European Polymer Journal 45 (2009) 1158–1168

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Effect of mixed solvent on solution properties and gelation behavior of poly(vinyl alcohol)

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ARTICLE INFO

Article history:
Received 26 February 2008
Received in revised form 17 December 2008
Accepted 5 January 2009
Available online 13 January 2009

Keywords:
Poly(vinyl alcohol)
Solution properties
Aging effect
Phase separation
Gelation kinetics

ABSTRACT

In this work, the static and dynamic light scattering measurements were used to investigate the solution properties and the aging effects on PVA/DMSO/water ternary system in dilute region at 25 °C. It was found that the phase separation and aggregate behavior occurs rapidly and obviously when DMSO mole fraction (X_1) in the solvent mixture is between 0.2 and 0.33, especially at 0.25. In this solvent composition range, a broad peak which indicates phase separation and chain aggregation can be observed from static light scattering measurement. However, when DMSO mole fraction is increased to 0.37, no such peak is present. For this ternary system, the gelation mechanism and the relationship between the phase separation behavior and the gelation of the formed physical gels were also investigated through the gelation kinetic analyses in the dilute and semi-dilute region. It is concluded that the cononsolvency effect in the dilute solution is not the sole origin that affects the phase separation, aggregation, and gelation behavior for the ternary system in a higher polymer concentration range. The hydrodynamic factors such as the higher viscosity and slower polymer chain diffusion that are resulted from higher polymer concentration should be also considered.

1. Introduction

Poly(vinyl alcohol) (PVA) exhibits important commercial applications due to its water-soluble and biocompatible properties and nowadays it is widely applied to the hydrogels as biomaterials. Mixtures of DMSO and water have also been used in biological applications ranging from antibacterial activity to membrane permeability [1]. On the other hand, PVA gels are also well known in preparing high-modulus PVA fibers by the drawing of gel films from the crystallization of semidilute solutions [2]. It is generally recognized that the degree of polymer–solvent interaction would affect significantly the physical and chemical properties of polymer solutions. It is also accepted that the formation of co-solvent complex could play an important role on the preferential adsorption phenomenon and the thermodynamic properties of polymer solutions.

In order to study the solution properties of a ternary system PVA/DMSO/water, the phenomenon of cononsolvency which is related to the molecular interaction is needed to be addressed. Tacx et al. [3] gave a possible explanation for the different affinity between the two solvents and PVA. It was concluded that PVA could be molecularly dissolved in DMSO and the formed solutions would not age. However, water could only be a moderate good solvent for PVA, the formation of aggregates would be easy to occur. From the viewpoint of chemical structures, the dipole moments and the donor-acceptor properties of each component could clarify these molecular interactions which would change with the compositions of the solvent mixture and the formation of a third component i.e., co-solvent complex. In our previous study [4], it was concluded that the formation of a third component would give rise to various phenomena of preferential adsorption coefficient for dilute PVA/DMSO/water ternary solution. It is

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doi:10.1016/j.eurpolymj.2009.01.005

therefore important to further discuss on the solution properties, the phase separation, coil aggregate and gelation behaviors in the semi-dilute region with different concentration and composition of co-solvent mixture. Takahashi et al. [5] reported that the fastest gelation and phase separation rate for a PVA/DMSO/water ternary system would occur at the volume fraction of DMSO $\Phi_{DMSO} = 0.6$. It was ascribed to the cononsolvency effect due to the formation of stable DMSO/(water)$_2$ complexes at $\Phi_{DMSO} = 0.66$. They also pointed out that spinodal decomposition type of phase separation would occur before gelation for the PVA solution with $\Phi_{DMSO} = 0.6$, resulting in polymer-rich and polymer-poor phases. The formation of junction points (PVA crystallites) of gel network would occur mainly in the polymer-rich phase, purposing that overall gelation rate should be affected by the phase separation process. Kaji et al. [5–11] have reported a serious of studies on PVA gels formed in DMSO/water mixtures by various scattering techniques in a broad composition range ($\Phi_{DMSO} = 0.3–0.8$). It was found that the mixed solvent would exhibit the poorest affinity to PVA at DMSO, $\Phi_{DMSO} = 0.6$. Takeshita et al. [9] also confirmed the spinodal decomposition type of phase separation actually would occur in the formation process of the opaque gel using time-resolved light scattering measurements. Wolf et al. [12] suggested that cononsolvency would usually occur either when the two solvents were close to demixing or when the complex was formed. On the other hand, Schild et al. [13] reported that perturbation of solvent–solvent interaction parameter would not be the origin of cononsolvency and the gel collapse transition in a ternary system. It is believed that the phase separation, the aggregation behavior and the gelation kinetics of PVA solutions might be strongly dependent on the composition of co-solvent mixture and the PVA concentration. However, the composition usually studied at $\Phi_{DMSO} = 0.6$ is actually nearer the 1/3 ratio, corresponding to $X_{DMSO} = 0.25$. The aim of this study was to investigate if the cononsolvency would be the origin of phase separation and gelation in the compositions near the formation of cononsolvency.

2. Experimental

2.1. Materials

The PVA powder (M_w = 124,000–186,000, from Aldrich) with a high degree of hydrolysis (about 99.9%) was used in this work. The solvent, dimethylsulfoxide DMSO, was purchased from Aldrich and used as received. The PVA/DMSO/water ternary solutions with various compositions were prepared by dissolving PVA in mixed DMSO/water solvent. The combined mixtures were heated at 95 °C then cooled to 25 °C. The PVA concentration was controlled in both dilute and semi-dilute region. The DMSO compositions (V/V) in the mixed solvent ranged from 10/0 to 0/10.

2.2. Dynamic light scattering

For dynamic light scattering experiment, the solvent, DMSO and water were repeatedly filtered using a 0.02 μm Millipore filter to remove dusts before using. The as-received PVA powder was purified by the following method before using. First, a 10 gL^{-1} PVA aqueous solution was prepared at 95 °C, and then the homogeneous PVA solution was filtered through a 0.45 μm Millipore filter to remove the dusts. Finally, the purified PVA sample was obtained from the precipitation of the solution by adding dust-free acetone. The precipitated PVA was collected and dried in vacuum oven at 70 °C for 3 days. Mixed solvents with various compositions of DMSO/water mixture, 0/10, 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 6.6/3.4, 7/3, 8/2, 9/1, 10/0 (V/V) were used to prepare PVA solutions. Four dilute solutions for every studied composition of co-solvent mixture were prepared at least. Homogeneous PVA solutions were obtained by heating at 95 °C for 5–6 h, and then sealed in the Pyrex tube. The solutions were heated to become homogeneous again, and then quenched rapidly to 25 °C for dynamic light scattering measurements.

The dynamic light scattering was conducted on a Malvern series 4700 apparatus equipped with the 7132 multiple-τ autocorrelator recording on 128-channels. The light source was an Argon ion laser, operating at power of 20–50 mW with a wavelength of 514.5 nm. The light was vertically polarized and focused on the sample cell through a temperature-controlled chamber filled with dust-free distilled water. The measurements were carried out at the scattering angle θ, from 30° to 120°. The data was collected from the intensity autocorrelation function. Given that the polymer chain obeys Gaussian statistics, the measured normalized intensity correlation function $g^{(2)}(t)$ is related to the normalized electric correlation function $g^{(1)}(t)$ through Siegert relation [12–15]:

$$g^{(2)}(t) = 1 + \beta|g^{(1)}(t)|^2 \tag{1}$$

where β is an optical factor related to the coherence area viewed by the detector. Some useful parameters related to the solvent quality such as hydrodynamic radius R_h, diffusion coefficient D, and second virial coefficient K_d can be determined by this operation.

2.3. Kinetics of gelation

The homogeneous PVA solutions with different polymer concentrations and compositions of co-solvent mixture were prepared in the sealed test tubes which were then kept in an oven at 95 °C for 2 h to make the solutions homogeneous again. The hot solutions were rapidly transferred into a water bath at 25 °C. The quenched temperature (25 °C) was always kept constant for different polymer concentration and compositions of co-solvent mixtures to prevent temperature effect which could weaken the DMSO/(water)$_n$ hydrate obviously. The test tube tilting method was used to determine the gelation time, t_{gel} which was defined as the time (minutes) required for the cessation of the solution flow inside the test tube when it was tilted. The reciprocal of gelation time of the solution is referred as the apparent gelation rate t_{gel}^{-1} which can be expressed as a function of polymer concentration and temperature: [8,17,18]

$$t_{gel}^{-1} \propto f(C)f(T) \tag{2}$$