Behaviour of gels based on (hydroxypropyl) cellulose methacrylate

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Abstract

A new class of gels obtained from aqueous solutions of hydroxypropylcellulose partially esterified with methacryloylchloride was prepared by UV crosslinking. Measurements of swelling degree and the elastic properties of samples having different esterification degree were treated according to the theory developed for semirigid chains: the values of the ν (number of elastically active chains) and χ (polymer–solvent interaction parameter) were calculated and used to interpret some experimental behaviours. Moreover, thermosensitive response was evidenced and related to the trend of the enthalpic and entropic components of χ as functions of temperature. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

(Hydroxypropyl) cellulose methacrylate (HPCM) is a polymer that was recently obtained by reaction between (hydroxypropyl) cellulose (HPC) and methacryloylchloride [1]. A repeat unit of a HPCM chain may be represented as follows:
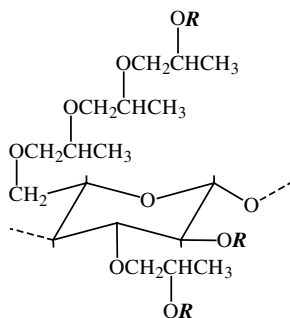
where **R** is the methacrylic residue ($-CO-C(CH_3)=CH_2$). The molar etherification (MS) is 4 and the molar esterification (DE) is 3. Obviously, the actual values of MS and DE for a macroscopic sample represent an average on the whole of units. Moreover, we can notice that the maximum DE value is 3, while in principle no limit exists for MS, even if commercial samples generally have MS between 3 and 5.

HPCM retains the mesogenic nature of HPC, although the presence of a few methacrylic residues noticeably influences many physical behaviours [1]. For instance, HPCM samples are soluble in water at room temperature only when DE ≤ 0.2, in spite of the fact that HPC gets mixed with water in all proportions. Moreover, all the lyotropic and thermotropic transition temperatures are function of DE: in particular, the cloud temperature, that is the temperature at which an aqueous solution becomes cloudy, decreases from $\approx 40°C$ for HPC (DE = 0) to $\approx 30°C$ for HPCM (DE = 0.2).

Also the anisotropic ↔ isotropic transition temperature (T_i) of the neat sample decreases by about 60°C in the same DE range, as well as the critical polymer concentration (C_p') for the appearance of the anisotropic phase, in aqueous solution, which decreases from 40 to 34% w/w [1].

Consequently, the phase diagram of HPCM in water, even if qualitatively similar to that of HPC, is quantitatively modified with regard to the field of stability of the isotropic and anisotropic phases [1,2].

A further interesting behaviour of HPCM concerns the presence of some double bonds along the chain: they may give crosslinking reaction under UV radiation as long as the radiation time increases. A first consequence is that the number of crosslinks does not involve the chemical composition of the system, which only depends on DE and radiation time. In this paper, the characterisation of hydrogels obtained from HPCM at low DE value was performed by measuring the weight swelling degree (SW_p), and the shear
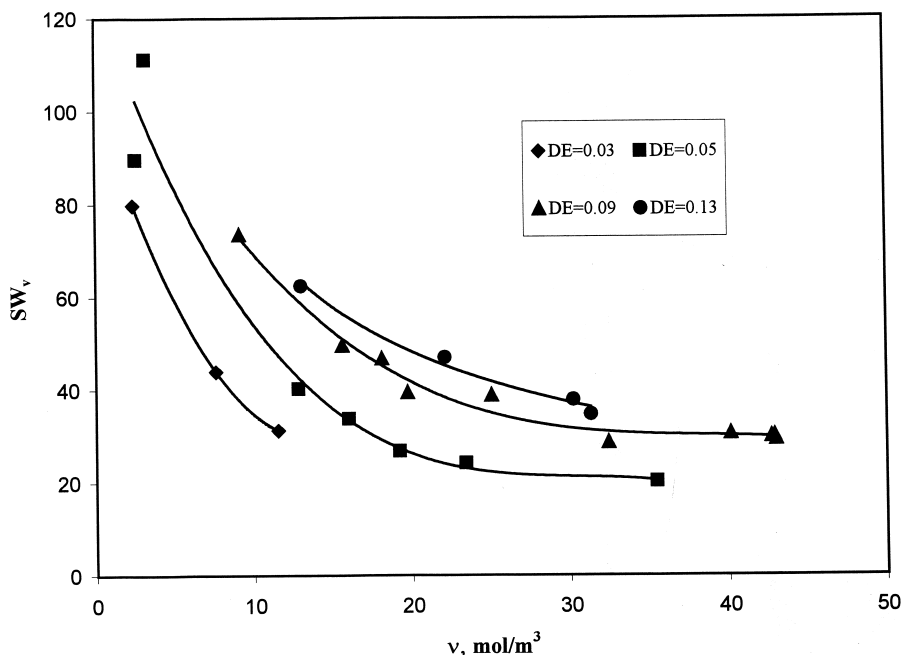
Fig. 1. Dependence of the degree of swelling (SW_v) on the crosslinking density ν for samples of HPCM at different degree of substitution (DE); ν was calculated from compression modulus data according to theory valid for flexible polymers [5–8].

modulus (*G*) at room temperature and discussed according to the theories used for polymeric gels [3–9]. Moreover, the effect of temperature on the swelling behaviour at different DE was examined for some samples.

2. Experimental

2.1. Materials

HPC sample, supplied by Hercules Inc., similar to that used in a previous work [1], was utilised for all syntheses. Its M_w and MS were 150 000 and 4 ± 0.5, respectively. The sample was dissolved in water at polymer concentration $C_p = 5\%$ w/w, centrifuged at 10 000 rpm for 30 min to eliminate suspended particles and freeze dried. Dimethylacetamide (DMAc) was supplied by Fluka, distilled under vacuum and kept on molecular sieves. Methacryloylchloride (MACl) (Fluka) was used as received and stored at low temperature under dried nitrogen. Doubly distilled water was used for all solutions.

2.2. Methods

Synthesis of hydroxypropylcellulose methacrylate (HPCM) was performed as reported in a previous work [1]. A suitable amount of MACl was added at constant temperature, 0°C, to a solution of HPC in DMAc at $C_p = 3\%$ w/w, under nitrogen flow and left to react for 22 h. The products were precipitated with ether, filtered, dissolved in water and freeze dried.

Gel preparation: Aqueous solutions of HPCM samples at concentration 5–10% (w/w) were placed inside quartz

tubes, having 5 mm diameter and 5 cm length. The tubes were accurately sealed after elimination of dissolved oxygen by vacuum soft treatment alternated to nitrogen flowing, for at least five times. Then, the tubes were irradiated with UV light between 60 and 500 min. The radiation apparatus was a UV Rayolet RPR-200, Southern New England, $\lambda = 2537$ Å. All crosslinked samples were easily extracted from the tube, showing good self supporting behaviour.

Gel swelling: The weight swelling degree SW_p of a gel is defined as the ratio between the weight W_g of the swollen gel in the solvent, and the weight W_p of the dried polymer network ($SW_p = W_g/W_p$). In order to measure SW_p a piece of gel, previously dried in vacuum oven at 80°C and weighed, was located in a stainless steel basket and put into water at constant temperature. By measuring the weight of the gel at different times *t*, it is possible to have a trend of SW_p vs *t*; the swelling generally increases to a plateau (SW_p equilibrium value) in 20–100 h, depending on the crosslinking extent and temperature. SW_p may be converted to SW_v (volumetric swelling = ratio between the gel and the polymer volumes), provided that the density of the solvent δ_1 and of the polymer δ_2 are known and assuming additivity of the volumes.

$$SW_v = [1 + \delta_2/\delta_1(SW_p - 1)] \tag{1}$$

The reciprocal of SW_v represents the polymer volume fraction ϕ_2, that is the variable used in theoretical approach of swelling phenomena.

The density of HPCM at different DEs was measured at room temperature by using a density gradient column obtained by mixing *n*-heptane and carbon tetrachloride.
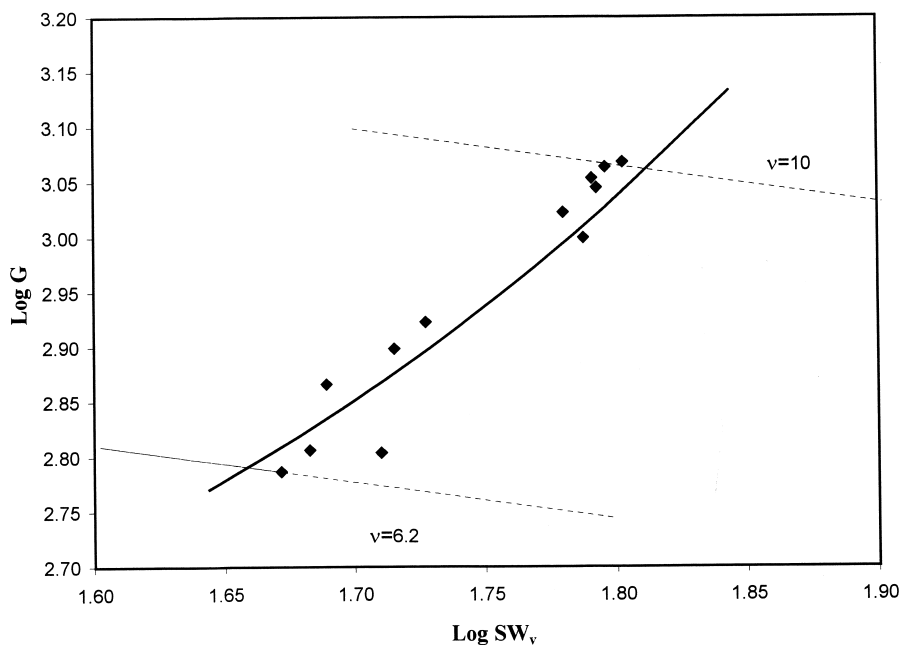
Fig. 2. Dependence of the compression modulus on the degree of swelling. (◆) HPCM at DE = 0.13 (sample 21, Table 1). The full line, which interpolates the experimental results, was calculated according the theory valid for semiflexible polymers [5–8] using $\nu = 1.3$ mol/m^3. Dashed lines were calculated according to the theory for flexible polymers using $\nu = 6.2$ and 13 mol/m^3, respectively.

The density varies linearly from 1.17 g/ml at DE = 0 to 1.22 g/ml at DE 0.19. Due to the low-crosslinking degree, it is acceptable to assume that the polymer density be the same in the network and in the uncrosslinked state. The density of water was taken equal to 1 g/ml. Each value of the swelling in Figs. 1–4 are the average of three measures. The error is evaluated ±3%.

Mechanical properties: The mechanical properties of the swollen gels were obtained using an Instron dynamometer, mod. 5500. Discs of gel (height ≅ 2 cm), having parallel limit surfaces, were obtained from the gel cylinder, using a device equipped with a sharp steel blade, and placed between dynamometer plates. The plates were coated with a Teflon film to avoid barrelling phenomena. The shear
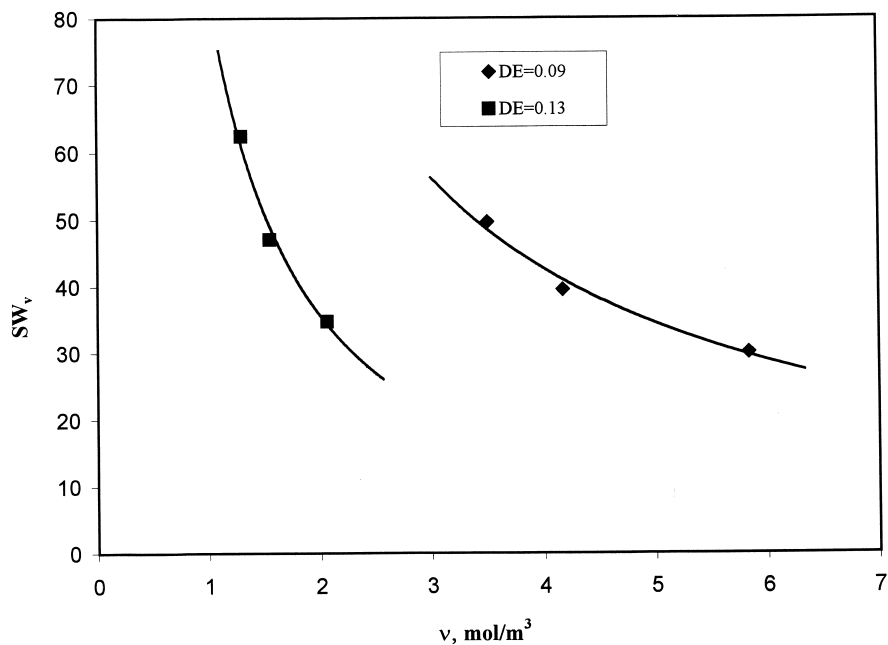

Fig. 3. Dependence of the degree of swelling (SW$_\nu$) on the crosslinking density for hydrogels of crosslinked HPCM at two degree of substitution; ν was calculated from compression modulus data according to theory valid for semiflexible polymers [3].
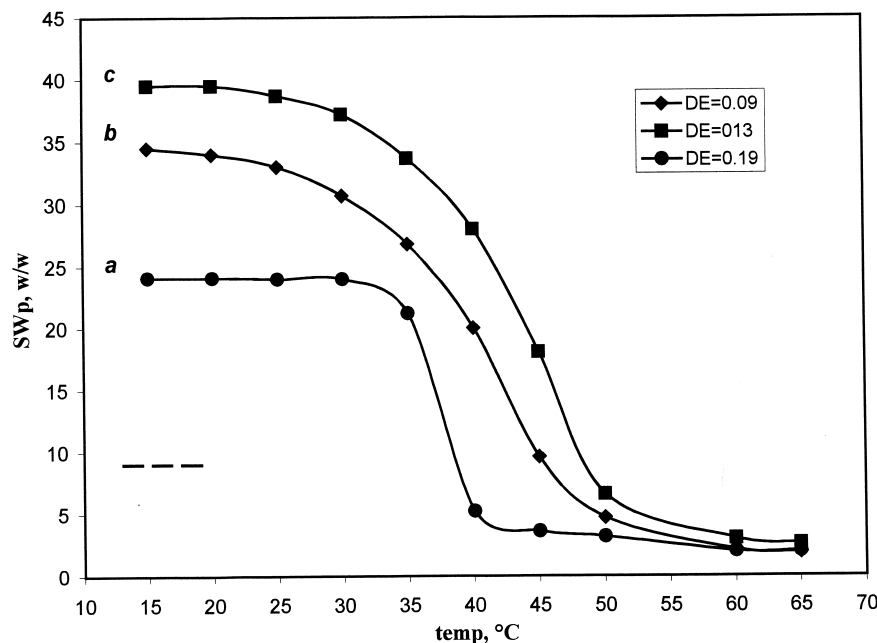
Fig. 4. Equilibrium swelling of crosslinked HPCM at different degree of substitution in water as function of temperature. The critical swelling ratio at which an anisotropic phase is observed between 20 and 25°C is reported as a dashed segment.

modulus G was evaluated from the curve of the mechanical stress (σ) vs ($\lambda - 1/\lambda^2$), where λ is the extension ratio [4,5]. In some cases, G was also measured during the swelling process at predetermined times.

Optical microscopy: The critical swelling degree, and hence the critical polymer concentration C_p', at which anisotropy may be observed for a sample placed between crossed polarizers, at room temperature, was determined by using a polarized Reicther Polyvar Pol microscope.

3. Results and discussion

3.1. Gel characterisation

Table 1 provides characterisation data of 24 gels obtained according to the procedure described in the experimental section. Second column gives DE value of the precursor HPCM samples: its value varies between 0.03 and 0.13. SW_p at the swelling equilibrium in water and the corresponding SW_v (at room temperature) are reported in the third and fourth columns, respectively. The decrease of SW_p, at constant DE, depends on the increase of irradiation time (= crosslink extent). Finally, the fifth column gives the shear G modulus at room temperature.

Starting from these data, a complete characterisation of gels in terms of ν (moles of elastic effective chains for unit of network dry volume) and χ (Flory–Huggins interaction parameter) may be made on the basis of theoretical considerations. The sixth and seventh column show the ν and χ values, obtained as explained in the following. Some authors [6–9] for networks of conventional polymers,

following the Gaussian statistics, firstly faced the general problem. The well-known basic hypothesis is that the total variation of the Gibbs free energy ΔF of the system from the unswelled to the swelled state is the sum of two terms, one related to the free energy of mixing (ΔF_m) [7] and the other to the elastic expansion of the network ΔF_{el} [6–8]. The corresponding variation of the chemical potential $\Delta\mu_1$ of the solvent may be obtained by differentiating ΔF with respect to the number of solvent moles n_1 at constant T and P. When the crosslinking process is performed in solution at polymer volume fraction $\phi_{2,0}$, it was demonstrated that [9]

$$\Delta\mu_1 = RT(\text{In } \phi_1 + \phi_2 + \chi\phi_2^2 - V_1\nu\phi_2/2 + \phi_{2,0}^{2/3}\phi_2^{1/3}V_1\nu)$$

(2)

where V_1 is the molar volume of the solvent, ϕ_1, ϕ_2 the solvent and polymer volume fraction, respectively. At the equilibrium swelling $\Delta\mu_1 = 0$.

It was also demonstrated [4] that the shear modulus G of the above-mentioned gel follows the relation:

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

(3)

For a specific set of values $\phi_{2,0}$, V_1 and T, known ϕ_2 and G from experiments, Eqs. (2) and (3) allow us the calculation of ν and χ, that is the complete characterisation of the gel. The values reported in Table 1 were obtained by applying the described procedure. Two main conclusions are inferred from these data: firstly, SW_v decreases with ν at constant DE, as expected, secondly, SW_v increases with DE, at constant ν. This last result, highlighted from the sequence of the SW_v vs ν curves in Fig. 1 does not agree with the

Table 1
Characteristic of HPCM hydrogels: ν and χ obtained according to the theory valid for flexible polymers [5–8]

Sample	DE	SW_p (w/w)	SW_v (w/w)	G (kPa)	ν (mol/m^3)	χ
1	0.03	67.9	79.8	0.47	2.4	0.48
2	0.03	37.4	43.9	1.79	7.6	0.49
3	0.03	26.6	31.2	3.07	11.5	0.49
4	0.05	94.1	111.2	0.36	3.2	0.47
5	0.05	75.9	89.6	0.30	2.6	0.49
6	0.05	34.2	40.3	1.99	12.8	0.49
7	0.05	28.7	33.8	2.63	16	0.49
8	0.05	22.8	26.8	3.42	19.2	0.50
9	0.05	22.4	26.3	4.19	23.4	0.50
10	0.05	20.6	24.2	6.50	35.3	0.49
11	0.09	61.8	73.6	0.77	9.1	0.48
12	0.09	41.7	49.6	1.54	15.6	0.49
13	0.09	39.3	46.7	1.77	18.1	0.49
14	0.09	33.2	39.4	2.04	19.7	0.49
15	0.09	32.7	38.8	2.61	25	0.46
16	0.09	25.7	30.5	4.54	40.1	0.49
17	0.09	25.3	30.0	4.89	42.9	0.49
18	0.09	25.2	29.9	4.85	42.7	0.49
19	0.09	24.7	29.3	4.99	43	0.49
20	0.09	24.1	28.6	3.73	32.4	0.50
21	0.13	52	62.4	1.12	13	0.48
22	0.13	39.2	47.0	2.13	22.1	0.48
23	0.13	29	34.7	3.34	31.3	0.49
24	0.13	31.6	37.8	3.13	30.2	0.49

Table 2
HPCM hydrogels: ν, χ and n parameters obtained according to the theory valid for semiflexible polymers [2]

Sample	ν (mol/m^3)	χ	n
DE = 0.09			
12	3.5	0.49	3.3
14	4.17	0.49	2.77
17	5.83	0.50	1.98
DE = 0.13			
21	1.3	0.50	3
22	1.55	0.51	2.38
23	2.06	0.49	1.79

increasing hydrophobicity of the network as DE increases. This misleading conclusion suggests that the experimental data concerning HPCM gels need a different treatment. In particular, the semiflexibility of the polymer chain should be taken into account, as the conformation of partially extended chains inside the network may not be described by the Gaussian statistics, even at low ν values.

Very recently, Schröder and Opperman [3] considered networks of highly extended chains, as in the case of charged polyelectrolite gels, and derived the equation for the elastic contribution to $\Delta\mu_1$, by using the well-known treatment based on Langevin function (L^{-1})

$$\Delta\mu_{1el} = 1/3RT\nu V_0\phi_{2,0}(\phi_2/\phi_{2,0})^{2/3}n^{1/2}L^{-1}[(\phi_{2,0}/\phi_2)^{1/3}n^{-1/2}]$$
(4)

where

$$L^{-1}(y) \cong 3y + 9/5y^3 + 297/175y^5 + 1539/875y^7$$
$$+ 126117/67375y^9 + \cdots$$
(5)

n is the number of statistical segments per network chains; this parameter includes the chain stiffness, that is the non-Gaussian character of the network. Obviously, when n approaches infinity, the Gaussian statistics is again valid.

Moreover, the above authors [3] calculated the mechanical stress σ of a swollen network uniaxially deformed, as a function of the deformation λ.

$$\sigma = 1/3RT\nu V_0\phi_{2,0}(\phi_2/\phi_{2,0})^{2/3}n^{1/2}[\lambda L^{-1}((\phi_{2,0}/\phi_2)^{1/3}n^{-1/2})$$
$$- \lambda^{-1/2}L^{-1}(\lambda^{-1/2}(\phi_{2,0}/\phi_2)^{1/3}n^{-1/2})]$$
(6)

The shear modulus G corresponds to the initial slope of σ vs $(\lambda^2 - \lambda^{-1})$. When $n \to \infty$ (flexible chain), the log G vs SW_v trend is linearly decreasing; when n is finite (extended chains), the curve initially decreases then shows an upturn and progressively increases with the swelling [3,10]. The upturn occurs at lower SW_v value as n is lower. From an experimental point of view, we need to measure G at different SW_v for each sample. The best fit between experimental data and theoretical values according to Eq. (6) gives the couple of values n and ν.

Results concerning sample 21 of Table 1 are reported on Fig. 2. Log G strongly increases with log SW_v: the best fit of the experimental points according to the equation was obtained by using the pair of values $n = 3$, $\nu = 1.3$. The low n value explains why only the increasing branch of the curve was observed (in other terms, the previously mentioned upturn is very close to the y-axis).

Curves calculated according to Eq. (3) (flexible chains) are also reported on the same figure for $\nu = 13$ and 6.2 to evidence that the trend for flexible polymers is strongly influenced by small ν variations and is decreasing throughout the whole range of the measured SW_v.

Table 2 shows the values of ν, χ and n for samples 12, 14, 17, 22 and 23 of Table 1, besides the previously considered sample 21. Finally, Fig. 3 shows the trend SW_v vs ν at DE = 0.09 and 0.13: the position of the curves is correctly inverted with respect to Fig. 1 according to the expected increases of hydrophobicity with DE (lower swelling at higher DE and fixed ν). An unsolved problem is why χ values show no dependence on DE.

3.2. Sensitive behaviours

Volume phase transitions, consisting in a discrete change in gel volume with a very small change of environmental variables, is a well-known feature of flexible and semirigid polymer gels [15–25]. Interest in this kind of behaviour,
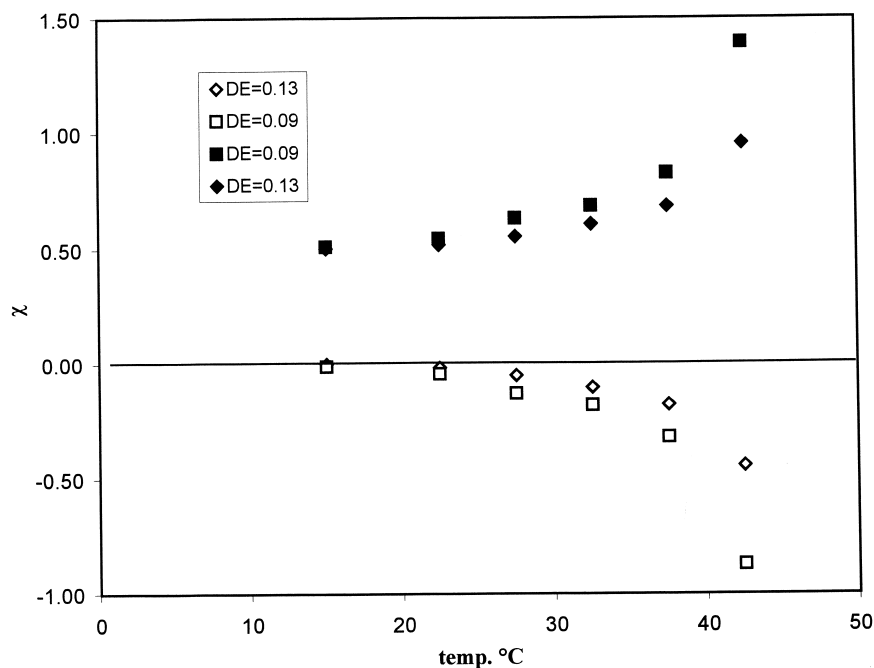
Fig. 5. Enthalpic (χ_H, open symbol) and entropic (χ_S, full symbol) polymer–water interaction parameters of crosslinked HPCM having different DE as a function of temperature.

when temperature is the variable considered, has stimulated wide theoretical and experimental work. While in the field of flexible polymers, NIPA gels are undoubtedly the most studied [15,19] in the field of semirigid polymers, cellulose derivatives are probably the kind of gels which attracted a greater interest [20,25].

During a preliminary study of thermal behaviour of a gel not completely characterised, except for the DE of the original HPCM sample (DE $\cong$ 0.19), we measured $SW_p = 24$ at room temperature and $SW_p = 3$ at 60°C. The SW_p decrease was not smooth, but showed a jump from the swollen to the shrunken state at $\approx$ 37°C (see curve a, Fig. 4).

This result suggested the extension of this kind of study to two other samples, having different DE and ν. The curves b and c in Fig. 4 refer to the pairs of values DE = 0.09/ν = 4.17 and DE = 0.13/ν = 1.55, respectively. Both of them show a jump of SW_p vs T, sample b at $T \sim 40$°C and sample c at $T \sim 43.5$°C. By comparing the curves of the three samples, the order of the jump temperature does not follow clearly the order of DE. Not only curve c lies over curve b indicating that the effect of ν increase from 1.55 to 4.17 prevails over the decrease of DE, which should promote better interaction with the solvent [1].

The dashed line in Fig. 4 shows the swelling ratio at which the concentration of the crossinked polymers reaches the critical value for the appearance of an anisotropic phase at room temperature.

Similar volume–phase transitions were firstly observed for a partially ionised acrylamide gel by changing solvent composition [26]. Subsequently, it was found that not only the solvent composition [27–29], but also other environ-

mental variables like temperature [4,30–36], ionic strength and pH changes [37–39] may determine the same behaviour. These results supported the pioneering theoretical work by Dusek and Patterson [40], who predicted the possibility of a discontinuous volume change of a polymeric gel, by analogy with the coil–globule transition, observed for some polymers in solution.

From a thermodynamic point of view, the gel behaviour was treated by using the same approach utilised for van der Waals fluids. As known, these fluids are characterised by the presence of excluded volume and intermolecular interactions; they give a transition of gas → liquid by increasing the pressure when the temperature is lower than a critical T_c value (T_c = Boyle temperature, that is the temperature at which the term of the van der Waals attractive interactions balances the terms due to the translational entropy of the molecules). The treatment of volume–phase transition of polymer gels was similar in the sense that the swollen gel was considered in correspondence to the gas and the shrunk gel to the liquid. By using the free energy in Eqs. (2) and (3), it was found that a critical value (χ_c) of polymer–solvent interaction parameter exists: when $\chi > \chi_c$ (for example when T approaches the so-called θ temperature), a volume transition may be observed.

Of course, beside the van der Waals, other kinds of interactions may occur in particular cases. As an example, hydrophobic interactions can play a significant role for hydrogels: the mixing process (that is the swelling process) is characterised by heat development and decrease of entropy, due to the ordered structure of the water molecules around the hydrophobic groups of the polymer in the

network. As a consequence, an increase of temperature is accompanied by a volume decrease; the shrunk polymer becomes more ordered while the water molecules, sent off the network, are in a less ordered state. Therefore, changing the chemical nature of side chain groups [4–29] might control the extent of this contribution, which is opposite to that of Van der Waals interactions when T increases. Best information about a specific gel should derive from the knowledge of the enthalpic (χ_H) and entropic (χ_S) values which may be obtained from the variation of the χ parameter with temperature [4,41]. Negative values of χ_H and $\chi_S > 0.5$ were observed for hydrogels, confirming the fundamental role of the hydrophobic interactions.

Fig. 5 shows the trend of χ, χ_H and χ_S vs temperature for samples 14 and 22 of Table 1. χ_H is negative (exothermic mixing process) in both cases and becomes more negative as DE decreases, χ_S is positive and higher for the sample at lower DE. These results suggest that the main contribution to the polymer–water interaction parameter is an entropic basis as expected.

In the case of gels made of semirigid polymers, capable of forming a liquid crystalline phase at high polymer concentration, a further kind of driving force should be taken into account to determine the volume–phase transition, namely, the tendency of the rigid segments to interact, giving a more ordered concentrated phase. In fact, as the polymer concentration in a shrunk gel is higher than the critical concentration for the appearance of the liquid crystalline phase, the gel is in an anisotropic phase.

Therefore, many factors can influence the temperature at which a volume–phase transition occurs, such as hydrophobicity of the polymer chain correlated to the DE value, the degree of crosslinking and the tendency to form a LC phase. A more rigorous analysis must be performed to detect the role played by each of these parameters.

4. Conclusion

Precursor polymer HPCM is widely heterogeneous, due to a set of factors, that is the polydispersities of both molecular weight and hydroxypropyl and methacrylic groups distribution. However, due to the crosslinking process based on UV radiation, the chemical composition does not vary by increasing the crosslink degree for a specific HPCM sample. It is, therefore, possible in principle to obtain gels with different crosslinking density ν and the same chemical composition. Alternatively, it is also possible to have the same ν and different chemical composition by varying DE. This later aspect, which should be conveyed from different values of the interaction parameter χ, was not evidenced from our results. Tables 1 and 2 show that, whatever the applied theory, χ varies only by a few percent, practically assuming for all the gels the value ~0.5. We know that an uncrosslinked sample of HPCM having DE > 0.2 is practically insoluble in water, while it is completely soluble when

DE = 0 (underivatized HPC). This behaviour does not agree with the constant χ in the gel state. Analysis of χ vs temperature, allowed the determination of the enthalpic (χ_H) and entropic contributions (χ_S). Negative χ_H values indicate a lower endothermic mixing process during the swelling as DE increases, while the increasing positive χ_S values are related to a negative residual entropy which might be interpreted as a solvent condensation around the polymer chain.

Analysis of the swelling values and shear modulus G according to recent theories [3,10–14] demonstrated that the semirigidity of the chain, even when relatively weak, must be taken into account. We are unable to check whether ν values in Table 2 represent the real crosslinking density or not, but surely they enable us to obtain the expected dependence of SW_v on DE and ν (see Fig. 3).

Finally, environmental behaviours concerning temperature variation were observed. The existence of a jump on the swelling as the temperature increases is related to the existence of hydrophobic interactions between water and methacrylic side chain groups, as seen for other systems [4]. Furthermore, during the jump a swelling value corresponding to the transition from an isotropic to an anisotropic state of the gel is reached in all cases (Fig. 4). As the iso–aniso transition is entropically driven, it is reasonable that its contribution must be taken into account in a complete theoretical analysis of the swelling jump for gels made of semirigid polymer. Of course, it is foreseeable that responsive behaviours of HPCM gels may be shown even with respect to other environmental variables.

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