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ORIGINAL CONTRIBUTION

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Reentrant behavior of poly(vinyl alcohol)–borax semidilute aqueous solutions

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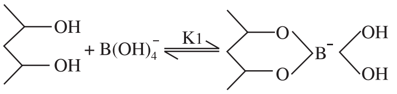
Abstract The reentrant behavior of Poly(vinyl alcohol) (PVA)–borax aqueous semidilute solutions with a PVA concentration of 20 g/l and borax concentrations varies from 0.0 to 0.20 M was investigated using dynamic light scattering (DLS) and dynamic viscoelastic measurements. Two (fast and slow modes) and three (fast, middle, and slow) relaxation modes of PVA semidilute aqueous solutions without and with the presence of borax, respectively, were observed from DLS measurements. The fast and middle relaxation modes were q^2-dependent (q is the scattering vector) characteristic of diffusive behavior; however, the slow modes were q^3-dependent, characteristic of intraparticle dynamics. The experimental results showed that the slow relaxation mode dominates the DLS relaxation. The DLS slow mode relaxation time, τ_s, and the viscoelastic modulus $G'(\omega)$ and $G''(\omega)$ data had a similar trend and demonstrated reentrant behavior as the borax concentration was increased from 0.0 to 0.20 M, i.e. τ_s, $G'(\omega)$, and $G''(\omega)$ fluctuated with increasing borax concentration. The excluded-volume effect of polymers, charge repulsion among borate ions bound on PVA molecules, and intermolecular cross-linking didiol–borate complexation caused an expansion of the polymer chain; however, the screening effect of free Na^+ ions on the negative charge of the borate ions bound on PVA and intramolecular cross-linking didiol–borate complexation led to a shrinkage of the polymer chain. The reentrant behavior was the consequence of the balance between expansion and shrinkage of the PVA–borate complex.

Key words Poly(vinyl alcohol) · Borax · Dynamic light scattering · Viscoelasticity

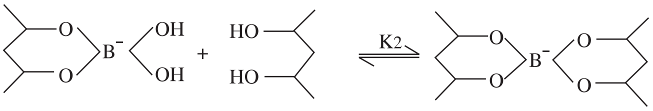
Introduction

Studies of polymer–ion complexes have continued vigorously in recent years due to the wide range of application of polymer–ion complexes. Poly(vinyl alcohol) (PVA) is one of the most typical capable of polymer–ion complexation [1]. PVA has several unique features: it is water-soluble, crystallizable, capable of hydrogen bonding, and forms ion complexes with various ions, such as borate [2–7], cupric [8], vanadate [9], and Congo red [10–12]. The structures and properties of aqueous solutions of the PVA–borate complex have been studied extensively in recent years [5–7, 13–21]. The mechanism of the cross-linking reaction of borate ion with PVA is believed to be a so-called "didiol" complexation, which is formed between two diol units and one borate ion [5, 14–16]. This phenomenon depends on the concentrations of PVA and borate ion and on temperature.

The PVA–borate cross-linking mechanism is divided into two reactions, i.e. monodiol complexation (reaction 1) and a cross-linking reaction (reaction 2) as shown by the following equations:



(1)



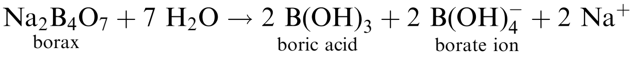
(2)

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. When the charges are partially screened by free ions, a "reentrant" behavior can be observed, i.e. the polymer chains expand then shrink then expand and so on, while the borate concentration increases; it results from a balance between the electrostatic repulsion among the charged complexes formed on the polymeric chain and the shielding effect on the charged complexes by free ions.

In dilute polymer solutions, the size of the chain is lowered due to intra-molecular cross-linking 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 size and stability of the PVA–borate complex system is ruled by electrostatic repulsion and intramolecular cross-linking. Leibler et al. [17], based on the data of Ochiai et al. [18] for the 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 size was the consequence of a balance among the elastic energy, the excluded volume effect, and the electrostatic potential.

In semidilute polymer solutions, both intramolecular and intermolecular cross-linking through reaction 2 may happen, and a gelation of the PVA–borate complex is expected. The reentrant behavior of PVA gel has been studied extensively in recent years [19–21]. Kurokawa et al. [19] studied the phase behavior and the sol–gel transition of the PVA–borate–water system by a viscometric method. Their results showed that at a given combination of PVA concentration and ionic strength, the system underwent a clear–opaque–clear reentrant transition with increasing boric acid concentration. Keita et al. [20] reported the reentrant phases for PVA–borate reversible gels, and they attributed this behavior to the balance between the electrostatic repulsions among the charged complexes formed on the polymeric chain and the cross-linking induced by the borate ions. Shibayama et al. [21] reported swelling/shrinking reentrant behavior of a chemically cross-linked PVA–borate complex gel. They showed that the gel shrinked and became turbid then swelled and became clear as the borax concentration was increased from 0.0 to 0.06 M.

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 [15]:



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

The borate ions and the PVA molecules form complexes which induce electrostatic charges on the polymeric chains. In present work, we report data from dynamic light scattering (DLS) and dynamic viscoelastic measurements of PVA–borax–water semidilute solutions at 25 °C with a PVA concentration of 20 g/l and borax concentrations ranging from 0.0 to 0.2 M. The formation of a gel depends on the PVA concentration, the molar ratio of boric acid and PVA concentrations, the pH value of the solution, and temperature. Though the concentration of PVA in the present solutions was slightly higher than overlap concentration, c^* ($c^* = 15$ g/l, in the present PVA solutions), the solutions did not show gelation phenomenon; however, the reentrant behavior was clearly observed from DLS and dynamic viscoelastic measurements.

Experimental

Materials

PVA (99% hydrolysis, $M_w = 1.1 \times 10^5$, Aldrich Chemical Co.) was dissolved in a 1-propanol–water system and dialyzed using a Spectra/Por 3 membrane (MWCO (molecular weight cut off) = 3500, Spectrum Medical Industries, Calif.) against water to remove any lower-molecular-weight species and was recovered by reprecipitation with acetone.

Sodium tetraborate (borax, $Na_2B_4O_7$, Riedel-de Haen Co.) was dried at 120 °C under reduced pressure for 1 day before sample preparation.

The PVA–borate complex solution was prepared as follows. The dialyzed PVA was dissolved in water at a concentration of about 10 g/l. 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 under clean room conditions for 1 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 20 g/l with various borax concentrations ranging from 0.0 to 0.2 M.

Intrinsic viscosity

The intrinsic viscosity of PVA in water was determined on a dilute PVA aqueous solutions at 25 °C using a Ubbelohde viscometer with a flow time of about 120 s for deionized water. A value of 0.659 dl/g was obtained. The overlap concentration, c^*, of the PVA–water solution, obtained from intrinsic viscosity measurement using the relation $c^* = 1/[\eta]$, was ~15 g/l.

Dynamic light scattering

The quasielastic light scattering was measured with a 256-channel autocorrelator (Brookhaven Co., model BI9000). The laser was a He-Ne (633 nm, operated at 30 mW) Spectra Physics model. The experiments were carried out at 25 °C and at scattering angles of 30°, 45°, 60°, 90°, and 120°. To obtain the distribution of relaxation times, Eq. (4), a heterodyne data analysis method [22–26] was used to calculate the field correlation function, $g^{(1)}(t)$:

$$g^{(2)}(t) = 1 + \beta\{2X(1-X)g^{(1)}(t) + X^2[g^{(1)}(t)]^2\} \ , \tag{4}$$

where $g^{(2)}(t)$ is the intensity correlation function, $g^{(1)}(t)$ the field correlation function, X the homodyne ratio, and β the instrumental parameter. X can be obtained from Eq. (5).

$$X = 1 - [1 + \beta - g^{(2)}(0)]^{1/2}]/\beta^{1/2} \ , \tag{5}$$

where $g^{(2)}(0)$ can be obtained by extending the $g^{(2)}(t)$ data to $t \to 0$, and β can be obtained from the initial amplitude, $g^{(2)}(0)$, of polystyrene latex measurements [25]. In this study the β value is around 0.90. An inverse Laplace transformation was made from $g^{(1)}(t)$ to obtain the distribution of relaxation times using CONTIN software.

Dynamic viscoelastic measurements

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

Results and discussion

Since the PVA concentration was higher than c^*, all the solutions in this work were in the semidilute regime. Both intramolecular and intermolecular cross-linking reactions may happen through reactions 1 and 2. The dissociation constant of borax (Eq. 3) depends on pH, temperature, and the concentration of PVA. The dissociation constant of borax may decrease as the PVA concentration increases. The field autocorrelation functions, $g^{(1)}(t)$, were obtained from intensity autocorrelation functions, $g^{(2)}(t)$, using a heterodyne data analysis method (Eqs. 4, 5). Figures 1 and 2 show the field autocorrelation functions $g^{(1)}(t)$, of DLS at scattering angles of 30°, 45°, 60°, 90°, and 120° for PVA–borax aqueous solutions with a PVA concentration of 20 g/l and borax concentration of 0.0 and 0.16 M, respectively. The relaxation time distributions, $\tau A(\tau)$, where τ is the relaxation time and $A(\tau)$ is the relative amplitude of τ, obtained from $g^{(1)}(t)$ using the nonlinear regression CONTIN program are also shown in Figs. 1 and 2. Two and three relaxation modes (their relaxation times are denoted as τ_f, τ_m, and τ_s for fast, middle, and slow modes, respectively) were observed for PVA–borax aqueous solutions without and with the presence of borax, respectively, as shown in Figs. 1 and 2.

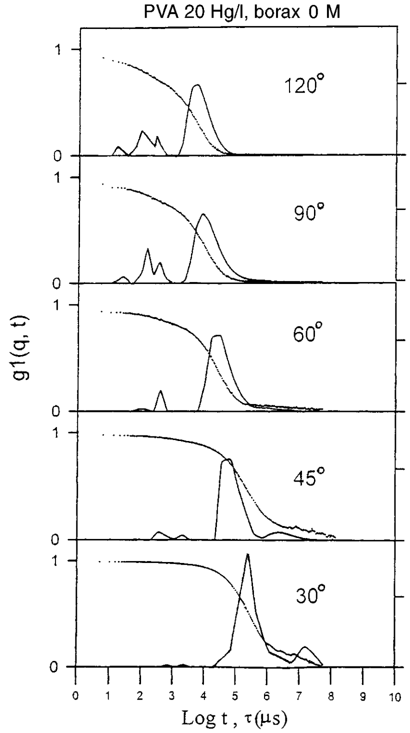


Fig. 1 Correlation functions, $g^{(1)}(t)$, and distributions of relaxation times, $\tau A(\tau)$, at various scattering angles for the poly(vinyl alcohol) (PVA)–water system. The designated *numbers* are scattering angles. *Dotted line*: $g^{(1)}(t)$; *solid line*: $\tau A(\tau)$. Borax concentration = 0.0 M

Fang and Brown [27] reported a bimodal distribution from DLS of PVA dilute and semidilute aqueous solutions (without borax). Their results showed that a dominant slow mode existed in semidilute PVA aqueous 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 borax (or with low borax concentrations) the cluster formation appears involving polymers associating or ordering through participation of hydrogen bonding. Similar DLS results of gelatin solutions, reported by Amis et al. [28], also revealed two decay processes. The fast process provided a diffusion coefficient with the same magnitude as the mutual diffusion coefficient in aqueous gels. The slow process provided a much smaller diffusion coefficient and was identified with the self-diffusion coefficient.

Two DLS relaxation modes from low-ionic-strength polyelectrolyte solutions have also been reported [29–43]. The fast mode has been attributed to coupled diffusion of polyions and low-molecular-weight counterions [29, 32–34, 44] or to thermally excited

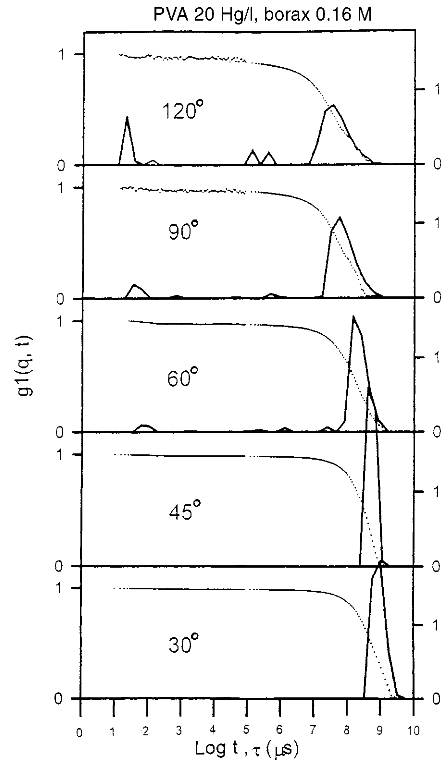


Fig. 2 Correlation functions, $g^{(1)}(t)$, and distributions of relaxation times, $\tau A(\tau)$, at various scattering angles for the PVA–borax–water system. The designated *numbers* are scattering angles. *Dotted line*: $g^{(1)}(t)$; *solid line*: $\tau A(\tau)$. Borax concentration = 0.16 M

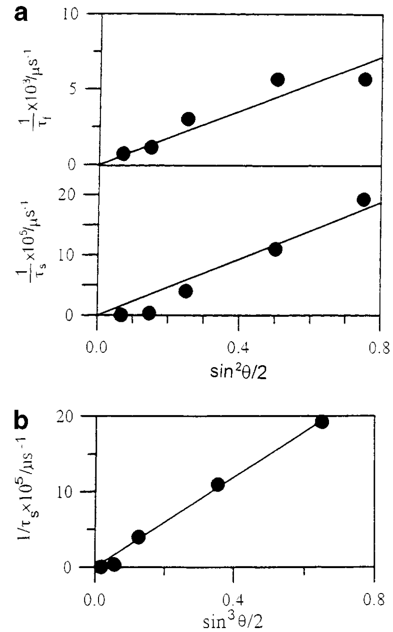


Fig. 3 **a** Relaxation rates, τ_f^{-1} and τ_s^{-1}, versus $\sin^2\theta/2$ for the PVA–water system. Borax concentration = 0.0 M. **b** Relaxation rate τ_s^{-1} versus $\sin^3\theta/2$ for the PVA–water system. Borax concentration = 0.0 M

displacements of polymer segments between entanglements [36]. The slow mode has been interpreted as representing supramolecular structures [29–31, 36–40, 44], as evidence of a reptation mechanism [34], or as impeded diffusion in a congested solution [36]. Recent experiments [41, 42] have shown that under certain conditions an intermediate mode is observed, which lies between the fast and slow modes. For example, Topp et al. [41] showed, in addition to fast and slow modes, the presence of a third, intermediate mode of poly(2-vinylpyridine) quaternized with ethyl bromide aqueous solution when the number of carbon atoms between the two charged groups exceeds a value $n \geq 12$. This result was similar to that of the present work. It was assumed that the intermediate mode was caused by the dynamics of intramolecular hydrophobic domains formed by uncharged segments of the polymer backbone at a low charged ion content of the polymer chains.

Figures 3a and 4a show the $\sin^2\theta/2$ dependency of three relaxation rates, i.e. $1/\tau_f$, $1/\tau_m$, and $1/\tau_s$, obtained from Figs. 1 and 2, respectively. As shown in Figs. 3a and 4a, good $\sin^2\theta/2$ dependencies of the fast and middle modes were observed. These results suggested that the fast and middle relaxation modes were diffusive; however, the $\sin^2\theta/2$ dependency of the slow relaxation rate, $1/\tau_s$, was not so good. The plots of $1/\tau_s$ versus $\sin^3\theta/2$ for PVA–borax aqueous solutions with borax concentrations of 0.0 and 0.16 M are shown in Figs. 3b and 4b, respectively. Comparing Fig. 3a with 3b and Fig. 4a with 4b, we found that a better $\sin^3\theta/2$ dependency, rather than a $\sin^2\theta/2$ dependency of $1/\tau_s$ was observed. Sedlak and Amis [39] reported that the fast mode of a salt-free polystyrene sulfonate semidilute solution was $\sin^2\theta/2$-dependent and the slow mode was also $\sin^2\theta/2$-dependent, but did not pass through the origin. They attributed the fast mode to the coupled diffusion of polyions and counterions. The slow mode was a combination of internal motion and translational diffusion of multichain domains (clusters) [31, 32, 35]. Sun and King [45] carried out DLS experiments on semidilute aqueous solutions of poly(*N*-vinyl-2-pyrrolidone). Two relaxation modes were observed. The fast mode had a typical $\sin^2\theta/2$ dependence, characteristic of diffusion, and the slow mode had an approximately $\sin^3\theta/2$ dependence, characteristic of intraparticle dynamics. The phenomenon of the $\sin^3\theta/2$ dependence of the slow mode of poly(*N*-vinyl-2-pyrrolidone) semidilute aqueous solutions was similar to that of PVA–borax semidilute aqueous solutions. These results indicated the presence of polymer clusters.

The slow mode amplitudes, A_s, of the correlation functions shown in Figs. 1 and 2 are plotted against scattering angle and are shown in Fig. 5. The data in Figs. 1, 2, and 5 indicate that the slow mode relaxation dominates the DLS autocorrelation functions and that A_s decreases with increasing scattering angle. The homodyne ratios, X, of the DLS correlation functions at a scattering angle of 30° of PVA–borax aqueous solutions are plotted against borax concentration in Fig. 6. These results showed that the X value of the PVA–borax aqueous solution was smaller than that of the same PVA aqueous solution without borax and that the X value fluctuated with increasing borax concentration.

De Gennes et al. [46] treated polyelectrolyte solution behavior as a function of the polymer concentration. According to their results, several concentration regions and corresponding critical concentrations can be distinguished. At very dilute concentrations, the polyions can be fully stretched and randomly oriented because of the large separation and the weak intermolecular interactions. At higher concentrations, the polyions cannot orient freely and may form an ordered lattice. Further increase of the polyion concentration causes an overlap of chains and the formation of a transient network. Under these conditions the polymer chains become more flexible and a characteristic correlation length, ζ, can be introduced similar to that of semidilute neutral polymer solutions, but there are no direct contacts between chains because of repulsive electrostatic interactions. In this regime there is no preferential orientation of polyions, i.e. the solution is isotropic.

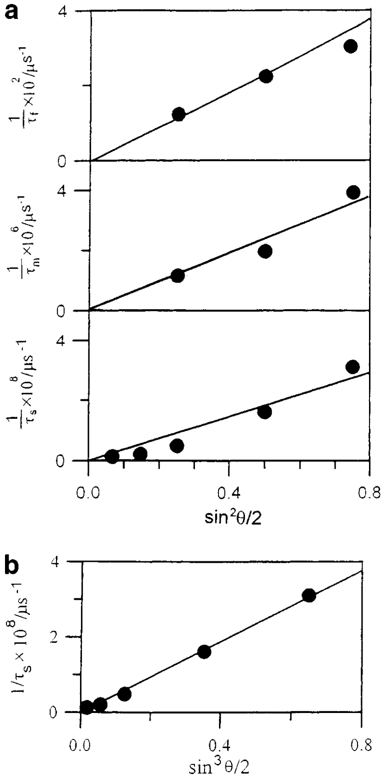


Fig. 4 **a** Relaxation rates, τ_f^{-1}, τ_m^{-1}, and τ_s^{-1}, versus $\sin^2\theta/2$ for the PVA–borax–water system. Borax concentration = 0.16 M. **b** Relaxation rate τ_s^{-1} versus $\sin^3\theta/2$ for the PVA–borax–water system. Borax concentration 0.16 M

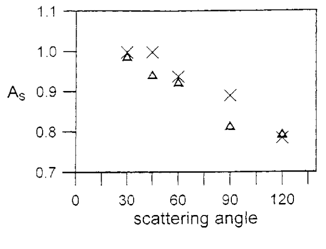


Fig. 5 Slow mode amplitude, A_s, versus scattering angle, θ. Borax concentration of 0.0 M (△) and 0.16 M (×)

As shown in Fig. 1, the PVA aqueous solution had a fast relaxation time of $\tau_f \sim 1.8 \times 10^2$ μs and a slow relaxation time of $\tau_s \sim 9.1 \times 10^3$ μs at a scattering angle of 90°. However, τ_f decreased to about 45 μs and τ_s increased to about 6.2×10^7 μs as the borax concentration was increased to 0.16 M (Fig. 2). For the PVA semidilute aqueous solution without borax, the fast mode was attributed to the cooperative diffusion of the transient network and the slow mode was considered to describe the translational motion of the aggregations of clusters formed through hydrogen bonding. The presence of borax in the PVA aqueous solution caused a decrease in τ_f and an increase in τ_s. The fast mode was due to the coupled motion of counterions and cooperative diffusion of the transient network and the slow mode was due to the translational motion of clusters formed through hydrogen bonding and borate–didiol complexation. The middle mode, as proposed by Woermann et al. [41], was due to the dynamics of intramolecular hydrophobic domains formed by uncharged segments of the polymer backbone.

Since it is easier to observe the whole molecular chain motion from DLS at a smaller scattering angle, the variation of τ_s at a scattering angle of 30° is plotted against borax concentration in Fig. 7. It is obvious that τ_s fluctuates as the borax concentration increases. We divide the plot of τ_s versus borax concentration into six regimes (i.e. regimes a–f). τ_s increases in regime a and decreases in regime b as the borax concentration increases, then similarly τ_s increases in regime c and

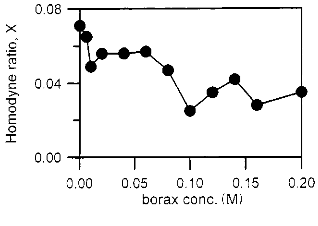


Fig. 6 Homodyne ratio, X, versus borax concentration

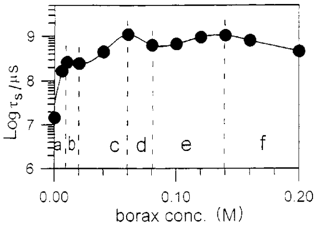


Fig. 7 Slow mode relaxation time, τ_s, of dynamic light scattering versus borax concentration for the PVA–borax–water system

decreases in regime d and so on. The fluctuation of τ_s with increasing borax concentration is the "reentrant phenomenon" of PVA–borax aqueous solutions [19–21].

In the PVA–borax system, the polymer chain may be viewed as a random copolymer with some units (monocomplexes) bearing electrostatic charges. The dicomplexes act as tie points, i.e. intermolecular or intramolecular cross-links. 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 equilibrium, but there are also some free ions present in the solution. These free ions shield the electrostatic charges even in the absence of a passive salt. As a result of the complexation equilibria, the polymer chains bear a certain amount of electrical charge. The interaction between these charged units modifies the chain conformation. According to Leibler et al. [17], the structure of the PVA–borate complex in aqueous solution depends on the following factors:

1. The excluded-volume effect of the polymer chain.
2. The intramolecular cross-linking reactions of PVA with borate ion.
3. The intermolecular cross-linking reactions of PVA with borate ion.
4. The charge repulsion among the complex units.
5. The electrostatic screening effect on the negatively charged complex units by free ions.

Factors 1, 3, and 4 cause an increase in the polymer chain size, whilst factors 2 and 5 result in a decrease in the polymer chain size.

Since the PVA concentration was higher than the overlap concentration, intermolecular reactions dominated reactions between PVA and borate ion while the borax concentration was lower than 0.01 M (regime a in Fig. 7). Owing to charge repulsion among the borate complex ions bound on PVA molecules and intermolecular cross-linking reactions, the polymer chain sizes increased with increasing borax concentration. Thus τ_s increased with increasing borax concentration. In regime b of Fig. 7 (0.01 M ≤ borax concentration ≤ 0.02 M), the polymer molecules had longer chains than those in regime a, which increased the chance for polymer molecules to undergo an intra-molecular cross-linking reaction. In regime b, not only intermolecular but also intra-molecular cross-linking reactions happened between PVA and borate ions. The intra-molecular cross-linking reaction reduced the particle sizes of the PVA–borate complexes; thus, τ_s decreased with increasing borax concentration. The other reason for the decrease in τ_s of the PVA–borate complex could be due to the increase in excess free Na^+ ions which shielded the negative charge of the PVA–borate complex molecules leading to the reduction of charge repulsion among the complex ions and the sizes of PVA–borate complex molecules. In regime c of Fig. 7 (0.02 M ≤ borax concentration ≤ 0.06 M), since the negative charges of the PVA–borate complex was highly shielded by excess free Na^+ ion at a borax concentration of 0.02 M, the electrostatic repulsion between the negatively charged PVA–borate complex and borate ions was lowered. As the borax concentration was increased from 0.02 to 0.06 M, free borate ions were easily bound on PVA molecules to form a negatively charged complex. Thus, the electrostatic repulsion among the negatively charged PVA–borate complex ions and the intermolecular cross-linking reaction of PVA molecules through didiol–borate complexation increased with increasing borax concentration which increased the polymer chain size. In regime d (0.06 M ≤ borax concentration ≤ 0.08 M), since the PVA–borate complex was highly negatively charged at a borax concentration of 0.06 M, the borate ions did not bind easily on the PVA molecules due to the highly electrostatic repulsion between the borate ions and the PVA–borate complexes. Thus increasing the borax concentration resulted in an increase in excess free Na^+ ions which shielded the negatively charged PVA–borate complexes and reduced the polymer chain sizes. Similarly, the polymer chain size increased in regime e (0.08 M ≤ borax concentration ≤ 0.14 M) and decreased in regime f (0.14 M ≤ borax concentration ≤ 0.20 M) with increasing borax concentration.

In order to understand further the PVA–borax aqueous solution properties, dynamic viscoelasticity measurements were also carried out at room temperature. Figures 8 and 9 show the data of log $G'(\omega)$ and log $G''(\omega)$ respectively, for PVA–borax aqueous solutions with a PVA concentration of 20 g/l and various borax concentrations. These results show that both $G'(\omega)$ and $G''(\omega)$ fluctuate with increasing borax concentration. $G'(\omega)$ at the plateau (at ω = 100 rad/s) and $G''(\omega)$ at the peak maximum (at ω = 5 rad/s) versus borax concentration are plotted in Fig. 10. Similar trends for G' (ω = 100 rad/s) and G'' (ω = 5 rad/s) versus borax concentration as for τ_s of the DLS measurements were observed. The data in Fig. 10 revealed that both $G'(\omega)$ and $G''(\omega)$ increased as τ_s increased and decreased as τ_s decreased.

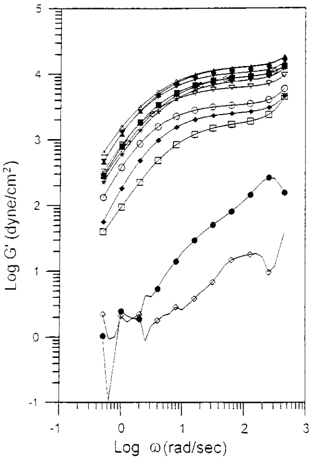


Fig. 8 Storage modulus, log $G'(\omega)$, versus log ω for the PVA–borax–water system with various borax concentrations. Borax concentration: 0.0 M (◇); 0.006 M (◆); 0.01 M (○); 0.02 M (●); 0.04 M (▽); 0.06 M (▼); 0.08 M (□); 0.10 M (■); 0.12 M (△); 0.14 M (▲); 0.18 M (★); 0.20 M (■)

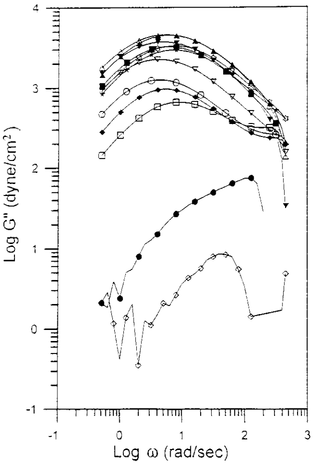


Fig. 9 Loss modulus, log $G''(\omega)$, versus log ω for the PVA–borax–water system with various borax concentrations. Borax concentration: 0.0 M (◇); 0.006 M (◆); 0.01 M (○); 0.02 M (●); 0.04 M (▽); 0.06 M (▼); 0.08 M (□); 0.10 M (■); 0.12 M (△); 0.14 M (▲); 0.18 M (★); 0.20 M (■)

It is known that $G'(\omega)$ and $G''(\omega)$ at low frequency have the following relations with regard to frequency: $G'(\omega) \sim \omega^{n'}$ and $G''(\omega) \sim \omega^{n''}$. The exponents n' and n'' are among the important characteristics of viscoelastic properties of polymer solutions. Most experimental data show that n' and n'' are 2 and 1, respectively, for dilute polymer solutions [47]. The n' and n'' data calculated from the low frequency of $G'(\omega)$ and $G''(\omega)$ of the present solutions are summarized in Table 1. These data reveal that both n' and n'' are lower than 2 and 1, respectively. The lower values of n' and n'' suggest that intramolecular cross-linking and branching reactions occurred among the PVA molecules through the didiol–borate reactions 1 and 2. Chambon and coworkers [48–51] studied the sol–gel transition using viscoelastic measurements; their results demonstrated that at the gel point both the storage, $G'(\omega)$, and loss, $G''(\omega)$, parts of the complex shear modulus obeyed the power law exponents of $n' = n'' = 0.5$–0.75. The data listed in Table 1 show that most of the n' values were located between 1.1 and 1.3 and that most of the n'' values were located between 0.5 and 0.8, indicating that these solutions were close to gelation but were not really in the gelation state. These results are consistent with those of DLS measurements.

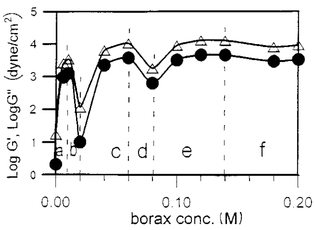


Fig. 10 Plateau storage modulus, log $G'(\omega)$, at ω = 100 rad/s and maximum loss modulus, log $G''(\omega)$, at ω = 5 rad/s versus borax concentration for the PVA–borax aqueous solution $G'(\omega)$ (△); $G''(\omega)$ (●)

Table 1 The exponents of $G'(\omega)$ and $G''(\omega)$ at low frequency for poly(vinyl alcohol)–borax aqueous solutions

Borax concentration/M	n'	n''
0.0	0.66	0.82
0.006	1.50	0.69
0.01	1.31	0.63
0.02	1.16	0.99
0.04	1.12	0.55
0.06	1.20	0.57
0.08	1.20	0.75
0.10	1.31	0.62
0.12	1.11	0.53
0.14	1.24	0.62
0.18	1.27	0.65
0.20	1.14	0.66

Conclusion

In the present work, we show the data of DLS and dynamic viscoelastic measurements of PVA–borax aqueous solutions with a PVA concentration slightly higher than the overlap concentration and borax concentrations varing from 0.0 to 0.20 M. The reentrant behavior of the PVA–borate complex in water was observed with increasing borax concentration. The experimental results revealed that the structures and conformations of the PVA–borate complex in water are strongly influenced by the intermolecular and intramolecular cross-linking reactions of PVA didiol–borate complex formation, the charge repulsion of borate ions bound on the PVA molecules, and the shielding effect of excess free Na^+ ions on the negatively charged borate ions bound on PVA molecules.

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References

1. Sakurada I (1985) Polyvinyl alcohol fibers. Dekker, New York
2. Deuel H, Neukom A (1949) Makromol Chem 3:113
3. Ochiai H, Kurita Y, Murakami I (1984) Makromol Chem 185:167
4. Sinton S (1987) Macromolecules 20:2430
5. Shibayama M, Sato M, Kimura Y, Fujiwara H, Nomura S (1988) Polymer 29:336
6. Shibayama M, Yoshizawa H, Kurokawa H, Fujiwara H, Nomura S (1988) Polymer 29:336
7. Kurakawa H, Shibayama M, Ishimaru T, Wu WL, Nomura S (1992) Polymer 33:2182
8. Saito S, Okuyama H (1954) Kolloid-Z 139:150
9. Shibayama M, Adachi M, Ikkai F, Kurokawa H, Sakurai S, Nomura S (1993) Macromolecules 26:623
10. Ikkai F, Shibayama M, Nomura S, Han CC (1996) J Polym Sci Polym Phys Ed 34:939
11. Shibayama M, Ikkai F, Moriwaki R, Nomura S (1994) Macromolecules 27:1738
12. Shibayama M, Ikkai F, Nomura S (1994) Macromolecules 27:6383
13. Wu W, Shibayama M, Roy S, Kurokawa H, Coyne LD, Nomura S, Stein RS (1990) Macromolecules 23:2246
14. Pezron E, Leibler L, Ricard A, Lafuma F, Audebert R (1989) Macromolecules 22:1169
15. Pezron E, Leibler L, Ricard A, Lafuma F, Audebert R (1988) Macromolecules 21:1121
16. Pezron E, Ricard A, Lafuma F, Audebert R (1988) Macromolecules 21:1126
17. Leibler L, Pezron E, Pincus PA (1988) Polymer 29:1105
18. Ochiai H, Kurita Y, Murakami I (1984) Makromol Chem 185:167
19. Kurokawa H, Shibayama M, Ishimaru T, Nomura S, Wu WL (1992) Polymer 33:2182
20. Keita G, Ricard A, Audebert R, Pezron E, Leibler L (1995) Polymer 36:49
21. Shibayama M, Takeshi T, Nomura S (1994) Macromolecules 27:5350
22. Pusey PN, van Megen W (1989) Physica A 157:705
23. Joosten JGH, Gelade E, Pusey PN (1990) Phys Rev A 42:2161
24. Joosten JGH, McCarthy JL, Pusey PN (1991) Macromolecules 24:6690
25. Horkay F, Burchaard W, Hecht AM, Geissler E (1993) Macromolecules 26:3375–4203
26. Horkay F, Burchard W, Geissler E, Hecht AM (1993) Macromolecules 26:1296
27. Fang L, Brown W (1990) Macromolecules 23:3284
28. Amis EJ, Janmey PA, Ferry JD, Yu H (1983) Macromolecules 16:441
29. Lin SC, Lee WI, Schurr JM (1978) Biopolymers 17:1041
30. Mathies P, Moutett C, Weisbuch G (1981) Biopolymers 20:2381
31. Schmitz KS, Lu M, Gauntt J (1983) J Chem Phys 78:5059
32. Drifford M, Dalbiez JP (1985) Biopolymers 24:1501
33. Borsali R, Nguyen H, Pecora R (1998) Macromolecules 31:1548
34. Koene RS, Mandel M (1983) Macromolecules 16:973
35. Sedlak M, Konak C, Stepanek P, Jakes J (1987) Polymer 28:873
36. Schmitz KS, Yu J (1988) Macromolecules 21:484
37. Schmidt M (1989) Makromol Chem Commun 10:89
38. Forster S, Schmidt M, Antonietti M (1990) Polymer 31:781
39. Sedlak M, Amis EJ (1992) J Chem Phys 96, 817
40. Ermi BD, Amis EJ (1996) Macromolecules 29:2701
41. Topp A, Belkoura L, Woermann D (1996) Macromolecules 29:5392
42. Nerling W, Nordmeir E (1997) Polym J 29:795
43. Brett DE, Amis EJ (1998) Macromolecules 31:7378
44. Muthukumar M (1997) J Chem Phys 107:2619
45. Sun T, King HE (1996) Macromolecules 29:3175
46. de Gennes PG, Pincus P, Velasco RM, Brochard F (1976) J Phys (Paris) Colloq 37:1461
47. Ferry JD (1980) Viscoelastic properties of polymers, 3rd edn. Wiley, New York, pp 190
48. Chambon F, Winter HH (1985) Polym Bull 13:499
49. Chambon F, Petrovic ZS, MacKnight WJ, Winter HH (1986) Macromolecules 19:2146
50. Chambon F, Winter HH (1987) J Rheol 31:683
51. Winter HH, Morganelli P, Chambon F (1988) Macromolecules 21:532