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Polymer 47 (2006) 577–584

polymer

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The application of attenuated total reflectance Fourier transform infrared spectroscopy to monitor the concentration and state of water in solutions of a thermally responsive cellulose ether during gelation

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Received 15 August 2005; received in revised form 17 November 2005; accepted 22 November 2005
Available online 15 December 2005

Abstract

This paper reports the use of ATR-FTIR with PLS data analysis to probe the thermal gelation behaviour of aqueous solutions of the cellulose ether, hydroxypropyl methylcellulose (HPMC). Spectroscopic changes in the ν(CO) region of the infrared spectra (collected using ATR) were shown to mark the onset of gelation and information about the temperature of gelation and the effect of the gel structure on the water hydrogen bonding network was elucidated. The use of PLS data analysis to quantify the water concentration within the gel at the ATR interface is highlighted. The dominance of intermolecular H-bonding over intramolecular H-bonding within the cellulose ether in solution was also observed. The ATR-FTIR data was in good agreement with rheological and DSC measurements conducted on the same systems. A discussion regarding the changes in shape of the ν(OH) band of the water within the gel is provided and an interpretation of these changes in terms of modifications of the hydrogen bond strength of associated water during syneresis is given.

Keywords: Cellulose ether; ATR-FTIR; Gelation

1. Introduction

The use of hydrophobically modified water soluble polymers to control the rheological properties of aqueous based systems is widespread, with the technology applied to food [1], oil recovery [2], cosmetics [3] and pharmaceuticals [4]. More esoteric studies on synthetic polymers have provided a rudimentary understanding of the link between the nature and number of hydrophobic substituents and their rheological behaviour [5]. But studies on the derivatives of natural materials are less well understood due in part to the heterogeneity of the substitution and a lack of suitable models. Kondo et al. [6–8] have tried to address this lack of understanding but, due to the similar reactivities of the OH groups at the 2 and 3 position on the cellulose backbone, the number of model compounds that can be made using their methodology is limited to 2,3-di-*O*-methylcellulose and 6-*O*-methylcellulose with different degrees of heterogeneous substitution.

The propensity of HPMC (shown in Fig. 1) and certain other cellulose ethers, to undergo a reversible sol–gel transition at elevated temperatures in aqueous solution, has been widely studied [9–13]. The heating of cellulose ether solutions eventually results in loss of solubility and a temperature is reached, at which precipitation of the polymer and/or gel formation occurs. Both solubility effects and gel formation are fully reversible, although a degree of hysteresis can occur, and are reproducible, irrespective of the thermal history of the sample [14]. Gelation of HPMC is thought to arise from increasing hydrophobic interactions and exclusion of water (syneresis) from heavily methoxylated regions of the polymer [15]. In contrast, hydroxypropyl cellulose (HPC), a closely related material that does not contain methoxyl substituents, precipitates on heating but does not form a gel [16,17]. It has also been observed that methylcellulose has a lower gelation temperature and formed firmer gels than HPMC of equivalent substitution and molecular weight, indicating that hydroxypropyl substituents inhibit gelation [18,19].

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doi:10.1016/j.polymer.2005.11.067

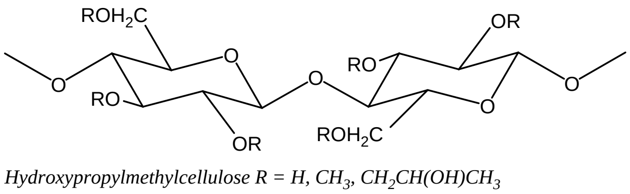

Fig. 1. Chemical structure of the cellulose ether used for this study.

ATR-FTIR has become a very important tool for characterising hydrogen bonding in aqueous systems [20–22] and determining the interactions between sorbed water and polymer matrices [23–25]. The detailed theory of attenuated total reflectance Fourier transformed infrared spectroscopy (ATR-FTIR) is available elsewhere [26] but it is worth summarising the salient points in relation to this paper. The most important feature of the ATR experiment is the evanescent field, which develops during the reflection of radiation at the interface of a material with a high refractive index (ATR crystal, n_2) and a material with a low refractive index (sample, n_1). Attenuation of this electric field by functional groups in the lower refractive index material results in a spectrum analogous to an absorbance spectrum. The depth of penetration (dp) of the evanescent field is governed by the wavelength of incident radiation (λ_1), the angle of incidence (θ_{inc}) and the ratio of the ATR crystal and sample refractive indices (n_{21}). This limits the sampling depth which can be estimated using Eq (1). In practice, the effective sampling depth is considered to be ~3dp.

$$\mathrm{dp} = \frac{\lambda_1}{2\pi\left(\sin^2\theta_{\text{inc}} - n_{21}^2\right)^{1/2}} \qquad (1)$$

As a result, the spectral information obtained will only be from the few microns close to the ATR crystal, regardless of the overall thickness of the sample. Therefore it is possible to obtain spectra from very strongly absorbing materials including water.

FTIR has been used to characterise the gel structure of a number of systems including synthetic polymers [27,28], proteins [29,30] and starches [31–34]. Iizuka and Aishima [31] used ATR-FTIR spectroscopy with evolved factor analysis to obtain information about the gelation processes of corn and potato starch. They reported profound intensity changes in the ν(CO) region of starch solutions during gelation and postulate that this is due to changes in the interaction of water with starch granules between 74 and 80 °C. Wilson et al. [32] and Bilkin et al. [33] used ATR-FTIR to study the gelation and retrogradation of waxy-maize starch and wheat starch gels, respectively. Once more, changes in the relative intensities of bands between 1200 and 800 cm^{-1}, indicated morphological changes and correlated well with rheological measurements. Lui et al. [34] have used FTIR in transmission mode to look at phase changes in potato starch solutions. They also reported increases in the intensity of bands between 1200 and 800 cm^{-1} during gelation. The authors also indicated changes in the types and nature of molecular interactions during gelation, suggesting that gelation was a hydration process.

Ostrovskii et al. have used a transmission FTIR method to study the thermal gelation of ethyl (hydroxyethyl) cellulose in the presence of an ionic surfactant [35]. The paper included a study of the changes in the 1200–900 cm^{-1} bands before and after gelation and indicated that a band around 1075 cm^{-1}, assigned to skeletal vibrations of the saccharide rings, decreased as a function of gelation. This, they postulate, was due to the rings being 'more bound' in the gel state. Conversely a band around 1120 cm^{-1}, assigned to C–O–C bridges, increased as a function of gelation, also as a result of a decrease in mobility of the cellulose rings. The authors also report interactions with SO_3^- groups in the surfactant, but because of the relatively large cell path length (25 μm) they were unable to obtain information regarding the structure of water in the gel state.

We have previously reported the significant and reproducible increase in intensity of the ν(CO) region of aqueous K4M HPMC solutions subjected to a temperature ramp in a sealed environment [36]. We observed a dependence of the measured gel point on the concentration of polymer and reported evidence of syneresis. These results were corroborated using a light scattering methodology. This investigation applies ATR-FTIR with partial least squares (PLS) data analysis to the study of thermal gelation phenomena in HPMC solutions and builds on our previous findings for K4M grade HPMC solutions.

This paper is part of a program of work examining the relationship between molecular interactions and the physical changes (thermal transitions, turbidity changes and rheological changes) that occur in thermally-responsive cellulose ether solutions. The role played by water in the sol–gel transition is poorly understood and in principle, vibrational spectroscopy readily facilitates the probing of water structure within the polymer network. Changes in the 'state' of water, and understanding factors affecting the gelation mechanism with respect to the sol–gel transition can potentially yield important information for intelligent formulation in food, cosmetic and pharmaceutical systems. Quantifying the water within the gel state may also provide significant information with respect to the syneresis process as it is unclear whether water loss leads to stronger hydrophobic chain interactions or if polymer/polymer interactions are the driving force for the proposed redistribution of water. Elucidating information on the state of the water in these systems may lead us part way to answering this question. This paper focuses on (i) establishing the viability of the technique for such studies (ii) characterising the state of the water in the gel network and (iii) quantifying polymer chain water loss (syneresis) during the sol–gel transition.

2. Experimental

HPMC solutions (Methocel E4M CR Premium USP/EP, hydroxypropyl content 9.3% and methoxyl content 29.5%, BN OD16012N32, Colorcon Ltd, Dartford, UK) were prepared using the method of Banks et al. [36].