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

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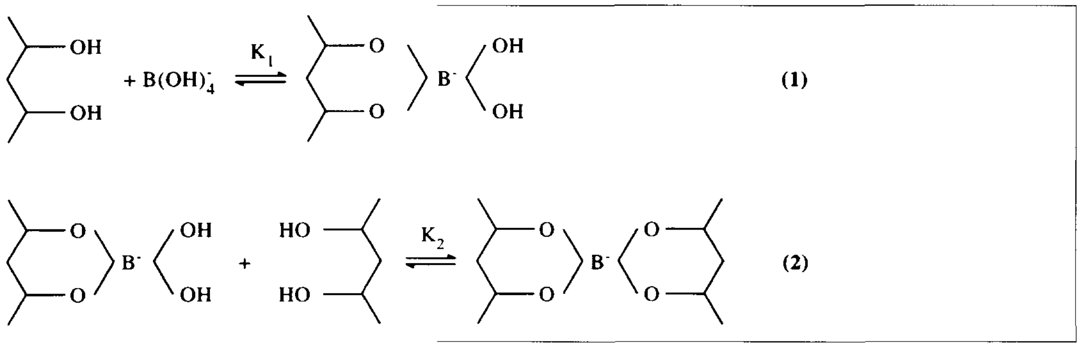
The physical properties of PVA–borax aqueous solutions with a PVA concentration near the overlap concentration and various borax concentrations were observed using dynamic light scattering and dynamic viscoelastic measurements. It had been proposed by Leibler *et al.* that the structure of PVA–borate 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 crosslinking mechanism is divided into two reactions, i.e. monodiol complexation (reaction (1)) and a crosslink reaction (reaction (2)) as shown by the equations:



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.

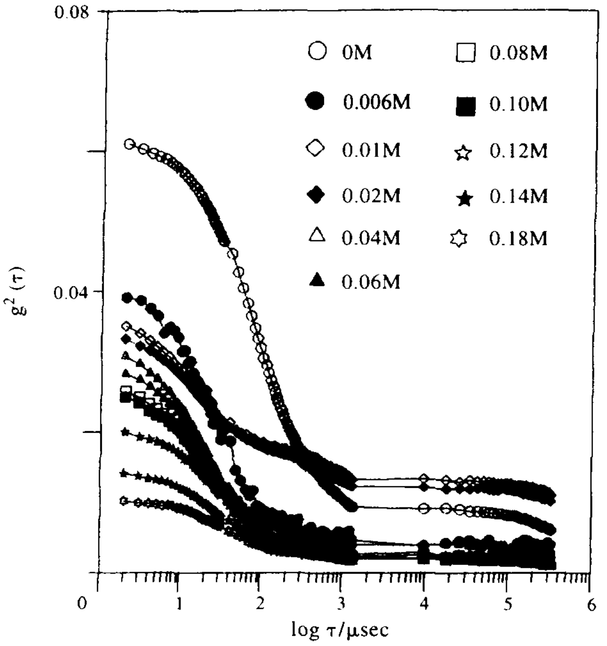


Figure 1 Correlation functions $g^{(2)}(\tau)$ for PVA–borax–water system with various borax concentrations and PVA concentration of 15 g l^{-1}

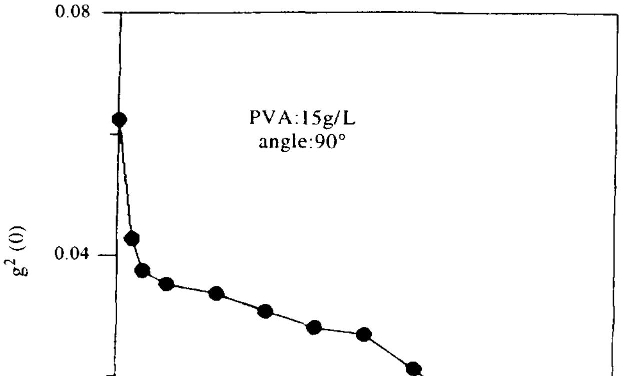


Figure 2 $g^{(2)}(0)$ vs borax concentration

Intrinsic viscosity

Intrinsic viscosity of PVA in water was determined on a dilute PVA aqueous solution at 25°C by Ubbelohde viscometer with a flow time of about 120 s for deionized water. A value of 0.659 dl g^{-1} was obtained.

Dynamic light scattering (DLS)

The quasi-elastic light scattering was measured with a 128-channel four multi-tau autocorrelator (Brookhaven 2030 AT). The laser was an argon ion (514 nm) Lyconix model. The experiments were carried out at 25°C and at a scattering angle of 90°. To obtain the distribution of

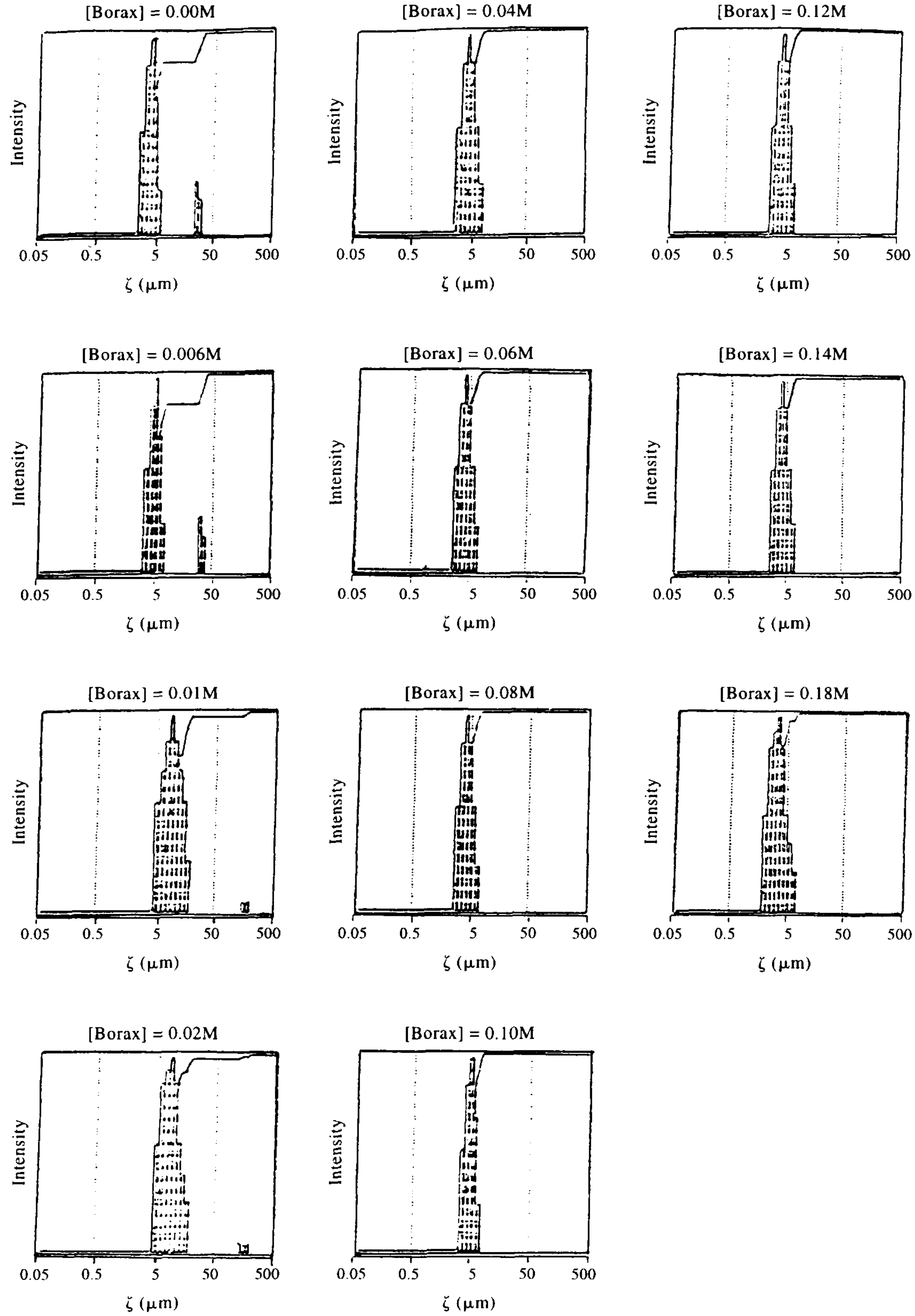

[Borax] = 0.00M
[Borax] = 0.04M
[Borax] = 0.12M
[Borax] = 0.006M
[Borax] = 0.06M
[Borax] = 0.14M
[Borax] = 0.01M
[Borax] = 0.08M
[Borax] = 0.18M
[Borax] = 0.02M
[Borax] = 0.10M

Figure 3 Distribution of correlation length of DLS for PVA–borax–water system with various borax concentrations (intensity and integration curves) relaxation times, inverse Laplace transformation (ILT) was made by using Exponential Sampling software provided by Brookhaven Co.

Dynamic viscoelastic measurements

Dynamic viscoelastic measurements were carried out under 10% strain at 25°C with a cone and plate geometry rheometer (Rheometric Inc., RDS-7000, plate diameter 50 mm, cone angle 0.04 rad).

RESULTS AND DISCUSSION

The PVA–borax solutions were prepared with PVA concentration at 15 g l^{-1} and borax concentration ranges 0.0–0.18 M. The autocorrelation functions $g^{(2)}(\tau)$ of dynamic light scattering (DLS) at scattering angle $\theta = 90°$ for PVA–borax systems are shown in *Figure 1*. *Figure 2* is the plot of the initial amplitude of the normalized intensity autocorrelation function of the scattered light, i.e. $g^{(2)}(0)$ vs borax concentration. It is obvious that $g^{(2)}(0)$ drastically decreased as the borax concentration increased from 0.0 M to 0.02 M, indicating the transition from 'sol' to the 'gel' state. Similar observations had also been reported for actin–heavy meromyosin complexes, argose, and polyacryamide gels[21,22]. Another drastic reduction of $g^{(2)}(0)$ occurred as the borax concentration increased from 0.10 M to 0.14 M, revealing another transition caused by the screening effect of excess free Na$^+$ ions on the electrostatic charges of PVA–borate complexes (see text in the following sections).

In polymeric gel, the polymer segments are restricted by the crosslinks to particular regions of the sample and are only able to perform limited Brownian motion around fixed average positions. Wun *et al.*[21] proposed a model with a harmonically bound particle to interpret the phenomenon of drastic reduction of $g^{(2)}(0)$ from 'sol' to 'gel' state. Geissler *et al.*[23] attributed the origin of the static scattering to microscopic heterogeneities formed during crosslinking. These authors treated the intensity correlation function as the heterodyne mode because the static scattering from the sample could be much larger than the dynamic scattering, and the former to be considered as a reference intensity. A recent theory of DLS by nonergodic media developed by Pusey and van Megen[24] provided a method to extract time-averaged intensity correlation function resulting from constrained motion of the polymeric segments. Joosten and Pusey[25,26] provided a theoretical framework which described the main features of dynamic light scattering by gels and used experimental data to test their theory. Fang and Brown[27] mentioned that while the initial amplitude of the intensity of correlation function is smaller than 0.01, the scattering should be treated as fully heterodyne. By evaluating diffusion coefficients of polymer gels, they found that the diffusion coefficients derived from the nonergodic method were almost the same as those from the heterodyne method when inverse Laplace transformation (ILT) was used. In the present work, since the initial value of $g^2(\tau)$ was larger than 0.01 (see *Figure 2*), the correlation lengths of 'sol' and 'gel' states were evaluated through ILT (software provided by Brookhaven Co.) with a homodyne method.

The distributions of correlation length ζ for PVA–borate complex solutions calculated from $g^{(2)}(\tau)$ at the scattering angle $\theta = 90°$ are shown in *Figure 3*. Since the intrinsic viscosity of PVA in aqueous solution at 25°C was $[\eta] = 0.659$ dl g^{-1}, thus the overlap concentration ($C^* = 1/[\eta]$) of PVA aqueous solution was around 15.4 g l^{-1}. The concentration of PVA of the present system was close to the overlap concentration. Both intra- and intermolecular crosslinking reactions through reactions (1) and (2) might happen. As shown in *Figure 3*, two relaxation modes were found for the present system with borax concentration lower than 0.02 M (i.e. [borax] $\leq$ 0.02 M), whilst one relaxation mode was found as [borax] $\geq$ 0.04 M. Fang and Brown[28] reported bimodal distribution of DLS for PVA dilute and semidilute aqueous solutions (without the presence of borax). Their results showed dominant slow mode existed in semidilute PVA solutions. The slow mode was considered to describe the mobility of clusters of chains (or ordered domains interspersed with disordered regions), while the fast mode was considered to correspond to the collective motions of the transient network. For PVA aqueous solutions without the presence of borax (or low borax concentration) the cluster formation appears involving

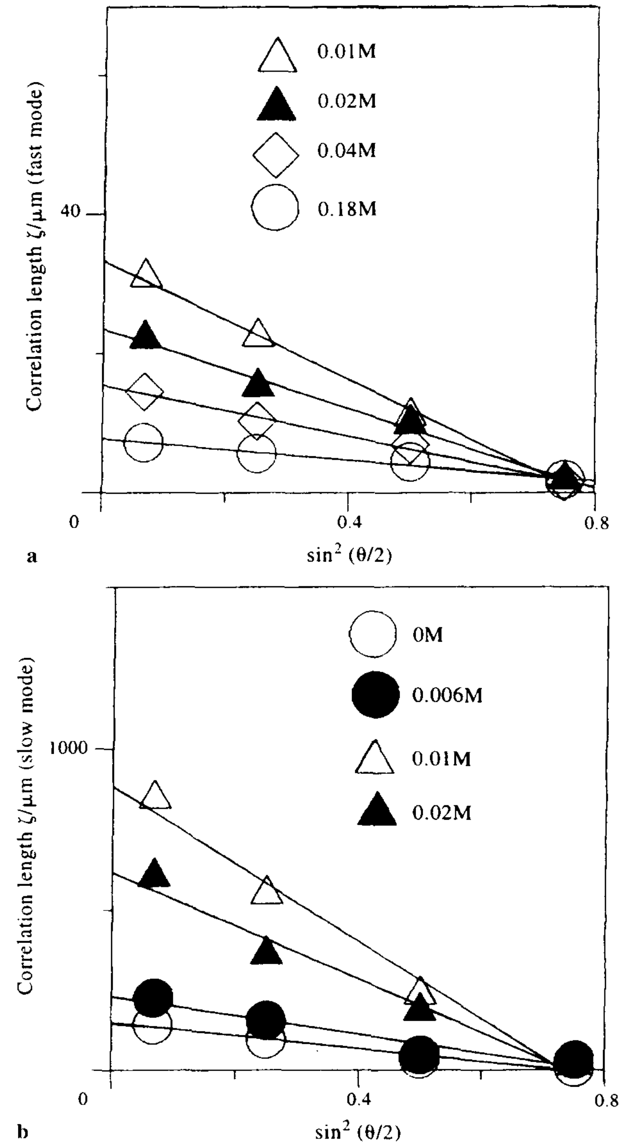


Figure 4 Dependence of correlation length ζ vs $\sin^2\theta/2$ for PVA–borax–water system with PVA concentration of 15 g l^{-1} and various borax concentrations. (a) Fast mode; (b) slow mode

polar polymers which can associate or order through participation of hydrogen bonding. Light scattering experiments for size polydispersity system such as polymer-1/polymer-2/solvent ternary mixture where polymer-1 and -2 are identical in chemical structure and differ only in molecular sizes, the signal from one species is modulated by the second, and leads to a bimodal autocorrelation function. The two modes of PVA–borax–water system were both q^2-dependent (q is the scattering vector) as shown in parts (a) and (b) of *Figure 4* in plots of correlation length ζ vs $\sin^2 \theta/2$ for the fast and slow modes at various borax concentrations. Similar dynamic light scattering results had also been reported for gelatin aqueous solutions and gels by Amis *et al.*[29]. These dynamic light scattering data of gelatin gels were analysed in terms of a single decay process, which was identified with the mutual diffusion coefficient, D_c. However, the DLS results of gelatin solutions revealed two decay processes. The fast process provided a diffusion coefficient with the same magnitude as mutual diffusion coefficient in aqueous gels. The slow process provided a much smaller diffusion coefficient and was identified with the self-diffusion coefficient of the gelation.

Figure 5 is the plot of fast mode correlation length ζ vs borax concentration for PVA–borate complex system with a PVA concentration of 15 g l^{-1}. As shown in *Figure 5*, there were two maximum correlation lengths ζ which corresponded to the borax concentrations at 0.01 M and 0.12 M. Thus, the fast mode correlation length increased and decreased sharply with the borax concentration as it increased from 0.0 M to 0.06 M. However, as the borax concentration increased from 0.06 M to 0.18 M, the correlation length increased and decreased slowly. The maximum correlation length corresponding to the borax concentration of 0.12 M was much lower than that corresponding to borax concentration of 0.01 M.

Figure 6 shows the plots of storage modulus $G'(\omega)$ vs frequency ω for PVA–borate aqueous solutions with a PVA concentration of 15 g l^{-1} and various borax concentrations. The plots of $G'(\omega)$ at frequency $\omega = 158$ rad s^{-1} (the frequency at the plateau region) vs borax concentration for the same solutions (*Figure 6*) are shown in *Figure 7*. A similar trend for the variations of correlation length ζ and $G'(\omega)$ vs borax concentration was observed. In the PVA–borate system, the chain may be viewed as a random copolymer with some units (monocomplexes) bearing electrostatic charges. The dicomplex act as tie points, i.e. inter- or intra-molecular crosslinks. These systems are very different from polyelectrolytes bearing fixed charged groups. Not only is the number of charges on the chain determined by the chemical equilibria, but also there are some free ions present in the solution. These free ions shield the electrostatic charges even in the absence of passive salt. As a result of complexation equilibria, the polymer

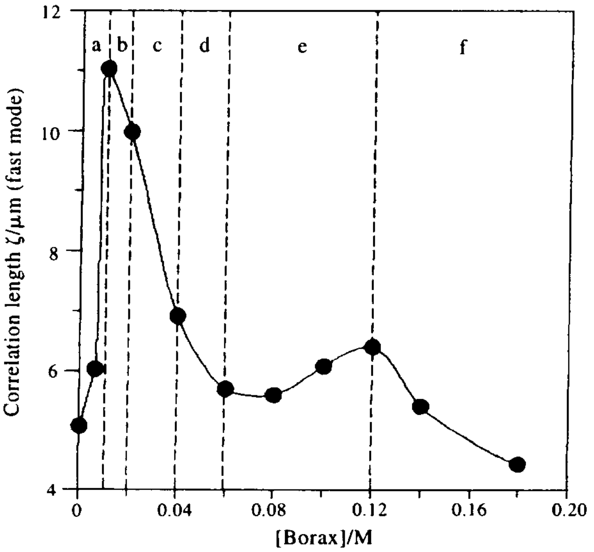


Figure 5 Fast mode correlation length ζ of DLS vs borax concentration for PVA–borax–water system, [PVA] = 15 g l^{-1}

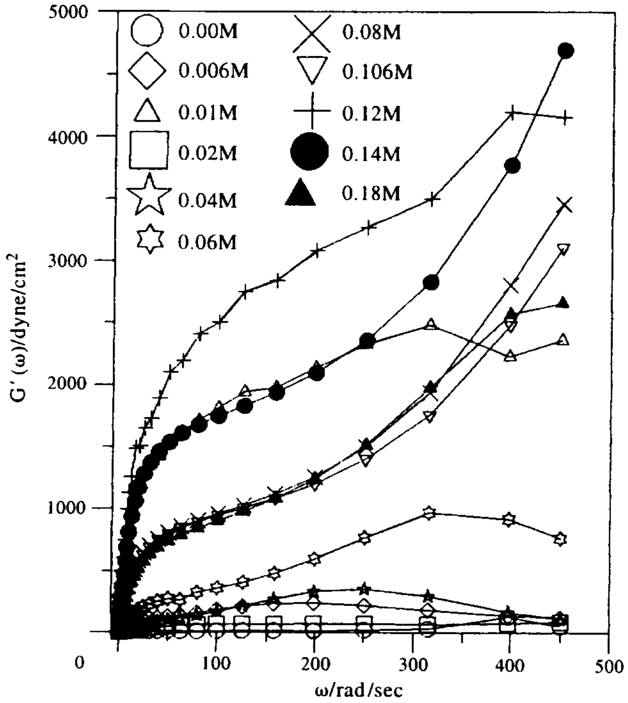


Figure 6 Storage modulus $G'(\omega)$ vs $\log\omega$ for PVA–borax–water system with various borax concentrations, [PVA] = 15 g l^{-1}

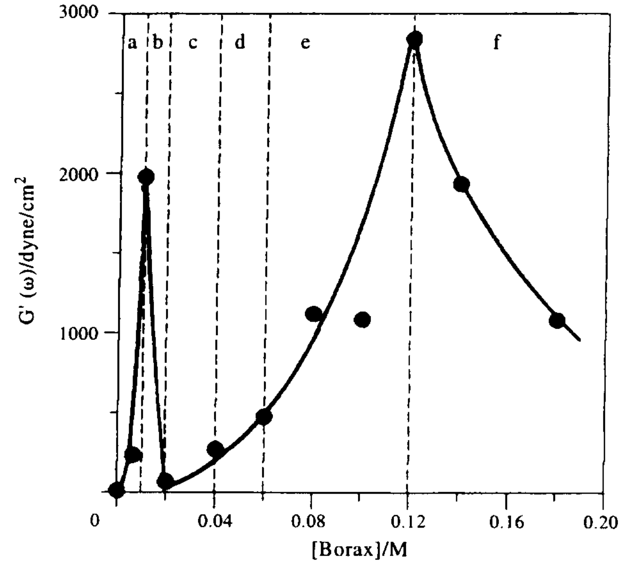
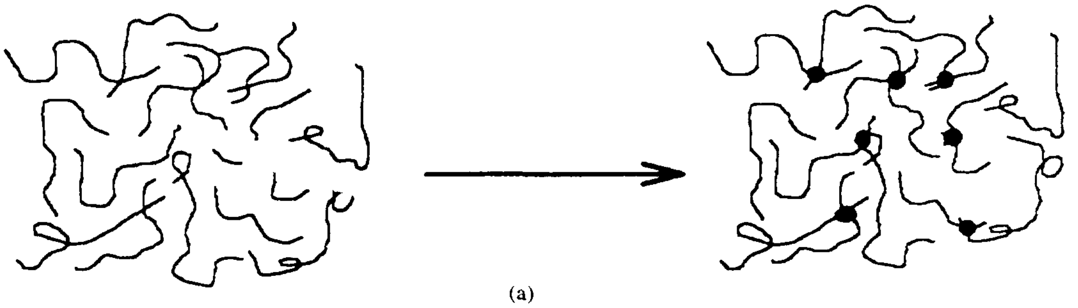


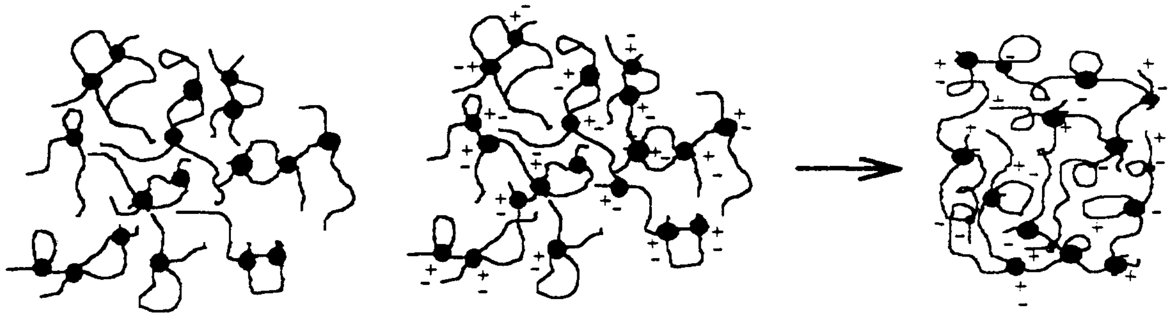
Figure 7 $G'(\omega)$ vs borax concentration at frequency $\omega = 158$ rad s^{-1} for PVA–borax–water system, [PVA] = 15 g l^{-1}



(a)

[Borax] = 0.00M

0.00M < [Borax] ≤ 0.01M



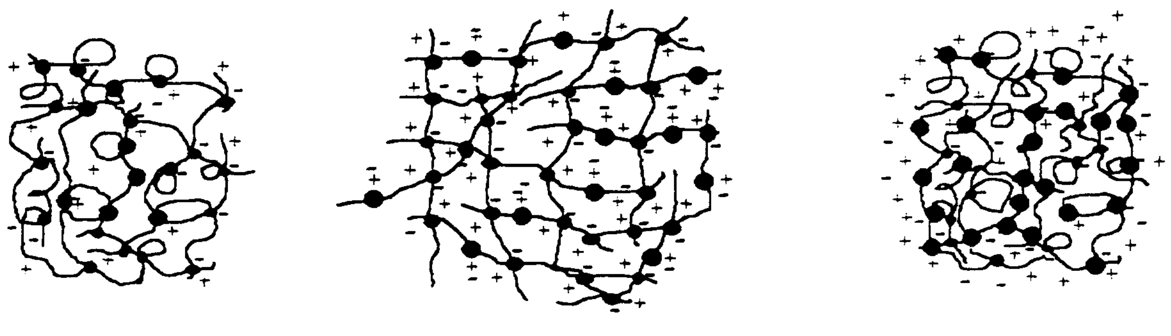
(b)

0.01M ≤ [Borax] ≤ 0.02M

0.02M ≤ [Borax] ≤ 0.04M

(c)

[Borax] = 0.04M



(d)

0.04M < [Borax] ≤ 0.06M

(e)

0.06M < [Borax] < 0.12M

(f)

0.12M ≤ [Borax]

Figure 8 Structures of PVA–borate complex in water with [PVA] = $15\,\mathrm{g\,l^{-1}}$ and various borax concentrations

chains bear a certain amount of electrical charge. The interaction between these charged units modifies the chain conformation. In chemical equilibrium no charge is fixed on a polymer chain without the presence of an excess of free complexing ions in solution. Applying a simple Flory model and considering the effects of excluded-volume interaction, electrostatic interaction, and the crosslink reaction, Pezron and Leibler *et al.*[5–7] proposed a model to predict the Flory energy and chain dimension of PVA–borate complex chain in aqueous solution. Using their model, the phenomenon of demixing transition of polymer aqueous solutions[5,6] and chain dimension of PVA–borate chains in dilute solution[7] can be successfully explained.

According to Leibler and Pezron *et al.*[7] the structure of PVA–borate complex in aqueous solution depends on the following factors: (1) the intra- and inter-molecular crosslinking reactions of PVA and borate; (2) the charge repulsion among the complex units; and (3) the electrostatic screen effect on the negative charge complex unit by free ions. Based on the experimental data, a scheme of the proposed structures for the present system is shown in *Figure 8*. While the concentration of borax was lower than 0.01 M, inter-molecular reactions dominate the reactions between PVA and borate ion (*Figures 5a*, *7a* and *8a*), the polymer chain length increased with the borax concentration. The fast mode of DLS data corresponded to the self diffusion of polymer chains and the slow mode of DLS data to the relaxation of polymer clusters. Both the fast mode correlation length ζ and storage modulus $G'(\omega)$ increased with the borax concentration. Between 0.01 M ≤ [borax] ≤ 0.02 M, not only inter-molecular reactions but also intra-molecular crosslink reactions happened between PVA and borate ions. The intra-molecular crosslink reaction reduced the particle sizes of PVA–borate complexes (*Figures 5b*, *7b* and *8b*). Both the fast mode correlation length ζ and $G'(\omega)$ decreased with borax concentration. For borax concentration between 0.02 M and 0.04 M, both inter- and intra-molecular crosslink reactions proceeded, and the system was close to gelation (*Figures 5c*, *7c* and *8c*). The polymer particles might overlap and the fast mode relaxation of DLS was considered to correspond to the collective motions of the transient network. The fast mode correlation length decreased while $G'(\omega)$ increased with borax concentration.

While the borax concentration was lower than 0.04 M, the slow mode of DLS corresponding to the relaxation of PVA clusters was observed. As the borax concentration was higher than 0.04 M, gel formed in the PVA–borate system (the solution did not flow while the test tube was tilted) and only one mode relaxation process was observed in DLS data (*Figure 8c*). The correlation length ζ of DLS corresponded to the collective motions of the permanent gel. For borax concentration between 0.04 M and 0.06 M, the crosslink density of the polymer gel was higher than that of regime-*c* (i.e. $0.02\,\mathrm{M} \leq [\text{borax}] \leq 0.04\,\mathrm{M}$). The correlation length ζ decreased with borax concentration whilst $G'(\omega)$ increased with borax concentration (*Figures 5d*, *7d* and *8d*). For borax concentration located between 0.06 M and 0.12 M, a highly crosslinked network was formed. The gel was highly swelled and rigid due to the charge repulsion among the borate ions bound on PVA molecules (*Figures 5e*, *7e* and *8e*). Thus, both correlation length ζ and $G'(\omega)$ increased with borax concentration due to electrostatic repulsion. As the concentration of borax was higher than 0.12 M, a lot of excess free borate ions were not bound with PVA molecules, the negative charges of PVA–borate complexes were largely shielded by the excess free Na^+ ions. The effect of charge repulsion decreased and resulted in a decrease of the degree of gel swelling (*Figures 5f*, *7f* and *8f*), leading to the decrease of both correlation length ζ and $G'(\omega)$ with borax concentration.

CONCLUSION

In the present work, we showed the dynamic light scattering and storage modulus data of PVA–borax aqueous solution near the PVA overlap concentration with various borax concentrations. The PVA–borax–water system was in a 'sol' state as the borax concentration was lower than 0.04 M, two relaxation modes were found in DLS data. Whilst the PVA–borax–water system was in 'gel' state as the concentration of borax was higher than 0.04 M and only one relaxation mode was found in DLS data. The experimental results revealed that the structures of PVA–borate complex in water were strongly influenced by the inter- and intra molecular reactions between borate ions and PVA molecules, the charge repulsion of borate ions bound on the PVA molecules, and the shielding of the negative charge bound on PVA molecules by the excess free Na^+ ions.

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