the experimental results of SR as a function of the crosslinking density on the basis of varying the value of the interaction parameter χ_{12} as a function of LAM/AM.

Fig. 2 shows the experimental results of SR as a function of the crosslinking density for 0, 5 and 10% LAM hydrogel with corresponding fitted curves obtained by using Eq. (1). If an arbitrary value of χ_{12} is chosen to fit the data of 0% LAM hydrogel, a relative increase of the interaction parameter $\Delta\chi_{12} = 0.15$ and $\Delta\chi_{12} = 0.23$ is necessary to fit the experimental data for 5% LAM hydrogel and for 10% LAM hydrogel, respectively. An increase in the interaction parameter χ_{12} is an indication of a decrease of polymer–solvent interactions.

Fig. 2 shows that Eq. (1) fits nicely the experimental results of SR as a function of the crosslinking density for 0% LAM hydrogel. The fits are not of such good quality as soon as LAM is incorporated in the hydrogel. In that case the theoretical curves fit the first two points but not the points corresponding to the highest crosslinking densities. That can be explained if it is considered that the carbohydrate incorporation is restricted when the crosslinking density increases. The level of

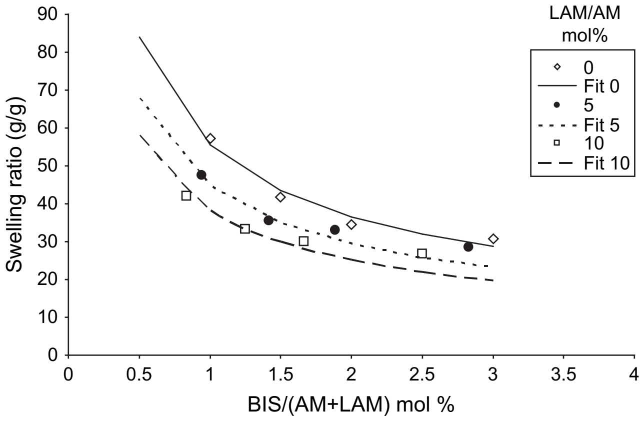


Fig. 2. Experimental results of the swelling ratio as a function of the crosslinking density for 0, 5 and 10% LAM hydrogel with corresponding fitted curves obtained by using Eq. (1) (see text).

carbohydrate incorporation is finally less than that is theoretically expected from the initial feed ratio.

To conclude, difference in swelling behavior between PAM and carbohydrate-containing hydrogels can be explained on the basis of considering the difference of solvent quality between PAM and carbohydrate-containing polymers. This swelling ratio study also shows that the incorporation of LAM into the final hydrogel is not complete especially in the case of the highest crosslinsking densities. ATR–FTIR and TGA experiments are then used to assess that at least a part of the incorporation of the carbohydrate monomers into the hydrogels has been realized.

3.2. ATR–FTIR experiments

Fig. 3 shows ATR–FTIR spectra of 0% LAM, 2% LAM and 10% LAM hydrogels. For the 0% LAM hydrogel, the characteristic bands of polyacrylamide are obtained (for example mainly, 3200–3330 $\mathrm{cm^{-1}}$: –N–H stretching, 2940–2885 $\mathrm{cm^{-1}}$: –C–H stretching, 1650–1660 $\mathrm{cm^{-1}}$ and 1600 $\mathrm{cm^{-1}}$: carbonyl –C=O (amide) and –C=N– resonance peaks coming from the amide group, respectively, 1450 $\mathrm{cm^{-1}}$ and 1410 $\mathrm{cm^{-1}}$ angular deformations of $-\mathrm{CH_2}-$). The ATR–FTIR spectrum of a 2% LAM hydrogel clearly reveals the incorporation of the carbohydrate moiety due to the presence of two additional absorption bands at 1080 and 1020 $\mathrm{cm^{-1}}$ which are in a typical range of C–O stretching absorption bands. These two additional bands compared to PAM are even more intense in the ATR–FTIR spectrum of a 10% LAM hydrogel.

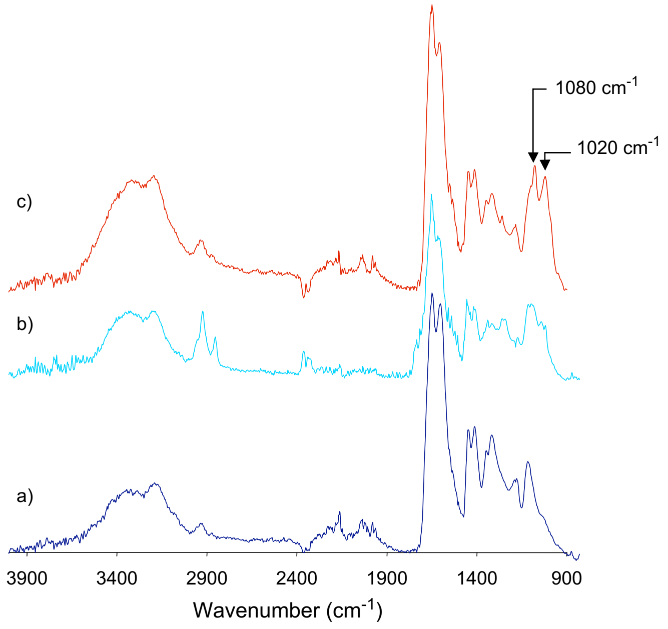


Fig. 3. ATR–FTIR spectra of (a) 0% LAM, (b) 2% LAM and (c) 10% LAM hydrogels.

3.3. TGA results

The incorporation of LAM into the hydrogel was also assessed by TGA experiments. Fig. 4 shows the thermal behavior of 0, 2, 5 and 10% LAM hydrogel for a crosslinking concentration of 3 mol%. No influence of the crosslinking concentration in the range 1–3 mol% was observed.

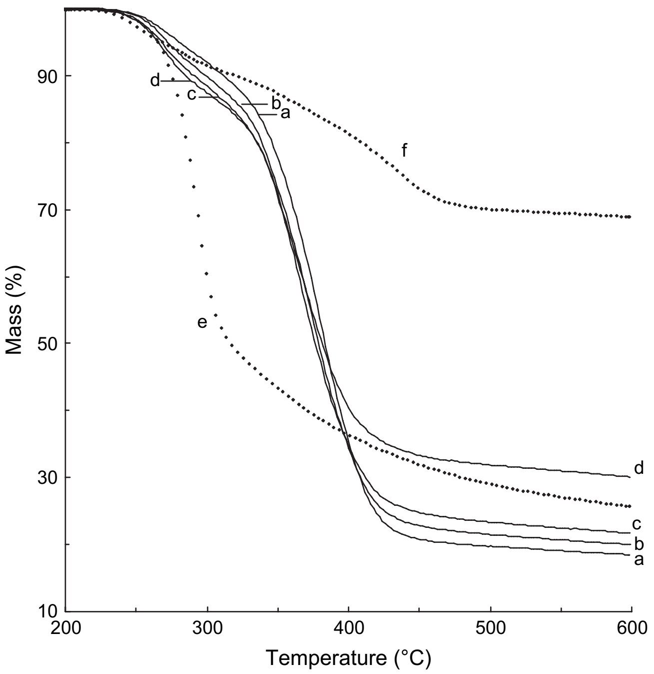


Fig. 4. TGA curves for (a) 0%, (b) 2%, (c) 5% and (d) 10% LAM hydrogels with a crosslinking amount of 3 mol% AM/BIS and TGA curves for (e) pure lactose and (f) pure LAM.

The TGA curve or spectra of 0% LAM (PAM) shows two degradation steps. The main loss of mass is obtained during the second event. The thermal degradation of PAM occurs with degradation temperatures $\mathrm{Td_1}$ of 268 ± 2 °C and $\mathrm{Td_2}$ of 384 ± 2 °C, and weight losses of 9 ± 1% and 74 ± 3%, respectively. The residue at 600 °C is found to be 19 ± 2%.

Minsk et al. [25] showed that PAM was decomposed above 285 °C with liberation of ammonia and formation of an imide group.

In the case of carbohydrate-containing hydrogels, the TGA curves also show two degradation steps (Fig. 4) but the results are slightly different as compared with PAM hydrogel. Whereas the degradation temperature of the first event ($\mathrm{Td_1}$) was not influenced by LAM incorporation, the degradation temperature of the second event ($\mathrm{Td_2}$) decreased significantly from 384 °C for 0% LAM, to 373 °C for 2% LAM and 5% LAM, down to 366 °C for 10% LAM. So the presence of LAM in the hydrogel structure decreases the thermal stability of the polymer.

Weight losses occurring during the first event increases steadily from 9, 10, 11 up to 14%, for 0% LAM, 2% LAM, 5% LAM and 10% LAM, respectively.

Weight losses occurring during the second event decreases steadily from 74% for 0% LAM, down to 69, 65 and 57%, for 2% LAM, 5% LAM and 10% LAM, respectively.

At the same time, the residue at 600 °C increases from 19, 21, 24 up to 30%, for 0% LAM, 2% LAM, 5% LAM and 10% LAM, respectively.

The TGA of pure lactose and pure LAM have been investigated in order to find a tentative explanation of the degradation behaviors of the carbohydrated hydrogels. Fig. 4 also shows the TGA curves mass loss versus temperature for pure lactose and pure LAM. In fact the degradation behavior of pure lactose is relatively simple consisting of only one degradation step with a degradation temperature of 294 °C which demonstrates the low thermal stability of the carbohydrate alone. However, the residue at 600 °C is still relatively high (26%).

In the case of LAM, the degradation behavior is more complex as it consists of at least a two-stage degradation characterized by degradation temperatures in the range 250–438 °C. Also a very high residual weight of 69% at 600 °C has been obtained. We can explain these results either by a possible combination of polymerization and heat resistance due to the carbohydrate moiety of the monomer during heating or by interactions between amide groups and carbohydrate moieties leading to hydrogen bonding causing heat resistance or both.

The presence of a lactosyl substituent decreases Td_2 and hence the thermal stability of the polymer. Zhou et al. [15] performed TGA studies on a copolymer of acrylamidolactamine-*co*-NIPAM with a carbohydrate monomer amount from 0 to 100%. They obtained a two-stage degradation for the copolymer; they associated the first degradation with the sugar moieties, and the second with the thermal degradation of the polyacrylamide main chain. The onset degradation temperature for polyNIPAM and polyvinyl-saccharide are 400 and 312 °C, respectively. The increase in residue as the amount of carbohydrate increases can also be observed in their thermogravimetric curves (Fig. 6 in Ref. [15]). Zhou et al. [26] also performed TGA experiment on a lactose-containing copolymer with a polystyrene main chain. They also obtained a two-stage degradation for the copolymer and they associated the first degradation with the sugar moieties.

So, finally TGA characteristics of the hydrogels are strongly influenced by the presence of LAM even at the lowest level of incorporation (2% LAM).

3.4. NMR results

The properties of water confined inside gels or porous materials can be accurately obtained from ^{2}H NMR analysis: ratio of crystallization and glass transition [27,28]. The virgin materials are swollen with D_2O, and the total water uptake is measured by weighing and are found similar to those obtained with normal water. Area of the deuterium NMR signal (A) is proportional to the amount of mobile water inside the sample. It is measured on cooling and heating the swollen material. The ratio $R = A(T)/A_0$ indicates the amount of non-frozen water at temperature T (where A_0 is the area of the peak at 300 K). A typical curve is presented in Fig. 5. An abrupt decrease of R is observed at 271 K corresponding to the crystallization of most of the water. The non-crystallizable water is determined from the low temperature plateau (2.6% in this material). Below 255 K, decrease of the intensity signal is related to the hindrance of mobility of the water molecules which are connected to the polymer network. An hysteresis for the water melting is observed. This is a rather usual feature for the crystallization/melting events.

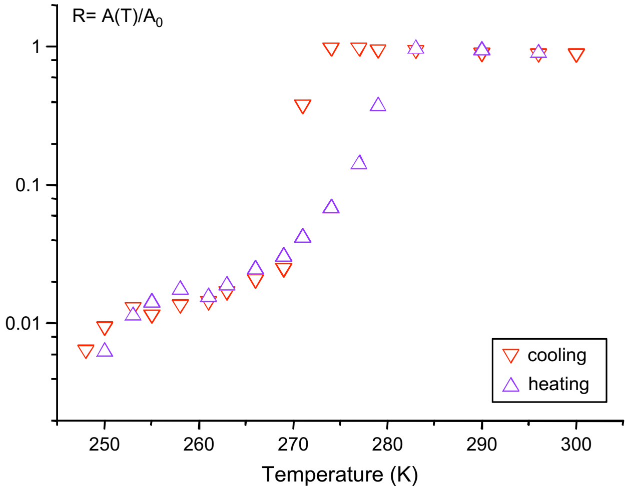


Fig. 5. $R = A(T)/A_0$ versus temperature for a 10% LAM hydrogel with a crosslinking amount of 1.5%.

NMR experiments were performed for six hydrogels corresponding to two different amounts of BIS/LAM and three different LAM contents.

Fig. 6 shows the non-frozen water mol% versus BIS/AM for three different amounts of LAM content: 0, 5 and 10%. The amount of non-frozen water is higher in the case of the 0% LAM hydrogel than that in the carbohydrate-containing hydrogels. For the 1.5% crosslinking amount, the non-frozen water is 4% for 0% LAM hydrogel and decreases down to 2.4 and 2.6%, for 5% LAM and 10% LAM hydrogels, respectively. In the case of 3% crosslinking amount, the non-frozen water is 5.2% for 0% LAM hydrogel and decreases down to 3.9% and 3.6%, for 5% LAM and 10% LAM hydrogels, respectively. No significant differences are observed between

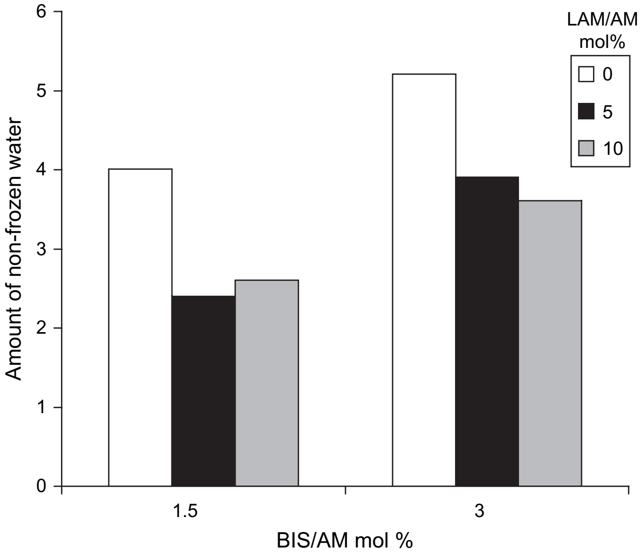


Fig. 6. Amount of non-frozen water obtained by NMR versus BIS/AM for LAM content of 0, 5 and 10%.

5 and 10% LAM polyacrylamide hydrogels. These results show that for a fixed amount of crosslinker, the non-frozen water decreases when the amount of carbohydrate increases. That means the water affinity is higher for PAM hydrogel than that for carbohydrate-containing hydrogel. So NMR results confirm the thermodynamic explanation of solvent quality.

For a constant value of LAM, the percentage of non-frozen water increases with the crosslinker amount. That means the water crystallization is restricted when the crosslinker amount increases. That trend correlates with the decrease of the water swelling ratio of the hydrogel as soon as the crosslinker density increases.

4. Conclusion

We have studied the effect of the incorporation of a carbohydrate-containing monomer on some physical-chemistry features of a crosslinked polyacrylamide hydrogel. Results obtained by simple water uptake measurements and by using NMR show that water has higher affinity for the non carbohydrate-containing hydrogel than for the carbohydrate-containing ones. Even if incorporation of the carbohydrate monomer into the 3-D network was not quantitative, FTIR and TGA assessed the incorporation of a part of the glycomonomer into the final hydrogel. The conditions of the polymerization have to be improved in order to increase the level of carbohydrate-containing monomers incorporated into the final copolymer. This is particularly tricky in the case of complex carbohydrate-containing monomers. This work could be now continued aiming at understanding the relationship between carbohydrate's chemical structure and property.

Acknowledgements

The authors thank Marc Tilloy (ICMMO) for the making of the quartz crucibles and Jocelyne Jegoudez and Patrick Berthet (LPCES, ICMMO) for the use of the TGA equipment.

References

[1] Hoffman AS. Adv Drug Deliv Rev 2002;43:3–12.
[2] Wichterle O, Lim D. Nature 1960;185:117.
[3] Lim F, Sun AM. Science 1980;210:908–10.
[4] Yannas IV, Lee E, Orgill DP. Proc Natl Acad Sci USA 1989;86:933–7.
[5] Lee KY, Mooney DJ. Chem Rev 2001;101:1869–79.
[6] Hutmacher DW. J Biomat Sci Polym Ed 2001;12:107–24.
[7] Martin BD, Ampofo SA, Linhardt RJ, Dordick JS. Macromolecules 1992;25:7081–5.
[8] Sakamato N, Suzuki K, Kishida A, Akashi M. J Appl Polym Sci 1998;70:965–72.
[9] Kim B, Peppas NA. J Biomat Sci Polym Ed 2002;13:1271–81.
[10] Okada M. Prog Polym Sci 2001;26:67–104.
[11] Ladmiral V, Melia E, Haddleton DM. Eur Polym J 2004;40:431–49.
[12] Lubineau A, Augé J, Drouillat B. Carbohydr Res 1995;266:211–9.
[13] Kallin E, Norberg T. J Carbohydr Chem 1989;8:597–611.
[14] E Silva MESR, Dutra ER, Mano V, Machado JC. Polym Degrad Stab 2000;67:491–5.
[15] Zhou WJ, Kurth J, Hsieh YL, Krochta JM. J Polym Sci Part A Polym Chem 1999;37:1393–402.
[16] Narain R, Jhurry D, Wulff G. Eur Polym J 2002;38:273–80.
[17] Renaudie L. PhD thesis. University Paris-Sud 11; 2004.
[18] Flory PJ. Principles of polymer chemistry. Ithaca, New York: Cornell University Press; 1953. p. 580.
[19] Livney YD, Portnaya I, Faupin B, Fahoum L, Ramon O, Cohen Y, et al. J Polym Sci Part B Polym Phys 2003;41:3053–63.
[20] Lepoittevin B, Masson S, Huc V, Haut C, Roger P. e-Polymers 2006:032.
[21] Renaudie L, Le Narvor C, Lepleux E, Roger P. Biomacromolecules 2007;8:679–85.
[22] Bech L, Meylheuc T, Lepoittevin B, Roger P. J Polym Sci Part A Polym Chem 2007;45:2172–83.
[23] Munk P, Aminabhavi TM, Williams P, Hoffman DE, Chmelir M. Macromolecules 1980;13:871–6.
[24] Klein J, Herzog D. Makromol Chem 1987;188:1217–32.
[25] Minsk LM, Kotlarchik C, Meyer GN, Kenyon WO. J Polym Sci 1974;12:133.
[26] Zhou WJ, Wilson ME, Kurth J, Hsieh YL, Krochta JM, Shoemaker CF. Macromolecules 1997;30:7063–8.
[27] Rault J, Neffati R, Judeinstein P. Eur Phys J B 2003;36:627–37.
[28] Judeinstein P, Carmo Lanca M, Marat-Mendes J, Rault J. Polymer 2000;41:8151–4.