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A reappraisal of the ‘thermoreversible’ gelation of aqueous poly(vinyl alcohol) solutions through freezing–thawing cycles

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Abstract

We report on a study of the gelation phenomenon of poly(vinyl alcohol) in water through freezing–thawing cycles. From self-exclusion chromatography experiments carried out on redissolved gels and microcalorimetry measurements performed on gels we come to the conclusion that gelation is rather of chemical than of physical nature.

Keywords: Gelation; Poly(vinyl alcohol); Freezing–thawing cycles

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1. Introduction

Aqueous solutions of atactic poly(vinyl alcohol) (PVA) do not produce physical gels when merely cooled at low temperature unlike what is commonly observed with atactic poly(vinyl chloride) [1–3]. Gelation of PVA solutions can, however, be achieved by submitting them to a series of freezing–thawing cycles [4–6]. The elastic modulus is seen to increase and a fibrillar network can be seen.

The freezing–thawing process can be accounted for from a thermodynamic viewpoint by realizing that water crystallization results in creating interstitial domains of high polymer concentrations. If some of the polymer chains (the chains of highest syndiotacticity for instance) belonging to these highly concentrated domains stand in a situation of appropriate undercooling, then they are liable to crystallize leading eventually to the gelation of the whole system. Yet, it is not clear why the number of freezing–thawing cycles should play such a major role. Indeed, there is no thermodynamic argument to state that polymer concentration would be further increased in the highly concentrated domains or to suppose that chains of lower syndiotacticity should eventually crystallize. In this paper, we report on a self-exclusion chromatography (SEC) analysis of the polymer chains recovered from the dissolution of gel samples obtained from various numbers of freezing–thawing cycles as well as on a study by means of microdifferential calorimetry of the resulting gels. The outcomes of the present study have led us to a reappraisal of the phenomenon in terms of the existence of a permanently cross-linked gel (chemical gel) rather than in terms of a thermoreversible gel.

2. Experimental

2.1. Materials

The PVA used in this study is a commercial product (ERKOL 28/99) with a degree of hydrolysis of 99.8%. The weight-average molecular weight as determined by GPC is 107,000 g/mol with a polydispersity of 1.77. The tacticity as measured by ^{1}H NMR spectroscopy is *syndio* $= 0.2$, *hetero* $= 0.5$ and *iso* $= 0.3$.

2.2. Sample preparation

PVA solutions (polymer concentrations of 5, 10, 15 and 20 wt%) were prepared in Pyrex tubes by mixing the appropriate amount of polymer and water (milli-Q grade) at 90 °C under conditions of vigorous stirring until the polymer was completely dissolved. Solutions were stored at 80 °C overnight and were then cooled to room temperature for 1 h prior to the freezing–thawing cycles. The PVA solutions were frozen by cooling down to −26 °C in a cryostat for

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5 min. After the freezing process, solutions were allowed to thaw at room temperature for 25 min. Different numbers of freezing–thawing cycles (4, 8, 12 and 16) were used to prepare cryogels.

2.3. SEC measurements

SEC analysis was carried out by using a multidetection device consisting of a LC-10AD SHIMADZU pump (throughput 0.5 ml/mn), an automatic injector WISP 717 + from WATERS, 3 coupled 30 cm-Shodex OH-pak columns (803 HQ, 804 HQ, 806 HQ), a multi-angle light scattering detector DAWN F from WYATT TECHNOLOGY, a differential refractometer R410 from WATERS. Distilled water containing 0.1 M $NaNO_3$ was used as eluent. The solutions for the SEC analysis (3 g/l) were prepared in distilled water by dissolving an appropriate amount of a piece of cryogel prepared as described earlier. Investigations were made from gels of same polymer concentration (20 wt%) prepared from different numbers of freezing–thawing cycles (4, 8, 12 and 16 cycles) on the one hand, and from cryogels of different concentration (5, 10, 15 and 20 wt%) of same number of freezing–thawing cycles (16 cycles) on the other hand.

2.4. Micro DSC measurements

A micro DSC from SETARAM (Micro DSCIII) has been used with stainless steel measuring cells. The DSC measurements were carried out on PVA cryogels of polymer concentration of 20 wt% having undergone 16 freezing–thawing cycles. Approximately 200–250 mg of gel material were transferred to the measuring cell. Samples were cooled from 25 to 5 °C at 1 °C/min, hold at 5 °C for 5 min and then scanned from 5 to 90 °C at different heating rates: 0.1, 0.25, 0.5 and 0.8 °C/min.

3. Results and discussion

A SEC study had already been made by Lozinsky et al. [7] but after only one freezing–thawing cycles. These authors had then detected no change with respect to the starting polymer. Here, again a comparison has been made between the PVA starting material and the polymer that has been gelled through several freezing–thawing cycles. Typical SEC spectra observed for all samples after more than two cycles are shown in Fig. 1. Both the variation of the concentration C_i, and the determination of C_iM_i of species i are displayed as a function of the elution volume. Two salient features are seen: (i) the appearance of materiel with high molecular weight (typically above $M = 10^6$), and (ii) the increase of the concentration in species of lower molecular weight. Here it is worth emphasizing that increasing the number of freezing–thawing cycle made the dissolution of the gel samples more and more difficult. This most probably means that species with still higher molecular weight are produced.

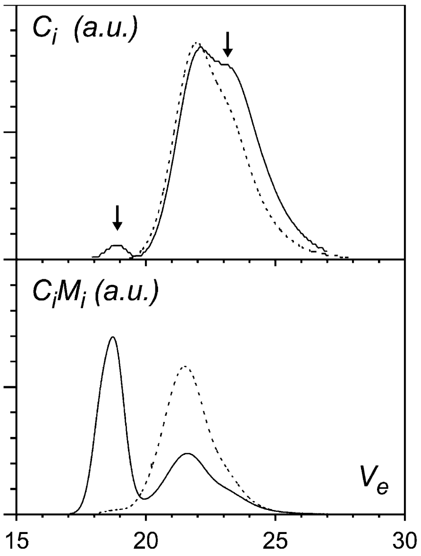

Fig. 1. SEC spectra of the material recovered by dissolution in hot water from a gel sample obtained after four freezing–thawing cycles. Gel concentration $C_{pol} = 0.20$ g/cm^3. Dotted line corresponds to the original PVA polymer while the full line stands for the SEC spectrum of the material recovered from the gel. Upper: variation of the species concentration C_i as measured from refractive index. Arrows highlight the appearance of both high and low molecular weight species. Lower: variation of the product C_iM_i as measured from light scattering.

These results suggest that the freezing–thawing procedure simultaneously leads to the breaking up PVA chains and the making of material of higher molecular weight. This may be accounted for by considering that the growing water crystals induce a shearing effect within the polymer solution which breaks up polymer chains and correspondingly creates free radicals [8,9]. Such an effect has already been reported for proteins [10–12]. These free radicals are liable to react with other chains leading to chemical cross-links, which produce high molecular weight material. Manifestly, increasing the number of freezing–thawing cycles increases the fraction of cross-linked material. This would imply that the gelation through the freezing–thawing procedure does not arise from physical interactions but rather from chemical interactions (chemical gels).

It has been, however, reported that a gel melting enthalpy could be measured whose magnitude increases with the number of freezing–thawing cycles. It should be stressed that these experiments have been carried out at only one heating rate. In the case of PVC Mutin and Guenet have shown that artifacts can occur under these conditions [13]. They have observed that the melting enthalpy for some heating rates would give irrelevant degrees of crystallinity. In fact, the melting enthalpy obtained after extrapolation to zero heating rate is virtually nought. This phenomenon has been shown to arise from mechanical effects due to the collapse of a piece of gel of undefined shape at the melting point. Clearly, the value of the melting enthalpy can be

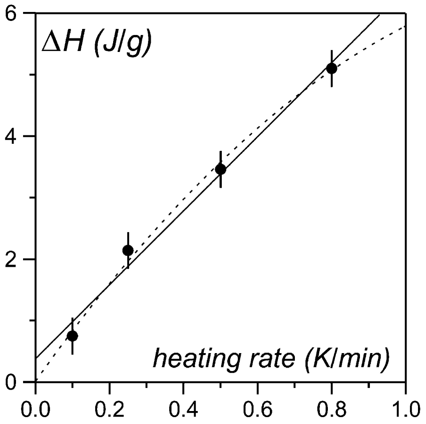

Fig. 2. Variation of the gel melting enthalpy ΔH as a function of the heating rate. For each heating rate a new sample is used. In all cases $C_{\mathrm{pol}} = 0.20$ g/cm^3. Solid line shows extrapolation to zero by using a linear variation while the dotted line corresponds to a polynomial variation (degree 2).

grossly overestimated if proper extrapolation to zero heating rate is not performed.

We have carried out the same type of experiments on gels prepared under the same conditions (here $C_{\mathrm{PVA}} = 0.20$ g/cm^3). As can be seen in Fig. 2 the melting enthalpy is very dependent upon the heating rate. Extrapolation to zero heating rate yields $\Delta H = 0.38$ J/g by considering a linear variation while a polynomial extrapolation (degree 2) gives $\Delta H = 0$. These values indicate clearly that the fraction of crystalline material x_c is very low, even virtually zero. Indeed, using values commonly reported in the litterature for the melting enthalpy of 100% crystalline syndiotactic PVA ($\Delta H = 150$ J/g) [14] would give $0 < x_c < 0.016$. Interestingly, ageing the gel in the DSC furnace at 20 °C for 2 days after melting at 90 °C gives virtually undetectable melting endotherm. Yet, this piece of gel possesses all the characteristics of the material before melting, in particular the elastic modulus is practically unchanged. Also, this piece of gel cannot be dissolved in a good solvent, such as DMF (dimethyl formamide) in spite of its absence of crystallinity. Whether there is a little amount of crystallinity or not has apparently no bearing with the gel properties. This again points to PVA gelation through freezing–cooling cycles being of chemical origin.

4. Concluding remarks

The experiments presented here suggest to reconsider the origin of the gelation phenomenon in poly(vinyl alcohol) submitted to freezing–thawing cycles. The results hint at some chemical cross-linking possibly arising from the creation of free radicals due to the shearing produce while water crystals grow within the polymer solution. Investigations should focus on this point to throw some light on this most unusual gelation mechanism.

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