Stabilisation Effect of Calcium Ions on Polymer Network in Hydrogels Derived from a Lyotropic Phase of Hydroxypropylcellulose

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Summary: The process of crosslinking of the hydrogel, derived from lyotropic liquid crystalline (LLC) phases of hydroxypropylcellulose/acrylic acid-water, by calcium ions was studied by means of Raman and dielectric spectroscopy. Formation of salt by poly(acrylic acid) and calcium ions, resulting in hydrogel crosslinking, induces differences in Raman spectra of the hydrogel before and after the crosslinking. The crosslinking results in significant increase in the activation energy of β-relaxation of poly(acrylic acid). This is a direct consequence of restriction in motions of carboxylic groups of poly(acrylic acid) due to calcium salt formation. Thus, the crosslinking improves polymer network stability in the hydrogel in the swollen state.

Keywords: dielectric spectroscopy; hydrogels; hydroxypropylcellulose; Raman spectroscopy

Introduction

Hydrogels, three-dimensional polymer networks, are able to absorb a large amount of water, which makes them interesting and promising materials offering various application possibilities, especially in medicine, pharmacy, and biotechnology.[1,2] However, the application possibility depends on the swelling properties and stability of the polymer network in the swollen state in defined environment conditions. The low density of chemical crosslinks very often causes poor stability of the polymer network of the hydrogel in the swollen state. Therefore, long immersion processes of such hydrogels can lead to destruction of the polymer network.

Recently, special emphasis has been put on hydrogels with liquid crystalline organisation of polymer network because of their similarity to the gel networks present in living organisms.[3] As it was reported in our previous paper[4], the photopolymerisation of acrylic acid in the lyotropic liquid crystalline (LLC) phase of hydroxypropylcellulose in the mixture of acrylic acid (AA) and water leads to a formation of optically anisotropic hydrogel. The process of photopolymerisation of AA in lyotropic phase is faster than phase separation and, therefore,

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the hydrogel sample is transparent, although both polymers - HPC and poly(AA) - are not miscible. However, the obtained hydrogel exhibits limited stability of the polymer network during long-term immersion in the water. This is an outcome of the fact that the network of HPC-poly(AA)-H_2O hydrogel is stabilised only by hydrogen bonds between HPC, poly(acrylic acid) and water, which is in agreement with the results obtained previously for the anisotropic composite of HPC-poly(AA) derived from photopolymerisable lyotropic phase of HPC/AA.[5]

In this paper, the process of crosslinking of the hydrogel – derived from lyotropic phase of HPC/AA-H_2O by calcium ions – and its impact on the stability of the polymer network in the swollen state is presented. We have taken advantage of poly(AA) ability to creat a salt with metal ions[6], such as calcium. The influence of crosslinking of the HPC-poly(AA)-H_2O hydrogel by calcium ions on the relaxation phenomena of the polymer network is also discussed.

Experimental Part

(2-hydroxypropyl)cellulose (M_w=100 000 g/mol), acrylic acid and calcium acetate were supplied by Aldrich Chemical Co. Acrylic acid was further purified by distillation.

The hydrogel HPC-poly(AA)-H_2O was the object of the research. This compound was prepared by photopolymerisation (λ=365 nm) of AA in the LLC-phase of HPC/AA-H_2O (40:40:20 wt.%), according to the procedure described elsewhere.[4] The photoinitiator: Esacure 651 (Ciba-Geigy) was added in the amount of 0.3 wt.% on the basis of the AA weight. The hydrogel, obtained in such a way, was afterwards crosslinked by calcium ions (Ca^{2+}), by means of immersion of the hydrogel in the water solution of calcium acetate with Ca^{2+} concentration of 0.22 mol×dm^{-3}, during 72 hours at the room temperature. After immersion, the hydrogel samples were dried at the room temperature.

The Raman analysis was performed using dispersive spectrometer Jobin-Yvon T64000, equipped with confocal microscope, at 293 K using Argon laser wavelength of λ=514 nm.

Dielectric relaxation spectroscopy was performed in Max Planck Institute for Polymer Research in Mainz (Germany) by means of Alfa High Resolution Dielectric Analyzer (Novocontrol GmbH), for the temperature range of 130-430 K and the frequency range of 10^{-1}-10^{6} Hz.

The swelling study of the hydrogel (diameter $2R$=20 mm, thickness d=0.2 mm) was carried out at the room temperature by registering changes of water uptake (h=immersed water weight/dry hydrogel weight) vs. time.

Results

Figure 1a shows the effect of immersion time on the water uptake, obtained for the hydrogel crosslinked by calcium ions. This dependence is compared with the results reported earlier for the non-crosslinked hydrogel (HPC-poly(AA)-H_2O).[4] The hydrogel crosslinked by calcium ions has approximately constant value of the water uptake (*h*) even after longer than one month immersion in water, which indicates better stability of the polymer network of the crosslinked hydrogel in the swollen state, with respect to the non-crosslinked hydrogel. However, three-dimensional polymer network of the non-crosslinked hydrogel is destroyed after long immersion, which is a direct consequence of destruction of hydrogen bonds between HPC and poly(AA).

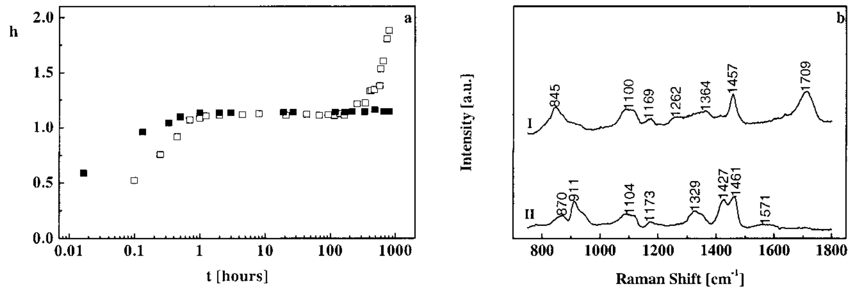

Figure 1. a) Dependence of water uptake on time for the hydrogels: non-crosslinked (open symbols) and crosslinked (solid symbols) by calcium ions. b) The Raman spectra of the dry sample of the hydrogel, non-crosslinked (line I) and crosslinked by calcium ions (line II).

The process of formation of calcium salt of poly(AA) was detected by means of Raman spectroscopy, when comparing the Raman spectra of the hydrogel before and after crosslinking by calcium ions (Figure 1b). The band at 1709 cm^{-1}, related to the carbonyl group of poly(AA), seen in the Raman spectrum of the non-crosslinked hydrogel (line I) disappears after crosslinking by calcium ions. At the same time, a new band at 1427 cm^{-1} comes to existence (line II). This band is typical for calcium salt of poly(AA) and is related to symmetric vibration of $-COO^-$ group (carboxylate anion) of created salt. Our results are similar to the Raman spectra of poly(AA) and its salts with calcium, sodium and aluminium at the range of 1400-1800 cm^{-1}, reported by M. Young et al.[6] The Raman spectroscopy results provide the evidence for the calcium salt formation by poly(AA) present in the HPC-poly(AA)-H_2O hydrogel.

It should be emphasised that the process of crosslinking of the hydrogel by calcium ions does not have a perceptible impact on mesomorphic organisation of the polymer network of the hydrogel. Therefore, this problem will not be discussed in this paper.

It is believed that formation of chemical bonds between poly(AA) and calcium ions in the hydrogel network affects the molecular motions of the hydrogel network, especially poly(AA). The relaxation processes of the polymer network in the hydrogel, before and after crosslinking, were analysed by dielectric relaxation spectroscopy.

Figure 2a shows the dependence of real (*M'*) and imaginary (*M''*) parts of electric modulus on temperature for the non-crosslinked hydrogel, containing water originating from LLC-phase of HPC/AA-H_2O as well as after its drying. Additionally, Figure 2b presents the activation map of relaxation times of the hydrogel.

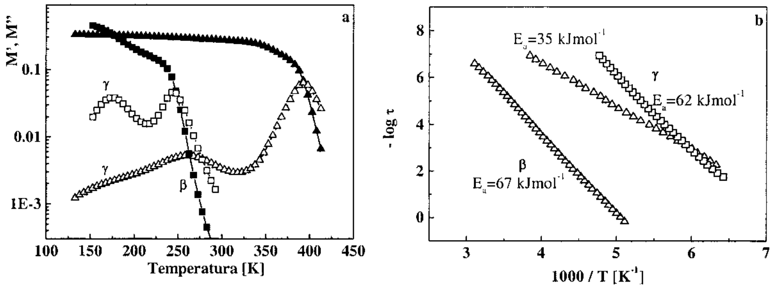

Figure 2. a) Temperature dependence of *M'* (solid symbols) and *M''* (open symbols) at f=1 kHz, and b) activation map obtained for the hydrogel containing 20 wt.-% of water from LLC-phase (squares) and after drying (triangles). $\tau = 1/(2\pi f)$, where τ - relaxation time and f – frequency.

In case of the hydrogel containing water coming from LLC-phase, two bands in the temperature dependence of *M'* and *M''* are observed. The band at 175 K (at 1 kHz) can be considered, according to the literature[7], as γ-relaxation of HPC, related to the local motions of side chains (hydroxypropyl groups) of HPC. The activation energy of registered γ-relaxation of HPC of the anisotropic hydrogel equals E_a=62 kJxmol^{-1}. This value is higher than the activation energy of γ-relaxation of pure HPC, reported by M. Pizzola (E_a=41 kJxmol^{-1}).[7] The difference between the obtained and literature value of E_a of γ-relaxation of HPC is a consequence of the presence of water molecules in the HPC-poly(AA)-H_2O hydrogel network. The hydration shell created by water molecules arround hydroxypropyl groups of HPC in the hydrogel network by results in significant increase in the E_a value of γ-relaxation of HPC. The band, observed at the temperature of 245 K (at 1 kHz), was not considered as it relates to the ionic conductivity. However, it should be emphasised that the amount of water in the hydrogel significantly influences the ionic conductivity.

In case of the dried hydrogel, the ionic conductivity phenomenon appears at much higher temperatures equal to 400 K (Figure 2a), which results from limited amount of water molecules in the hydrogel. Apart from the ionic conductivity effect, seen at 1 kHz at 400 K, a band at 255 K in the temperature dependence of *M'* and *M"* is also observed (Figure 2a). Dielectric spectroscopy results of the HPC-poly(AA) composites, reported by L. Okrasa et al.[5], indicate this band as the one related to β-relaxation of poly(AA). This relaxation process relates to the local motions of carboxylic groups of poly(AA)[5]. The value of E_a of β-relaxation, assessed for the dry hydrogel, equals E_a=67 kJxmol^{-1} and is similar to the literature value (E_a=56 kJxmol^{-1}).[5] The band of γ-relaxation of HPC in the dry hydrogel network is seen at 180 K in the temperature dependence of electric modulus at 1 kHz (Figure 2a). The assessed E_a of γ-relaxation of HPC of dry hydrogel network (E_a=35 kJxmol^{-1}) does not differ significantly from the value reported by M. Pizzola (E_a=41 kJxmol^{-1}).[7] One can conclude that the presence of water molecules in the hydrogel influences not only the ionic conductivity but also the γ-relaxation of HPC.

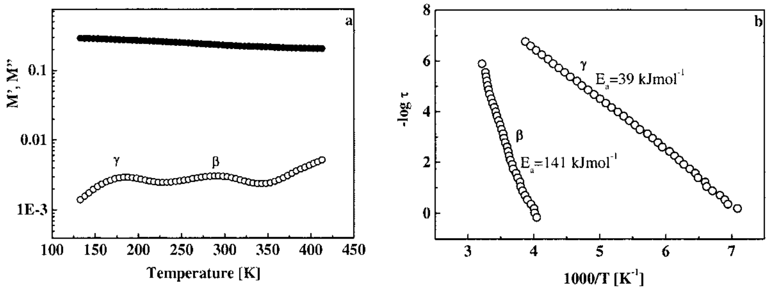

Figure 3. a) Temperature dependence of *M'* (solid symbols) and *M"* (open symbols) at *f*=1 kHz, and b) activation map obtained for dried hydrogel crosslinked by Ca^{2+}.

Figure 3a presents the influence of the temperature on the electric modulus of the hydrogel after its crosslinking by calcium ions and drying. Additionally, Figure 3b presents the activation map, showing relaxation times of this hydrogel network. For the crosslinked hydrogel, two bands: β-relaxation of poly(AA) and γ-relaxation of HPC are seen in the temperature dependence of electric modulus, similarly as it was observed for non-crosslinked hydrogel network. However, β-relaxation of poly(AA) shifts slightly at 1 kHz to 287 K after crosslinking process. Additionally, after crosslinking of the anisotropic hydrogel by calcium ions, the significant change in the value of activation energy of β-relaxation of poly(AA) is observed (Figure 3b). Due to crosslinking of the anisotropic hydrogel by Ca^{2+} ions, E_a of β-relaxation of poly(AA) (67 kJxmol^{-1} for non-crosslinked hydrogel) increases to the value of 141 kJxmol^{-1}. This suggests that the motions of -COOH group of poly(AA) in the polymer network of crosslinked hydrogel are strongly restricted, which can result from the process of formation of calcium salt of poly(AA), well revealed by Raman spectroscopy (Figure 1b). The value of E_a of γ-relaxation of HPC does not increase significantly (from 35 for non-crosslinked to 39 kJxmol^{-1} for crosslinked network) which suggests that calcium ions interact chemically during crosslinking process mostly with poly(AA).

Conclusion

Stabilisation of the polymer network of the HPC-poly(AA)-H_2O hydrogel in the swollen state results from the formation of chemical bonds between Ca^{2+} and poly(AA) present in the hydrogel, which has been revealed by Raman spectroscopy analysis. Hydrogel crosslinking leads to an increase in activation energy of relaxation processes of the main polymer constituents of the hydrogel network. This is especially visible for β-relaxation of poly(AA), present in the hydrogel network, which is a consequence of restriction in motions of polyacid carboxylic groups. Additionally, the water present in the hydrogel causes significant increase in the activation energy of γ-relaxation of HPC, related to the motions of side chains of polysaccharide chain of HPC, as well as shifts the ionic conductivity effect towards lower temperatures.

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