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Investigation of the relationships between the chain organization and rheological properties of atactic poly(vinyl alcohol) hydrogels

Rosa Ricciardi[a], Christine Gaillet[a], Guylaine Ducouret[b], Françoise Lafuma[b], Françoise Lauprêtre[a,*]

[a]*Laboratoire de Recherche sur les Polymères, UMR 7581-CNRS, 2 à 8 rue Henri Dunant, 94320 Thiais, France*
[b]*Laboratoire de Physicochimie Macromoléculaire, ESPCI, 10 rue Vauquelin, 75231 Paris cedex 05, France*

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Abstract

The structure and rheological behavior of atactic poly(vinyl alcohol) (a-PVA) hydrogels prepared by freeze/thaw cycles were investigated as a function of polymer concentration and number of freeze/thaw cycles. The presence of phases with different mobilities was observed using ^{13}C CP/MAS and DP/MAS NMR experiments. The degree of crystallinity of the a-PVA-rich phase was determined by ^{1}H NMR free decay experiments. Measurements of the shear storage and loss modulus were performed at a fixed frequency of 1 Hz and a strain value of 0.1%, i.e. under conditions where the deformation imposed on the gel structure is entirely reversible. Results thus obtained showed that an increase in the number of freeze/thaw cycles induces an increase in the degree of crystallinity in the polymer-rich phase together with an increase in the storage modulus. The a-PVA hydrogels became more fragile as the number of freeze/thaw cycles was increased. Moreover, both the percentage of protons in a rigid environment measured by ^{1}H NMR and the storage modulus values tended to a limiting value after six freeze/thaw cycles. These results show that the first five or six freeze/thaw cycles play a very important role in determining the hydrogel structure and rheological properties. A more detailed comparison of NMR and rheological data led to the conclusion that the storage modulus is mainly controlled by the a-PVA crystallinity while the hydrogen bond interactions have a much smaller contribution.

Keywords: Poly(vinyl alcohol) hydrogels; NMR; Rheology

1. Introduction

Atactic poly(vinyl alcohol) (a-PVA) is the largest volume, synthetic, water-soluble polymer manufactured in the United States and Japan [1]. It has vast applications in packaging, textiles and pervaporation membranes. The main characteristics of a-PVA are (i) its semi-crystalline character despite its lack of stereoregularity [2–4] and (ii) a strong tendency to exhibit both inter- and intra-molecular hydrogen bonds. Moreover, water solutions of a-PVA can transform into physically thermoreversible hydrogels under different conditions [5,6]. Hydrogels of a-PVA, obtained from dilute a-PVA water solutions by freezing at −20 °C and then thawing at room temperature repeatedly, show a number of interesting properties. They have good mechanical properties, high water content, they are stable at room temperature and are able to retain their original shape. In addition, they are biocompatible. All these properties make a-PVA hydrogels suitable for different biomedical and pharmaceutical applications [7,8]. In particular, their high mechanical strength and high elasticity are a few of the attributes of this material that make it suitable for applications as artificial tissues and contact lenses [9,10].

The final macroscopic properties of a-PVA hydrogels prepared by freeze/thaw cycles depend on parameters that describe the starting materials (concentration of a-PVA in water, molecular weight, degree of saponification, tacticity) and the processing steps (number of freeze/thaw cycles, temperatures and times of both the freezing and thawing steps). They are largely determined by the organization and interactions of the chains in the gel state. It must be noticed that, although numerous papers were devoted to a-PVA hydrogels, their structure is still not completely solved and the relationships with their mechanical properties are not clearly established. The phase diagram established by

* Corresponding author. Tel.: +33-1-4978-1286; fax: +33-1-4978-1208.
E-mail address: francoise.laupretre@glvt-cnrs.fr (F. Lauprêtre).

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Komatsu et al. [11] is of particular interest. It showed that gelation occurs with or without spinodal decomposition depending on the polymer concentration and temperature. According to Komatsu, the gelation starts by hydrogen bonding followed by crystallization. These conclusions were supported by small and wide-angle neutron scattering experiments [12]. In addition, NMR experiments performed on a-PVA hydrogels obtained by freeze/thaw cycles indicated the presence of hydrogen bonds and enabled the estimation of the number of monomer units involved in zero, one or two hydrogen bonds [13,14]. Moreover, they pointed out the presence of crystallites. Rheological studies of a-PVA hydrogels obtained by 1–5 freeze/thaw cycles [15,16] led to the conclusion that PVA hydrogels increase in rigidity when the number of freeze/thaw cycles is increased. Therefore, a-PVA hydrogels can be considered as complex systems whose structure and macroscopic properties depend on several phenomena (crystallization, hydrogen bonding and, in some cases, phase separation) occurring during gelation. Moreover, the propensity of a-PVA hydrogels to age by expulsion of water complicates the elucidation of all relevant factors in the gel structure formation [17].

The aim of this paper is to discuss how the crystallinity and hydrogen bonds control the rheological behavior of a-PVA hydrogels obtained by freeze/thaw cycles. The gels under study are characterized by a relatively low a-PVA concentration and, as described by Komatsu et al. [11], they undergo a phase separation at room temperature. The gel-state organization was determined by ^{1}H and ^{13}C NMR. The influence of polymer concentration and number of freeze/thaw cycles was considered. The results thus obtained have been correlated with measurements of the shear modulus.

2. Experimental section

2.1. Materials

The a-PVA powder (Aldrich ref. 36,315-4) used in this study had a molecular weight, $\bar{M}_w$, of 115,500 with a degree of hydrolysis of 98–99%.

The a-PVA microstructure was determined from the analysis of the ^{13}C NMR spectrum of a-PVA in deuterated water solution. The percentages of mm, mr and rr configurational triads were 22.1, 50.1 and 27.8%, respectively.

2.2. a-PVA gel preparation

Aqueous solutions of 11, 12.5 and 14.6% (w/w) a-PVA were obtained by dissolving the a-PVA polymer in deuterated water for 3 h at 96 °C under reflux.

The aqueous solutions were cast between glass slides with 1 mm spacers, or in glass microtubes, 3 mm in diameter, at room temperature. Gel samples were obtained by submitting the a-PVA solutions to one to eleven freeze/thaw cycles consisting of a freezing (20 h at $T = -22$ °C) and a thawing step (4 h at $T = 25$ °C). The gel samples were kept at room temperature. To minimize the influence of aging, NMR and rheological measurements on a given sample were performed within a few days.

2.3. Solid- and liquid-state nuclear magnetic resonance measurements

Solution-state ^{13}C NMR spectra were recorded at 75.47 MHz using a BRUKER AM 300 NMR spectrometer.

Proton and high-resolution solid-state ^{13}C NMR experiments were carried out at 300 and 75.47 MHz, respectively, using a BRUKER AVANCE 300 WB spectrometer.

Proton free induction decay experiments were performed on static samples by using a $\pi/2$ pulse duration of 3 μs. The percentage of rigid protons in a-PVA gel samples was determined by measuring the percentage of protons that relax during the first 20 μs. The error on each measurement was estimated to be of the order of ±0.5%.

In ^{13}C cross-polarization (CP) and direct polarization (DP) NMR experiments, proton dipolar decoupling (DD) and magic angle spinning (MAS) techniques were used. For all experiments performed using MAS, a HRMAS rotor was employed to avoid the loss of water from gel during spinning. The spinning rate was 5000 Hz. In the CP ^{13}C NMR spectra, the matched spin-lock CP transfers were carried out with ^{13}C and ^{1}H magnetic field strengths of 62.5 kHz, corresponding to a $\pi/2$ pulse duration of 4 μs. The proton decoupling field strength was 80 kHz. The CP contact time was taken as 1 ms to maximize the signal of ^{13}C carbons in the rigid regions of the samples. The delay time between two successive CP pulse sequences was taken as 5 s. In ^{13}C DP experiments the delay time was 2 s.

2.4. Rheological measurements

Rheological measurements were performed on a strain-controlled Rheometrics RFSII rheometer equipped with a parallel plates geometry (diameter 25 mm).

All rheological measurements were carried out at 25 °C. Disc shape samples (diameter 26 mm, thickness ~1 mm) of a-PVA gels were placed between the tools.

The samples were protected from drying by a homemade cover to prevent the water from evaporating. This protection ensured the sample stability over a time period long enough (i.e. 1 h) to perform the measurements of the shear mechanical properties. In all experiments, a weak normal force was applied on the surface of the sample discs in order to avoid the sweeping of the gel from the tool plates. This force ensured a slight compression of the sample.

In the frequency sweep experiments, the shear loss (G'') and elastic (G') moduli were measured in the linear viscoelastic regime, for frequencies ranging from 1 to 50 rad/s, at a maximum strain, γ, of 0.1%. This γ value was determined by preliminary strain sweep experiments, in

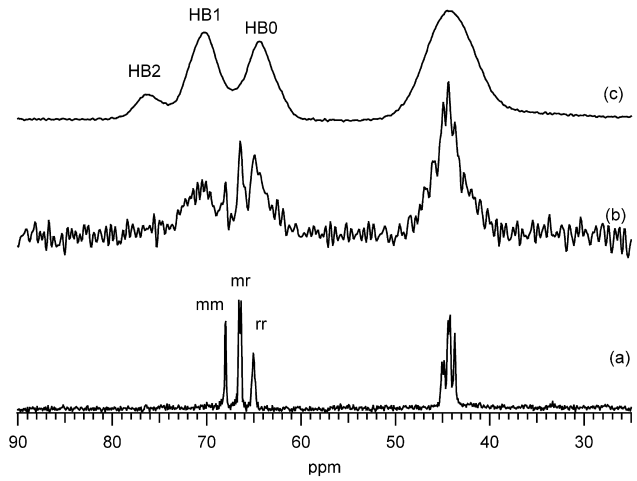

Fig. 1. (a) ^{13}C high-resolution solid-state DP/MAS NMR of a 11% w/w a-PVA hydrogel obtained after one freeze/thaw cycle. (b) ^{13}C high-resolution solid-state CP/MAS NMR of a 11% w/w a-PVA hydrogel obtained after one freeze/thaw cycle. (c) ^{13}C high-resolution solid state CP/MAS NMR of a-PVA dry powder.

which the storage and loss modulus were measured as a function of strain at a fixed frequency value of 1 Hz to check if the deformation imposed on the gel structure by the rheological experiment was entirely reversible. A strain value, γ, of 0.1% at 6.28 rad/s (1 Hz) was found suitable for all the samples investigated.

Each measurement was performed at least twice, on two different disc specimens from the same sample. The relative error on the modulus was of the order of 15%.

3. Results and discussion

3.1. Evidence for phase separation at the microscopic level

The evidence of a phase-separated structure in the a-PVA gels under study, obtained from freeze/thaw cycles, is provided by the fact that a-PVA gel samples are opaque. Moreover, as described by Kobayashi et al. [18], the presence of two different phases within the gels can be inferred by comparing the high-resolution solid-state ^{13}C CP/MAS and DP/MAS NMR spectra of the a-PVA gel samples.

As an example, Fig. 1a and b show two spectra obtained by ^{13}C DP/MAS and ^{13}C CP/MAS NMR, respectively, for an a-PVA gel sample at a 11% w/w polymer concentration after one freeze/thaw cycle only. The two spectra are very different, in agreement with the existence of phase-separated domains. In the ^{13}C DP/MAS NMR spectrum of the gel sample (Fig. 1a), the lines are quite narrow. The resonance due to the CH carbon gives rise to three lines at about 65, 66.5 and 68 ppm, which were assigned to rr, mr and mm triads, respectively, [19–21]. For the CH_2 carbon, the number of peaks observed are due to tetrad configurations. In terms of linewidth and resolution, the ^{13}C DP/MAS NMR spectrum of the a-PVA gel in Fig. 1a looks very much like the ^{13}C NMR spectrum of an a-PVA solution given in Fig. 2. In the phase-separated a-PVA gel, it corresponds to a water-rich phase.

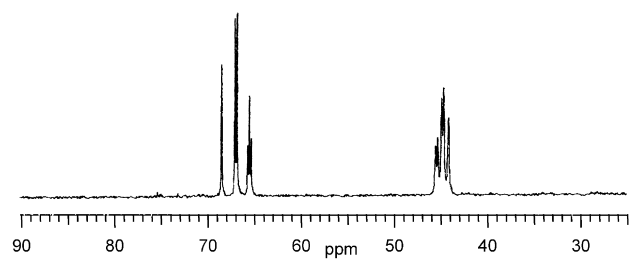

Fig. 2. ^{13}C NMR spectrum of a 11% w/w a-PVA solution.

3.2. Hydrogen bond interactions

As an example, the ^{13}C CP/MAS NMR spectra of an a-PVA gel at an 11% w/w polymer concentration after one freeze/thaw cycle and neat a-PVA are plotted in Fig. 1b and c, respectively. The natural linewidth of the a-PVA resonances in the a-PVA powder is much too large for the three narrow lines at 65, 66.5 and 68 ppm, characteristics of the a-PVA microstructure, to be observed. Three broad resonances (HB2, HB1, HB0) are observed at 77, 71 and 65 ppm for the CH carbon. They were assigned by Terao et al. [13] to methine carbons involved in two, one and zero hydrogen bonds, respectively. For the gel sample, the linewidths are much larger in the ^{13}C CP/MAS NMR spectrum than in the ^{13}C DP/MAS NMR spectrum. They are somewhat narrower than the lines observed in the solid powder. Besides, due to the low polymer concentration of the a-PVA gel sample, only lines HB1 and HB0, assigned to CH carbons involved in one (71 ppm) and zero hydrogen bonds (65 ppm) can be distinguished in Fig. 1b. These observations indicate that the chain mobility of the phase observed by the CP/MAS technique is much lower than the mobility in solution and somewhat higher than the chain mobility of the a-PVA powder. Therefore, the ^{13}C CP/MAS NMR spectrum can be assigned to a a-PVA-rich phase in the phase-separated a-PVA gel.

3.3. Crystallinity

The degree of crystallinity of all the a-PVA hydrogels was determined by measuring the fraction of rigid protons through ^{1}H free induction decay experiments as a function of polymer concentration and number of freeze/thaw cycles. As a first approximation, the free induction decay of a-PVA in the hydrogels exhibits two components characterized by a very fast gaussian-like decay with a relaxation time on the order of 20 μs and a much longer exponential decay. The former component, which corresponds to a small number of a-PVA protons, is characteristic of a rigid-lattice behavior, whereas the latter component involves protons with different mobilities. The rigid a-PVA component is very

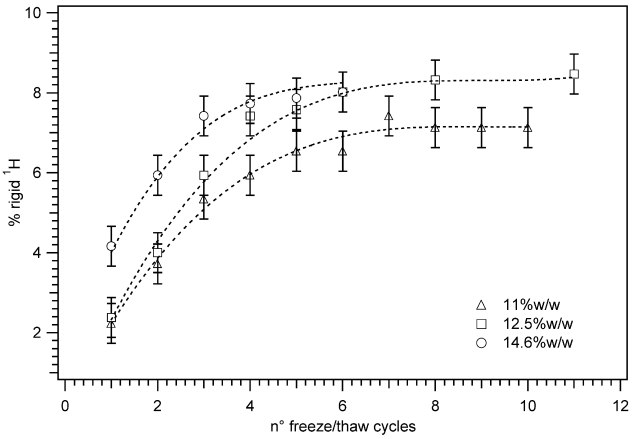

Fig. 3. Percentage of protons on rigid regions of PVA gels, at three different polymer concentrations, as a function of the number of freeze/thaw cycles: (△) 11% w/w a-PVA hydrogel; (□) 12.5% w/w a-PVA hydrogel; (○) 14.6% w/w a-PVA hydrogel. Lines are guides for the eye.

likely due to the a-PVA hydrogel crystallinity. The percentage of rigid a-PVA protons is plotted in Fig. 3 as a function of the number of freeze/thaw cycles for three polymer concentrations. For low numbers of freeze/thaw cycles, an increase in the number of freeze/thaw cycles or an increase in the polymer concentration induces an increase in the percentage of rigid protons. After five or six freeze/thaw cycles, the percentage of rigid protons tends to a limiting value.

These results show that the first five or six freeze/thaw cycles play a very important role in determining the hydrogel structure since they increase the crystallinity of the samples.

3.4. Rheological behaviour

Fig. 4 shows the strain dependence at 1 Hz of the storage, G', and loss, G'', modulus determined for 14.6% w/w a-PVA hydrogels obtained after different numbers of freeze/thaw cycles. The values of G' and G'' have been normalized by their respective maximum value, G'_0 and G''_0. At very low strain amplitudes, the loss modulus is lower than the storage modulus, in agreement with the existence of a network structure.

As shown in Fig. 4, the G''/G''_0 ratio dependence on the strain value undergoes a maximum which occurs at smaller values of percent deformation as the number of freeze/thaw cycles increases. In addition, it can be noted (Fig. 4) that, for small strain amplitudes, G' is independent of the strain amplitude. The latter result indicates that the deformation imposed on the network structure is entirely reversible. Indeed, repeated measurements on a given sample using the same protocol gave identical results proving that the gel structure is not modified by the experiment. At higher strain amplitudes, G' is a decreasing function of the strain amplitude and the deformation is no longer reversible. The higher the number of freeze/thaw cycles, the lower the strain amplitude, which characterizes the end of the constant regime, and the more fragile the a-PVA hydrogels. In the following, all the experiments were performed at the low strain amplitude of 0.1%, i.e. in the constant regime for G'.

As an example, the frequency dependence of G' is plotted in Fig. 5 for 14.6% w/w a-PVA hydrogels obtained after different numbers of freeze/thaw cycles. Repeated measurements, using the same protocol, gave reproducible results, in agreement with the reversible character of the deformation experienced by the sample at small strain amplitudes. For all the a-PVA gels investigated, at the three polymer concentrations (11, 12.5 and 14.6% w/w), G' and G'' (not shown on the graph) do not depend on the test frequency in the range between 0.1 and 30 Hz.

The values of the storage modulus, G', determined at 1 Hz for the different a-PVA gel samples are plotted in Fig. 6 as a function of the number of freeze/thaw cycles. The

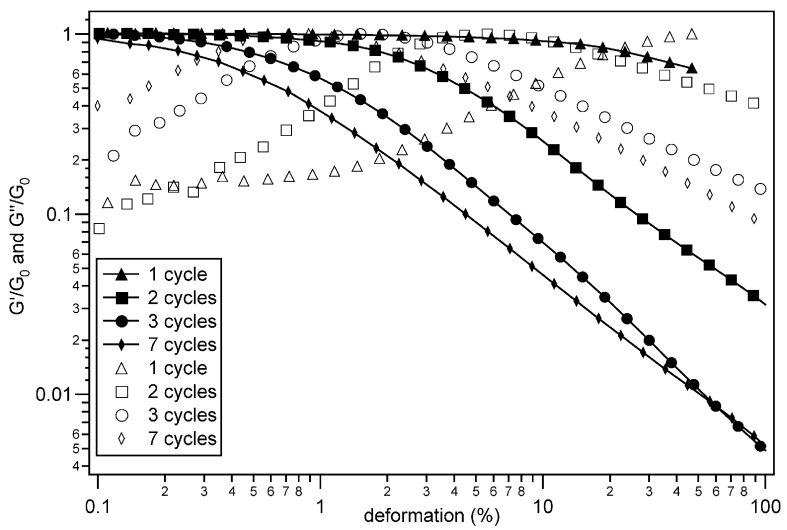

Fig. 4. G' and G'' modulus at 1 Hz as a function of different strain values, for14.6% w/w a-PVA hydrogels obtained after different numbers of freeze/thaw cycles. The G' and G'' moduli have been normalized with respect to their maximum values: filled symbols: G'; open symbols: G''. Lines are guides for the eye.

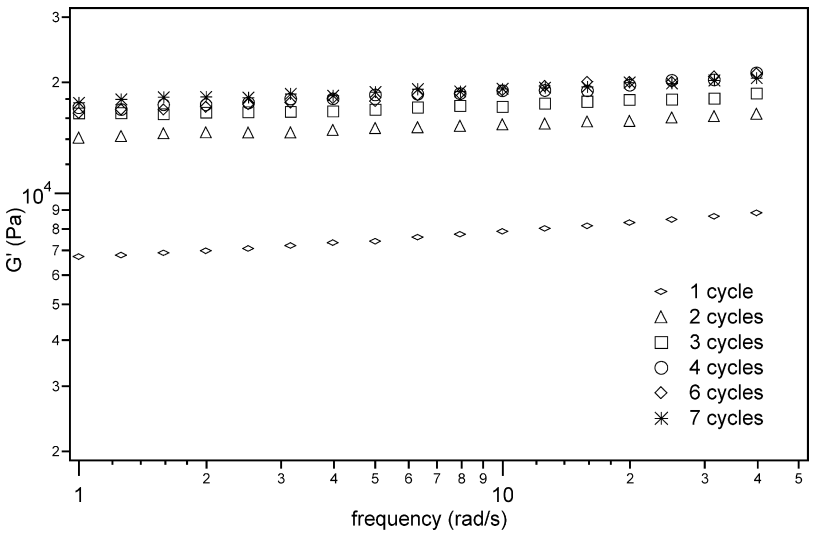

Fig. 5. Storage modulus, G', as a function of frequency for 14.6% w/w a-PVA hydrogels obtained after different numbers of freeze/thaw cycles.

storage modulus, G', increases with increasing polymer concentration. In addition, as shown in Fig. 6, for a given a-PVA concentration, G' increases with the number of freeze/thaw cycles and tends to a plateau value at high numbers of freeze/thaw cycles.

3.5. Comparison of NMR and rheological data

As shown by the ^{13}C NMR spectra plotted in Fig. 1a and b, the methine carbons of a-PVA which belong to the water-rich phase of the hydrogel are not involved in hydrogen bonds. On the opposite, a significant part of the methine carbons of a-PVA which belong to the a-PVA-rich phase is involved in one hydrogen bond. In agreement with conclusions derived by Kobayashi et al. [14], it is a clear evidence that hydrogen bonding contributes to the hydrogel crystallinity. It also infers that, in the systems investigated, the value of the storage modulus, G', should be mostly determined by the characteristics of the a-PVA-rich phase, i.e. the degree of crystallinity and density of hydrogen bond interactions in this phase. Therefore, to get a better understanding of the relationships between the network structure of the a-PVA hydrogels and their rheological behavior, the storage modulus values at 1 Hz, G', were plotted in Fig. 7 as a function of the percentage of protons in the crystalline phase, determined from the analysis of the ^{1}H free induction decays. For a given a-PVA concentration, the storage modulus, G', strongly increases as sample crystallinity increases. As a first approximation, the three data sets obtained for the three a-PVA concentrations can be fitted to straight lines. Extrapolation of these lines to G' equal to zero leads to a common value of the sample crystallinity, on the order of 1%. This result indicates that a minimum crystallinity is required for these a-PVA samples to exhibit gel behaviour. Moreover, it is interesting to note that, for a given crystallinity, the storage modulus increases slightly as polymer concentration increases. This phenomenon can be related to the increasing number of intermolecular hydrogen bonds that take part in the gel structure, in the a-PVA-rich

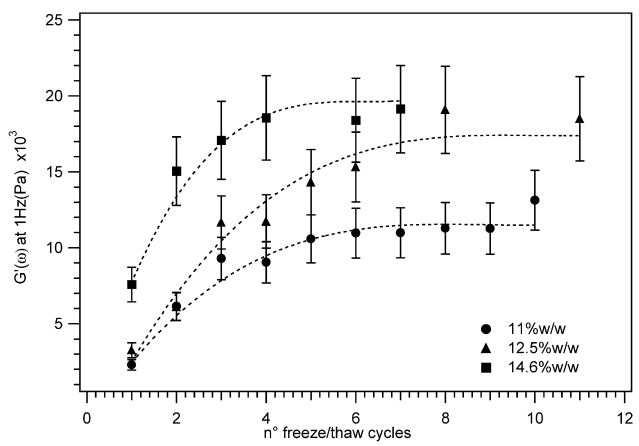

Fig. 6. Storage modulus, G', at 1 Hz, as a function of the number of freeze/thaw cycles for 11 (●), 12.5 (▲) and 14.6 (■) % w/w a-PVA hydrogels. Lines are guides for the eye.

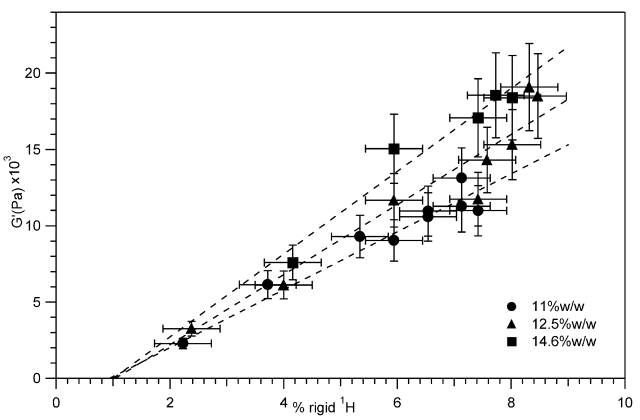

Fig. 7. Storage modulus, G', at 1 Hz, as a function of the percent of protons on rigid regions of the polymer, for 11 (●), 12.5 (▲) and 14.6 (■) % w/w a-PVA hydrogels.

phase of the hydrogel. Therefore, results displayed in Fig. 7 clearly show that hydrogel crystallinity is the main factor that controls the G' values at low strain amplitude, while the hydrogen bond interactions in the a-PVA-rich phase have a smaller contribution.

References

[1] Stephans LE, Foster N. Macromolecules 1998;31:1644.
[2] Bunn CW. Nature 1948;161:929.
[3] Bunn CW, Peiser HS. Nature 1947;159:161.
[4] Sakurada I, Fuchino K, Okada N. Bull Inst Chem Res Kyoto Univ 1950;23:78.
[5] Yokoyama F, Masada I, Shimamura K, Ikawa T, Monobe K. Coll Polym Sci 1986;264:595.
[6] Guenet JM. Thermoreversible gelation of polymers and biopolymers. San Diego: Academic Press; 1992.
[7] Peppas NA, Mongia NK. Eur J Pharm Biopharm 1997;43:51.
[8] Hassan CM, Hard JH, Peppas NA. Polymer 2000;41:6729.
[9] Hyon SH, Cha WI, Ikada Y, Kita M, Ogura Y, Nambu M. J Biomater Sci, Polym Ed 1994;5:397.
[10] Tamura K, Ike O, Hitomi S, Isobe J, Shimizu Y, Nambu M. Trans -Am Soc Artif Intern Organs 1986;32:605.
[11] Komatsu M, Inoue T, Miyasaka K. J Polym Sci, Polym Phys Ed 1986; 24:303.
[12] Kanaya T, Ohkura M, Kayi K, Furusaka M, Misawa M, Yamaoka H, Wignall GD. Physica B 1992;180/181:459.
[13] Terao T, Maeda S, Saika A. Macromolecules 1983;16:1535.
[14] Kobayashi M, Ando I, Ishii T, Amiya S. J Mol Struct 1998;440:155.
[15] Urushizaki F, Yamaguchi H, Nakamura K, Numajiri S, Sugibayashi K, Morimoto Y. Int J Pharm 1990;58:135.
[16] Kanekiyo M, Kobayashi M, Ando I, Kurosu H, Ishii T, Amiya S. J Mol Struct 1998;447:49.
[17] Willcox PJ, Howie Jr DW, Schimdt-Rohr K, Hoagland A, Gido SP, Pudjijanto S, Kleiner LW, Venkatraman S. J Polym Sci, Part B: Polym Phys 1999;37:3438.
[18] Kobayashi M, Ando I, Ishii T, Amiya S. Macromolecules 1995;28: 6677.
[19] Wu TK, Ovenall DW. Macromolecules 1973;6:582.
[20] Inoue Y, Chujo R, Nishioka A. J Polym Sci, Polym Phys Ed 1973;11: 393.
[21] Inoue Y, Chujo R, Nishioka A, Nozakura S, Iimuro H. Polym J 1973; 4:244.