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Dynamic light scattering of poly(vinyl alcohol)–borax aqueous solution near overlap concentration

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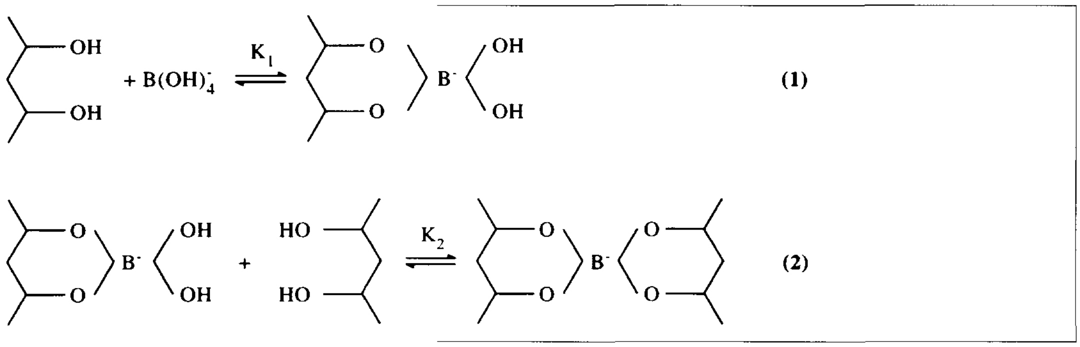
The physical properties of PVA–borax aqueous solutions with a PVA concentration near the overlap concentration and various borax concentrations were observed using dynamic light scattering and dynamic viscoelastic measurements. It had been proposed by Leibler *et al.* that the structure of PVA–borate complex in dilute aqueous solution strongly depends on: (1) excluded volume effect of polymers; (2) the intra- and inter-molecular crosslink reactions between di-diol of PVA and borate ion; (3) the charge repulsion among borate ions bound on the PVA molecules; (4) the screen effect of the free Na^+ ions on the negative charge of PVA–borate complex molecules. Based on the experimental data and the model of Leibler *et al.*, the structures of PVA–borate complexes near the overlap concentration in aqueous solutions were proposed. © 1997 Elsevier Science Ltd.

(Keywords: poly(vinyl alcohol); borax; dynamic light scattering)

INTRODUCTION

The structures and properties of aqueous solution of poly(vinyl alcohol) (PVA)–borate complex have been studied extensively in recent years[1–12]. The mechanism of the crosslink reaction of borate ion with PVA is believed to be a so-called 'di-diol' complexation, which is formed between two diol units and one borate ion[1,4–6]. This phenomenon depends on the concentrations of PVA and borate ion and temperature. The PVA–borate cross-linking mechanism is divided into two reactions, i.e. monodiol complexation (reaction (1)) and a crosslink reaction (reaction (2)) as shown by the equations:



(1)

(2)

Once a borate ion is attached to a polymer chain (reaction (1)), the polymer chain behaves as a polyelectrolyte unless the borate ion is removed from the chain. In this case, a significant contribution of electrostatic repulsion between monodiol units is expected, resulting in an expansion of the individual polymer chains.

In dilute polymer solution, the dimension of the chain is lowered due to intra-molecular crosslink formation through reaction (2), and an aggregation of polymer molecules may also be expected if the polymer–polymer attractive interaction is greater than the polymer–solvent interaction. The chain dimension and the stability of PVA–borate complex system is ruled by electrostatic repulsion and intra-molecular crosslink. Leibler *et al.*[7], based on Ochiai's data[8] of PVA–borax system, presented a theoretical Flory-type model describing the equilibrium size of the individual PVA–borax complex chain. Their model showed that the polymer chain dimension was the consequence of balance among the elastic energy, the excluded volume effect, and the electrostatic potential.

In semidilute polymer solutions, both intra- and inter-molecular crosslink reaction may happen through reaction (2), and a gelation of PVA–borate complex is expected. The gelation of PVA has been studied extensively in recent years[1–3,9,12–20]. Wu *et al.*[3] studied

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the temperature and concentration dependence of correlation length ζ of PVA aqueous hydrogels by small angle neutron scattering (SANS), and reported that a maximum polymer–polymer correlation length was observed for a PVA aqueous solution near the overlap concentration at melting temperature of the gel. Shibayama *et al.*[9] studied the temperature dependence of the correlation length of PVA–borate aqueous gels by SANS, showing that the correlation length ζ remained constant in the gel state and decreased sharply with increasing temperature in the sol state. Even at the highest temperature of observation (95°C), Shibayama *et al.* found that the correlation length ζ of PVA–borate molecules was a few times greater than the radius of gyration of the PVA molecules, indicating the presence of PVA clusters in the sol state. Geissler *et al.*[16] measured the swelling pressure and shear modulus of crosslinked PVA hydrogels and correlated these data to small angle X-ray measurements. They reported that the second moments describing the static concentration fluctuations increased strongly with the cross-linking density. Kurakawa *et al.*[17] studied the phase behaviour and sol–gel transition of PVA–borate–water system by viscometry method, and reported that at a given combination of PVA concentration and ionic strength, the system underwent a clear–opaque–clear transition with increasing boric acid concentration. The intrinsic viscosity decreased first then increased with increasing boric acid concentration. Mckenna *et al.*[19] measured the swelling pressure and shear modulus of PVA hydro-gels and studied the effect of the crosslinks on the polymer–solvent interaction parameter χ. Keita *et al.*[20] reported the 're-entrant phases' for PVA–borate reversible gels, and attributed this behaviour due to the balance between the electrostatic repulsions among the charged complexes formed on the polymeric chain and the crosslinking induced by the borate ions.

It is well known that borax (or sodium tetraborate, $Na_2B_4O_7$) is a good buffer. At low concentrations, it is totally dissociated into equal quantities of boric acid and borate ion[5]

$$\underset{\text{borax}}{Na_2B_4O_7} + 7H_2O \longrightarrow \underset{\text{boric acid}}{2B(OH)_3} + \underset{\text{borate ion}}{2B(OH)_4^-} + 2Na^+ \qquad (3)$$

In the present work, we reported the data from dynamic light scattering (DLS) and dynamic viscoelastic measurements for PVA–borax–water systems with PVA near the overlap concentration as well as various borax concentration. Based on the experimental results, the structures of PVA–borate systems near the PVA overlap concentration in water were proposed.

EXPERIMENTAL

Materials

(a) Poly(vinyl alcohol) (PVA) (99% hydrolysis, $M_w = 1.1 \times 10^5$, Aldrich Chemical Co.): It was dissolved in a *n*-propanol–water system and dialysed against water to remove any lower molecular weight species and recovered by reprecipitation with acetone.

(b) Sodium tetraborate (borax, $Na_2B_4O_7$, Riedel–de Haen Co.): It was dried at 120°C under reduced pressure for one day before sample preparation.

(c) Preparation of PVA–borate complex solution: The dialysed PVA was dissolved in water at a concentration of $\sim$10 mg ml^{-1}. The solution was then filtered through a Millipore filter (0.45 μm) to remove dust from the solution. PVA was then recovered by reprecipitation with acetone. The precipitated PVA sample was dried under vacuum at 60–70°C for one day to remove residual solvents. The PVA–borax solutions were then prepared by mixing PVA with various concentrations of borax–water solutions. The borax–water solutions were also filtered through a Millipore filter (0.45 μm) before mixing with PVA. Thus the final solutions had a PVA concentration of 15 g l^{-1} with a varying borax concentrations from 0.0 M to 0.2 M.

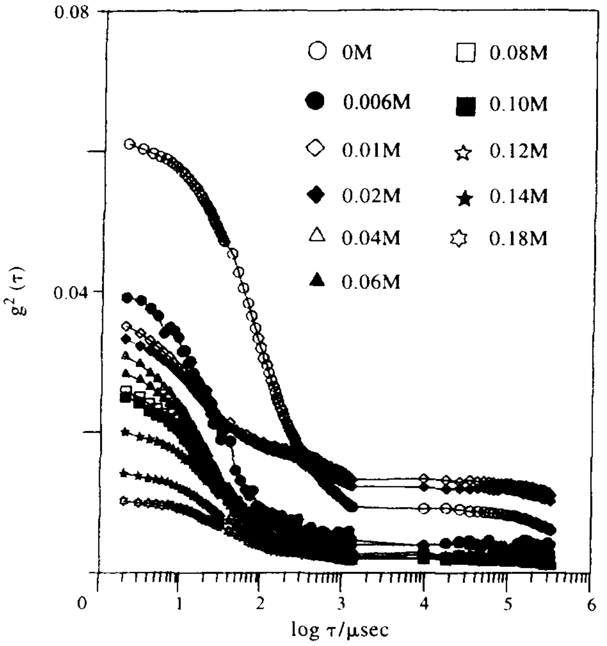

Figure 1 Correlation functions $g^{(2)}(\tau)$ for PVA–borax–water system with various borax concentrations and PVA concentration of 15 g l^{-1}

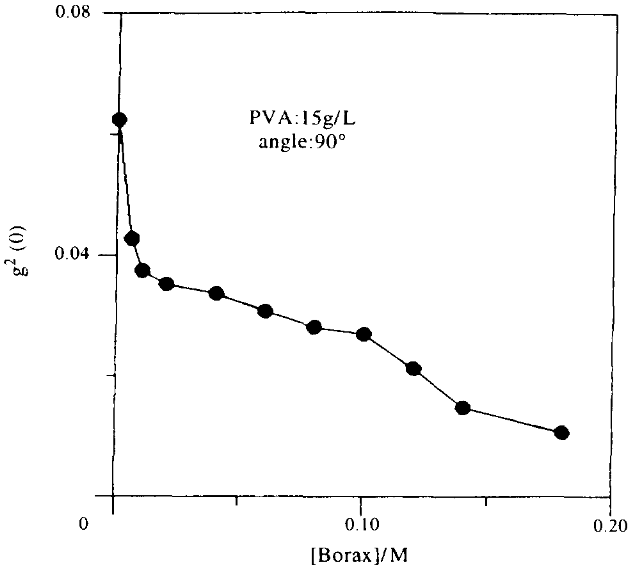

Figure 2 $g^{(2)}(0)$ vs borax concentration