

## Water-soluble temperature-responsive poly(vinyl alcohol-*co*-vinyl acetal)s

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Received: 15 December 2002/Revised version: 13 May 2003/ Accepted: 13 May 2003

### Summary

In order to obtain novel temperature-responsive copolymers, poly(vinyl alcohol) (PVA) was chemically modified by introducing cyclic acetal functionalities in the polymer chain. The acetalization reaction was carried out with acetaldehyde in water. The degree of acetalization was controlled in the range 10–25% by the initial aldehyde concentration. The copolymers obtained were characterized by 1D (<sup>1</sup>H, <sup>13</sup>C, DEPT) and 2D (COSY) NMR techniques as well as by viscometry. The thermo-responsive properties were evaluated by measuring the cloud point temperature ( $T_{cp}$ ) of the aqueous copolymer solutions.

### Introduction

Poly(vinyl alcohol) (PVA) is a water-soluble synthetic polymer, known to be truly biodegradable, biocompatible and of excellent film-forming properties and toughness. PVA is attracting renowned interest for the production of environmentally friendly fibers, membranes, high oxygen barrier films, etc. as well as for application in biotechnology and some medical fields. Basic properties of this polymer depend strongly on the degree of polymerization, degree of hydrolysis, distribution of hydroxyl groups, crystallinity, etc. [1,2]. PVA containing up to 20 % residual acetate groups is known to exhibit lower critical solution temperature (LCST) behavior in aqueous solution. Detailed investigations of the dependence of the LCST of series of poly(vinyl alcohol-*stat*-vinyl acetate) on the acetate content and the block sequence lengths have been reported [3,4].

PVA, like low molecular weight alcohols, is highly reactive and can undergo various modification reactions via the hydroxyl group [5–10]. Among them, reactions with aldehydes to form acetals such as poly(vinyl butyral) and poly(vinyl formal) are commercially utilized [11]. Many studies of the acetalization of PVA have been made since it was first investigated by Herrmann and Haehnel, the greatest part being focused on the products of high degree of acetalization [2,12]. To our knowledge, controlled synthesis of low percent acetalized PVA has not been investigated. The present paper reports for the first time the temperature-responsive properties of novel water-soluble copolymers synthesized by partial acetalization of PVA in aqueous solution.

## Experimental

### Materials

PVA 72000 (Fluka, reported degree of polymerization 1600, degree of hydrolysis 97.5-99.5 mol %), PVA 15000 (Fluka, reported degree of polymerization 300, degree of hydrolysis 86-89 mol %) and acetaldehyde (Fluka, >99% purity) were used as received.

### Synthesis of poly(vinyl alcohol-co-vinyl acetal)s of controlled degree of acetalization

The procedure applied in this work was based on the method elaborated in previous studies [8]. A solution of 1.25 g (56.8 mmol) PVA dissolved in 50 ml distilled water was placed in a two-neck flask, equipped with cooler and dropping funnel. 1 ml of the catalyst HCl (10-wt. %) was added, the solution was thermostated at 15°C and chosen amount of acetaldehyde (see Table 1) was added dropwise at vigorous stirring within 30 min. The temperature was raised to 40°C and the reaction was let to proceed for 4 hours. At the end, the temperature was raised to 60°C, the precipitated copolymer was isolated by decanting the solute, purified by repeating the isolation procedure in distilled water and finally dried at 60°C under vacuum.

### Measurements

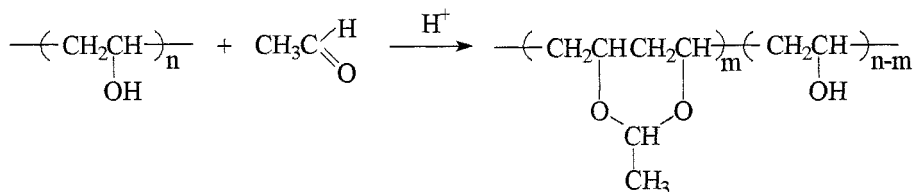
The NMR analyses were performed on a Bruker Avance DRX-250 spectrometer operating at 250.13 and 62.90 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively, using a dual 5 mm probe head. The measurements were carried out at ambient temperature in DMSO- $d_6$ , reference tetramethylsilane. The standard Bruker library pulse programs were used for all 1D and 2D NMR experiments. The typical conditions for the 1D experiment were: pulse width 30°, 1 s relaxation delays, 16K time domain points, zero-filled to 32K. Hard pulses with 90° pulse widths of 11.4  $\mu\text{s}$  for  $^1\text{H}$  and 6.0  $\mu\text{s}$  for  $^{13}\text{C}$  at a power level of 3dB below the maximum output were used. The distortionless enhancement by polarization transfer (DEPT) spectra were obtained under the same conditions as the  $^{13}\text{C}$  NMR spectra and  $\tau = (2 \text{ } ^1\text{J}_{\text{CH}})^{-1} = 3.45 \mu\text{s}$ ,  $\theta = 135^\circ$  was used. The 2D  $^1\text{H}/^1\text{H}$  homonuclear correlation spectra (COSY) were performed with a spectral width of ca. 1500 Hz, relaxation delay 2 s, mixing pulse width 45°, number of increments 256 and FT size 1K x 1K.

The viscosity measurements were carried out on an Ubbelode-type viscometer Schott Geräte CT1150 at 20°C in aqueous solutions.

Cloud point measurements were performed as follows: Aqueous polymer solutions of concentration 0.5g/dL were transferred in stopped test tubes and placed in a water bath which was heated at a rate of 1°C/min. The temperature at which the first opaqueness appeared in the solution was recorded. The solutions were also cooled from above this temperature at a rate 1°C/min and the temperature at which the finest opalescence disappeared was also recorded. The average of the two temperatures was reported as cloud point temperature ( $T_{\text{cp}}$ ).

## Results and Discussion

The reaction between PVA and acetaldehyde catalyzed by an acid leads to the formation of acetal rings along the polymer chain as shown in Scheme 1.



**Scheme 1.** Synthesis of poly(vinyl alcohol-*co*-vinyl acetal)

In order to obtain new materials with lower critical solution temperature (LCST) behavior, partial acetalization of PVA have been performed. Series of poly(vinyl alcohol-*co*-vinyl acetal)s have been synthesized, the degree of modification being controlled by the initial PVA-to-acetaldehyde ratio. Table 1 gives a survey of the copolymers obtained. The discussed copolymers are complex compounds exhibiting both stereo sequence and comonomer sequence distribution. Hence, a combination of several NMR techniques has been applied in order to assign the signals and to make the quantitative analysis of the copolymer composition possible.

**Table 1.** Synthesis of partially acetalized PVA <sup>a</sup>

| Sample | Starting PVA <sup>b</sup> | $\frac{[\text{PVA}]_0}{[\text{CH}_3\text{CHO}]_0}$ <sup>c</sup> | Theoretical degree of acetalization, mol.-% | Introduced acetal groups, mol.-% (NMR) | $\eta_{\text{inh}}$ , dL/g | $T_{\text{cp}}$ , °C |
|--------|---------------------------|---|---|--|----------------------------|----------------------|
| 1      | A                         | 10.0  | 10  | 12.9                                   | 1.1167                     | 41.0                 |
| 2      | A                         | 6.7   | 15  | 16.8                                   | 1.0434                     | 37.8                 |
| 3      | A                         | 5.0   | 20  | 21.4                                   | 0.9096                     | 34.5                 |
| 4      | A                         | 4.0   | 25  | 25.6                                   | 0.8380                     | 28.2                 |
| 5      | B                         | 10.0  | 10  | 9.4                                    | 0.2516                     | 29.5                 |
| 6      | B*                        | 10.0  | 10  | 11.2                                   | 0.3385                     | 38.9                 |
| 7      | B                         | 4.0   | 25  | 25.8                                   |                            | 17.0                 |
| 8      | B*                        | 4.0   | 25  | 26.3                                   |                            | 25.2                 |

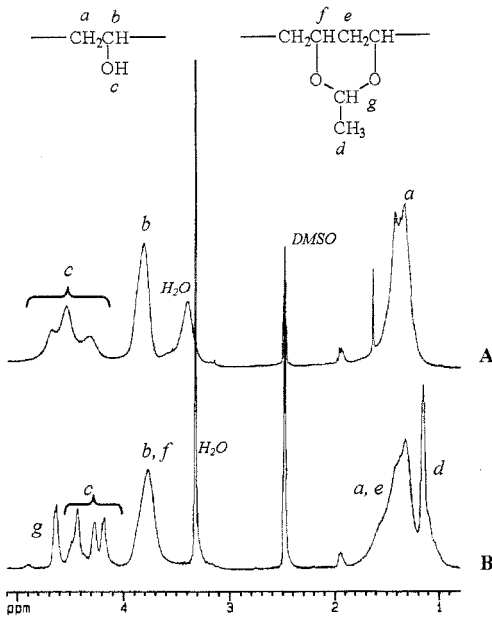
<sup>a</sup> Concentration of PVA 25g/L; acetalization reaction: 4 hours at 40°C

<sup>b</sup> A: PVA 72000,  $\eta_{\text{inh}}$  (A) = 0.6636 dL/g; B: PVA 15000,  $\eta_{\text{inh}}$  (B) = 0.2096 dL/g; B\*: completely hydrolyzed PVA 15000,  $\eta_{\text{inh}}$  (B\*) = 0.2194 dL/g

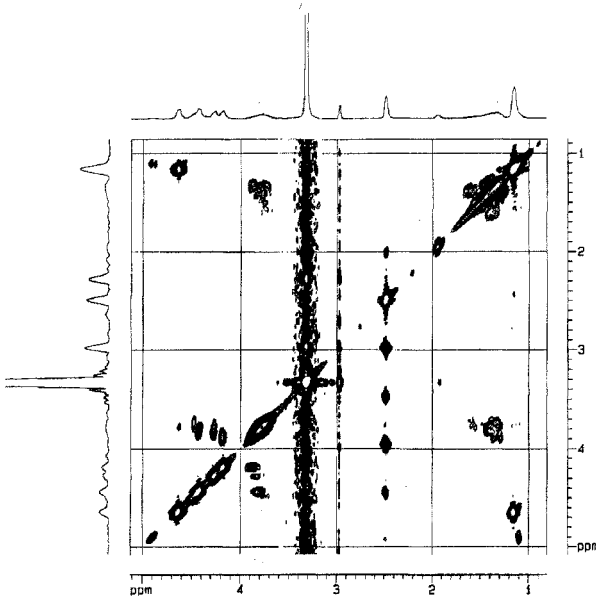
<sup>c</sup> Initial polymer-to-acetaldehyde molar ratio

In Figure 1, the <sup>1</sup>H NMR spectrum of the copolymer 4 (Table 1) is compared to those of the starting PVA. The resonance peaks of the methine protons in the main chains of both PVA and copolymer appear at 3.82 and 3.78 ppm, respectively, and those of the methylene protons in the 1.0–1.9 ppm spectral region. The peak at 1.16 ppm in the spectrum of the copolymer comes from the methyl group of the acetal ring.

The three resonance signals of the hydroxyl protons of the starting PVA appear at 4.69, 4.55 and 4.33 ppm and are attributed to the syndiotactic, heterotactic and isotactic triads, respectively [13,14]. In the same region of the spectrum of the copolymer, four equivalent signals are observed. The assignment of these signals was achieved by analyzing of the <sup>1</sup>H/<sup>1</sup>H COSY spectrum of the copolymer (Figure 2). The only resonance showing a cross-peak with the signal of the acetal methyl group is those centered at 4.64 ppm. It is clear that the resonance at 4.64 ppm in the spectrum of the copolymer corresponds to the O-CH-O protons of the acetal ring, whereas the



**Figure 1.** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) spectra of (A) starting PVA; and (B) poly(vinyl alcohol-*co*-vinyl acetal)



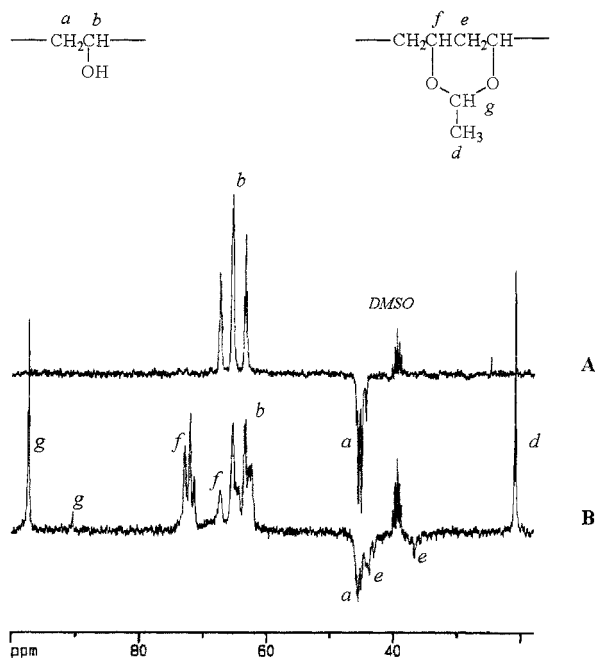
**Figure 2.** COSY NMR (DMSO-*d*<sub>6</sub>) spectrum of (poly(vinyl alcohol-*co*-vinyl acetal)

signals of the residual OH-groups are shifted upfield and appear at 4.46, 4.27, and 4.18 ppm, respectively.

Further details on the structure of the synthesized copolymers were obtained by analyzing DEPT NMR spectra and comparing the data with those published for poly (vinyl

butyral) [15]. The DEPT spectra of the starting PVA and the copolymer **4** are shown in Figure 3. The resonances of the hydroxymethine carbons of PVA were observed at 67.6, 65.6 and 63.6 ppm for the *mm*, *mr* and *rr* sequences, respectively, and those for the methylene carbons in the spectral area 44.4–46.0 ppm. In the spectrum of the copolymer, these resonances are observed in the areas 66–62 ppm and 46–43 ppm, respectively. Three new groups of signals due to the acetal rings appear: at 97.5 and 90.6 ppm for the O–CH–O carbons of the *meso* and *racemic* ring, respectively; at 72.3 for the CH<sub>2</sub>–CH–O carbons in the *meso* configuration and at 67.6 for those in *racemic* rings; and in the area 43–36 ppm for the methylene carbons of the acetal rings [14]. The difference in the intensities of the resonance signals of the *meso* and *racemic* O–CH–O carbons strongly indicates that the hydrolytically more stable *meso* acetal ring structure [11] prevail in the copolymer. More detailed investigation on the poly(vinyl alcohol-*co*-vinyl acetal)s copolymer stereo-structure is in progress and will be reported in a separate paper.

The composition of the copolymers was determined from the integrated <sup>1</sup>H NMR spectra. The degree of acetalization was calculated from the integral ratio of the signals assigned to the acetal O–CH–O protons to the signals of the methine groups in the main chain. As can be seen from Table 1, good agreement of the measured degree of acetalization with the theoretical one was achieved.



**Figure 3.** DEPT-135 NMR (DMSO-*d*<sub>6</sub>) spectra of (A) starting PVA; and (B) poly(vinyl alcohol-*co*-vinyl acetal)

The inherent viscosity values of the aqueous solutions of the copolymers measured at 20°C are higher than the viscosity of the starting PVA solution and decrease considerably with increasing the amount of the acetal groups introduces. This is

ascribed to the hydrophobic interactions leading to the shrinkage of the polymer chains in the solution.

The cloud point temperatures of the samples measured in aqueous solutions of concentration 5g/L are also listed in Table 1. The  $T_{cp}$  decreases considerably and continuously with increasing the portion of the acetal rings in the polymer chain. Thus the LCST-behavior of the reported copolymers could be easily controlled by the initial PVA-to-acetaldehyde ratio. The structural characteristics of the starting PVA have a decisive influence over the temperature-responsive properties of the final products. At the same degree of acetalization the copolymer derived from the lower molecular weight PVA (Samples 5 and 7; Table 1) showed a  $T_{cp}$  of 10°C lower than the higher molecular weight counterparts. This could be assigned to the presence of about 17 mol.-% residual acetate groups along with the introduced acetal groups, as the corresponding copolymers obtained from completely hydrolyzed parent PVA exhibited higher  $T_{cp}$  values close to those of the high molecular weight counterparts.

Further investigations on structure-properties relationship, and particularly the LCST behavior, of series of poly(vinyl alcohol-*co*-vinyl acetal)s of different structure and composition are in progress.

## Conclusion

Temperature-responsive copolymers were synthesized by partial acetalization of PVA with acetaldehyde in aqueous solutions. Thermo-responsive properties of the obtained poly(vinyl alcohol-*co*-vinyl acetal)s exhibited systematic change as a function of the copolymer composition. The cloud point temperatures of the aqueous copolymer solutions ranged from 41 to 17°C depending on the portion of the acetal functionalities introduced and the molecular characteristics of the starting PVA.

*Acknowledgments.* Financial support by the Bulgarian National Foundation for Scientific Research (Grant H-803) is gratefully acknowledged.

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