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A new class of hydrogels based on hydroxypropylcellulose and polyvinylpyrrolidone

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Abstract

Hydrogels based on hydroxypropylcellulose, cross-linked in the presence of vinylpyrrolidone, were prepared and characterized. They are more self-supporting as the percentage of polyvinylpyrrolidone in the copolymer increases. The influence of the cross-link degree and chemical composition on the trend of equilibrium swelling as a function of temperature was analyzed. A thermal cycle corresponding to a reversible process of solvent adsorption and deadsorption is illustrated. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hydrogels are a class of compounds which are very interesting for biotechnological and biomedical applications, thanks to their noticeable swellability in water, biocompatibility and biodegradability. Some of them, generally obtained from hydrophilic monomers [1], are 'conventional' in that they do not exhibit any significant volume transition to environmental changes (i.e. pH, temperature, etc.), while others show volume transition in response to small changes in environmental conditions.

This latter behaviour was observed both for conventional [2] and mesogenic semirigid polymers [3]. As an example, we may refer to a class of hydrogels prepared by partial esterification of hydroxypropylcellulose (HPC) with methacryloylchloride, followed by UV irradiation to cross-link the system [3]. These gels not only show a different swelling in water as a function of the esterification degree DE (moles of methacryloyl residues per repetition unit), but also a peculiar trend of the swelling with the temperature: in particular a fairly significant change in gel volume with a very small change in temperature was observed. The behaviour was related to the trend of enthalpic and entropic components of the polymer–solvent interaction parameter χ as a function of temperature. The main limit to possible applications of these gels concerns their stability over time. The ester linkages tend to hydrolyze with moisture and the network is destroyed after a few weeks. So we planned a new synthesis of HPC gels based on ether linkages between the –OH functions of HPC and the allylic groups, as well as introducing a suitable amount of vinyl pyrrolidone (VP) during the cross-linking process to modulate the hydrophilicity of the network.

2. Experimental

2.1. Materials

HPC sample, supplied by Hercules, was the same used in a previous work [3]. Its M_w was 10^5 and MS (molar hydroxypropyl etherification) was 4.2 ± 0.2.

Allyl bromide, potassium *tert*-butoxide, 1-hydroxycyclohexyl phenyl ketone and *N*,*N* dimethyl-acetamide (Aldrich) were used as received.

Vinylpyrrolidone (NVP) (Fluka) was distilled under vacuum before use to eliminate the stabilizer.

1-Hydroxycyclohexylphenylketone (Fluka) was used as photoinitiator.

Deuterated chloroform (Aldrich) was used as a solvent and tetramethylsilane (Aldrich) as an internal standard for chemical shift reference in H NMR analysis.

2.2. Methods

FTIR spectra were measured using a Bruker IF66 spectrometer and H NMR spectra using a Varian Gemini mod. 2000.

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Gel swelling was determined as described in Ref. [3].

The shear modulus of the gel was evaluated from the curve of the mechanical stress as a function of extension ratio using an Instron dynamometer mod. 5500 [3]. It was demonstrated that the shear modulus G of a gel can be correlated to cross-linking degree ν from the relation [4–8]

$$G = RT\nu(\phi_2/\phi_{2,0})^{3/2}\phi_2$$

where $\phi_{2,0}$ is the volume fraction of the polymer in the solution before the cross-linking reaction and ϕ_2 is the polymer volume fraction in the gel at the equilibrium swelling. The polymer weight concentration may be converted to volume fraction provided that the density of the polymer ($1.190\ \mathrm{g\ ml^{-1}}$) and of the solvent ($0.965\ \mathrm{g\ ml^{-1}}$) are known and assuming additivity of the volumes.

2.3. HPC allylate (HPC-al) synthesis and characterization

Solutions of HPC and potassium *tert*-butoxide in *N*,*N* dimethylacetamide were prepared in anhydrous conditions: aliquots containing equimolar amounts of potassium *tert*-butoxide and HPC (in terms of –OH function) were mixed and left to react under stirring for about 2 h at room temperature. Addition of allylbromide in equimolar proportions determines HPC-al and KBr formation. After precipitation of the salt by the addition of ethylether and filtration, the ethylether excess was eliminated by evaporation and the polymer was separated by water addition. The FTIR spectrum of a film of HPC-al, thickness ~50 μm, in comparison with that of underivatized HPC shows a few new peaks which refer to –CH and $-CH_2$ allylic groups ($3100\ \mathrm{cm^{-1}}$) and to C=C double bond ($1600\ \mathrm{cm^{-1}}$), while the intensity of the –OH peak at $3450\ \mathrm{cm^{-1}}$ decreases because of esterification. This analysis qualitatively confirms the introduction of allylic groups on the HPC chain. The quantitative DE determination was made by using the proton NMR technique, considering that each different proton structural group gives rise to peaks at a characteristic magnetic field strength with an area proportional to the concentration of the proton group.

The recorded spectrum of HPC-al (solvent $CDCl_3$, internal marker TMS) shows the following signals: 1.12 ppm – CH_3, 1.75 OH, 3–4 ppm CH and CH_2 of hydroxypropyl group, 5–5.3 ppm CH_2 of allylic groups, 5.75–6 ppm CH of allylic groups. Designating A as the integrated area from the proton of the CH of the allylic group and B as the area from the methyl proton of the hydroxypropyl group, the DE value may be calculated from the equation

$$\mathrm{DE} = \frac{A}{B/(3\mathrm{MS})}$$

where MS is the molar substitution degree of HPC.

In the present case, $\mathrm{DE} = 1.37 \pm 0.1$. The result indicates that the introduction of allylic groups is only partial, in the conditions examined.

It is worth observing that HPC-al is a hydrophobic polymer, as confirmed by the lack of solubility in water. A similar result was obtained by some of us studying the behaviour of HPC–methacrylate ester with a degree of esterification $\mathrm{DE} > 0.2$. The polymer is practically insoluble in water, while at lower DE the phase diagram is similar, but not identical, to that of HPC in the same solvent [4]. The fields of stability of the different phases as well as the transition temperatures are reduced when a few hydrophobic groups are introduced along the chain [9].

In the present case, the transition temperature (nematic phase → isotropic phase) (T_{ni}), determined by DSC, is 203 °C for neat HPC and 183 °C for HPC-al.

2.4. Gel synthesis

The method consists in preparing a solution containing 5% of HPC-al in dimethylacetamide (DMAc). Successively, a predetermined amount of NVP and photoinitiator were added and the mixture was exposed to UV radiation. Four samples having an HPC-al/NVP ratio (w/w) of 1:0.5, 1:1, 1:1.5 and 1:2, were prepared in cylindrical tubes. The gel corresponding to the first composition was not self-supporting and was therefore not utilized. The others were swelled in water for a long time to allow the diffusion of PVP free homopolymer towards the solvent, and then they were dried in vacuum oven for about three days.

The final composition (HPC-al/PVP, w/w) of the gels was determined by weight and reported in Table 1: all the samples are self-supporting. Their stiffness increases with the PVP percentage.

The presence of such a remarkable amount of PVP places these gels at the border between those based on conventional and semirigid polymers. This makes it difficult to choose the best treatment to calculate the degree value of cross-linking ν. However, taking into account that the amount of PVP in our samples in terms of moles of monomeric units is always higher than the corresponding amount of moles of glucosidic units (HPC-al), we considered it reasonable to obtain ν from the shear modulus of each gel by applying the method suggested by Flory [5–7] and Treolar [8] for networks of conventional polymers [3].

Fig. 1 gives the trend of the stress as the function of $\lambda - \lambda^{-2}$, where λ is the deformation for sample 3. ν values are listed in column 4 of Table 1 and they suggest that an increase in NVP content before the cross-linking reaction causes an increase in cross-link number. So the gels richer in PVP are stiffer not only because of the different chemical

Table 1
Gel composition and cross-linking degree

Sample	HPC-al/PVP initial ratio (w/w)	HPC-al/PVP ratio in the gel (w/w)	ν ($\mathrm{mol\ m^{-3}}$)
1	1:1	1:0.37	7.7
2	1:1.5	1:0.56	12.0
3	1:2	1:0.80	18.6

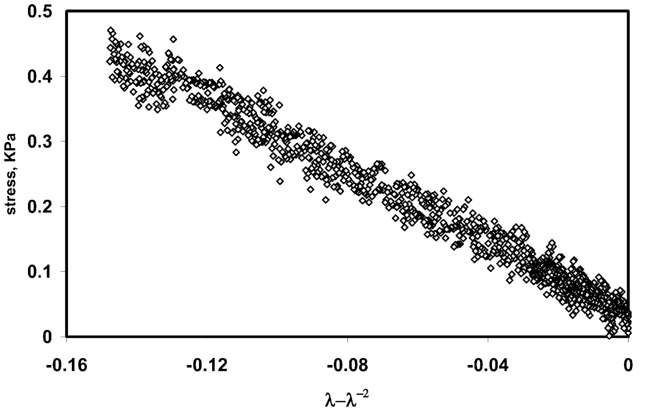

Fig. 1. Trend of the compression stress as a function of deformation.

composition, but also because of the higher ν value. These two factors are expected to play an opposite role on the swelling behaviour.

Fig. 2(a) shows the degree of swelling (SW), expressed as the ratio between the weight of the swelled and the dry network as a function of time at $T = 15$ °C.

Similar trends were observed at 30, 40 and 50 °C. All cases required about 10 h to reach the equilibrium state and the higher the PVP content, the greater the equilibrium swelling degree (SW_{eq}).

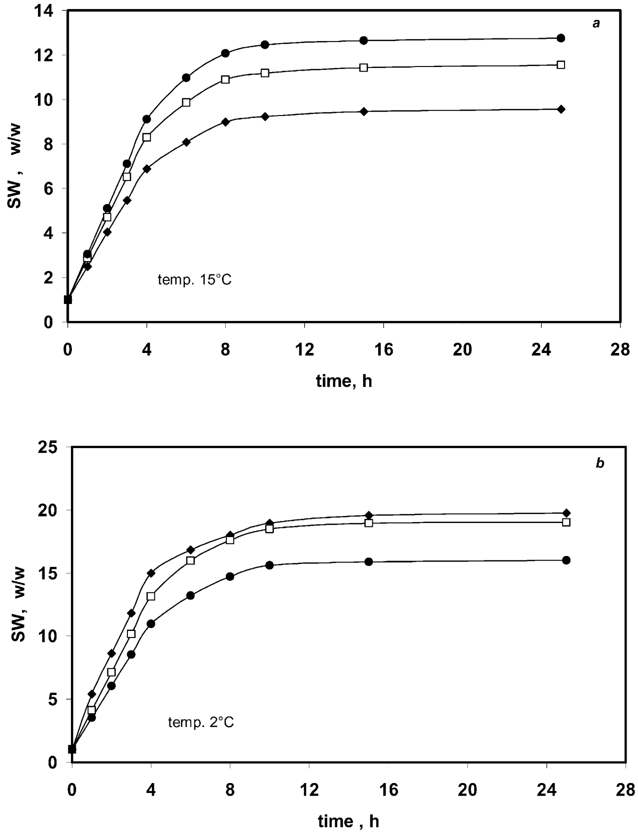

Fig. 2. Swelling variation with time at different temperatures: (a) 15 °C, (b) 2 °C. (◆) sample 1; (□) sample 2; (●) sample 3.

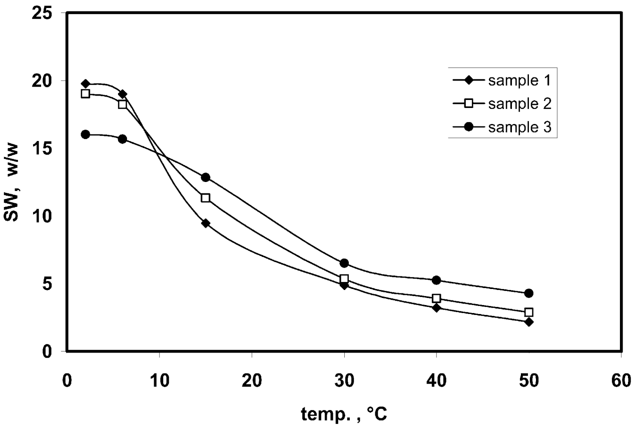

Fig. 3. Trend of equilibrium swelling SW_{eq} with temperature.

The situation is inverted at $T = 6$ and 2 °C and the swelling decreases as the PVP content increases (Fig. 2(b)).

Fig. 3 shows SW_{eq} as a function of the temperature: SW_{eq} decreases approaching the unit at about 50 °C. However, an inversion of the curve position is observed at $T < 10$ °C: at lower T, sample 1 tends to swell more than sample 2, and sample 2 more than sample 3. At higher T up to 50 °C, sample 3 shows the greatest equilibrium swelling, followed by sample 2 and then by sample 1.

Interpretation of this trend cannot be based only on the ν increase from sample 1 to 3: in that case, SW_{eq} should decrease at every temperature with the PVP content. So, the inversion observed at low temperature must take the polymeric composition into account. The interactions H_2O–HPC worsen with increasing temperature [9], and HPC in water shows a LCST behaviour, while the opposite may occur for PVP. The consequence is that sample 1, richer in HPC, is more swelled than 2 and 3 at low temperature (good interaction and low ν) and it is less swelled at high temperature.

Considering that the swelling is a reversible process, it is possible to study a thermal cycle characterized by a sequence of swelling and deswelling phenomena.

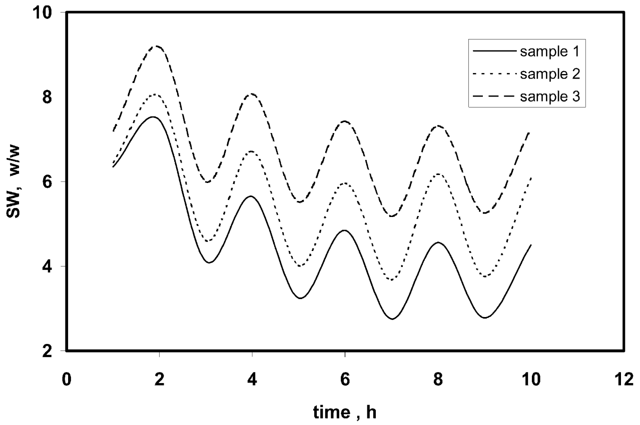

Fig. 4. Trend of SW as a function of time by varying the temperature between 11 and 50 °C every 60 min.

Fig. 4 shows the behaviour of the three samples subjected to a thermal cycle between 11 and 50 °C, remaining at each temperature for about 1 h. The reproducibility of the swelling and deswelling phenomena after the first cycle may be observed. These gels are an example of 'thermal sponges' as the release in the absorption of the solvent is not due to a mechanical action (squeezing and desqueezing) but due to an increase and decrease in temperature.

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