A Gel Network Constituted by Rigid Schizophyllan Chains and Nonpermanent Cross-Links

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A Gel Network Constituted by Rigid Schizophyllan Chains and Nonpermanent Cross-Links

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This work reports a gel network formed by rigid schizophyllan (SPG) chains with Borax as a cross-linking agent. The formed cross-links are nonpermanent and somewhat dynamic in nature because the cross-linking reaction is governed by a complexation equilibrium. Gelation processes are traced by dynamic viscoelastic measurements to examine the effects of Borax content, SPG concentration, temperature, salt concentration, salt type, and strain. The first-order kinetic model containing three parameters, t_0 (induction time), $1/\tau_c$ (gelation rate), and G'_{sat} (saturated storage modulus), is successfully applied to describe the gelation of the SPG–Borax system. Gelation occurs faster at higher Borax content, higher SPG concentration, higher salt concentration, or lower temperature. Moreover the gelation is cation-type-specific. Storage modulus is a linear function of both Borax content and SPG concentration. The linear relationship between storage modulus and Borax content can be explained by a modified ideal rubber elasticity theory with a front factor α to take into account the presence of ineffective cross-links and the effect of SPG chain rigidity. On the other hand, the linear dependence of storage modulus on SPG concentration could be explained on the basis of chain–chain contacting behavior of extended SPG chains. Apparent activation energy and cross-linking enthalpy are calculated to be −74.5 and −32.4 kJ/mol for the present system. Strain sweep measurements manifest that the elasticity behavior of this gel starts to deviate from Gaussian-chain network at a small strain of 10%.

1. Introduction

Generally, gels can be divided into two different categories on the basis of structural criteria: (i) chemical gels in which polymeric chains are cross-linked through covalent bonds and (ii) physical gels in which junction zones are formed by physical association of polymeric chains through noncovalent bonds such as hydrogen bond, hydrophobic interaction, and Coulombic interaction. According to different temperature dependences, physical gels can be further classified into four types:[1] (1) cold-set gels such as agarose,[2,3] carrageenans,[4] and gellan gum,[5] which are gelled by cooling the solutions, (2) heat-set gels such as methyl cellulose,[6–8] Curdlan,[9] and konjac glucomannan,[10,11] which are gelled by heating the solutions, (3) re-entrant gels such as xyloglucan,[12] which just forms a gel in a specific intermediate temperature range, and (4) inverse re-entrant gels, such as a mixed solution of methyl cellulose and gelatin, which form gels at higher and lower temperatures but stay as liquid in an intermediate temperature range. Here, we report a particular network formed by schizophyllan (SPG) with Borax as cross-linking agent, which cannot be readily attributed to chemical gel or physical gel. The SPG–Borax network is uncommon in the following two structural aspects: (i) the network chain is wormlike and rigid, which is scarce for chemical gels, and (ii) the cross-linking is an equilibrium complexation reaction; thus, the cross-links are dynamic in nature.

It is well-known that solutions of poly(hydroxyl) compounds such as poly(vinyl alcohol)[13–21] and galactomannans[22–26] form gels when treated with borate. The gelation results from the formation of a didiol complex between borate and the two pairs of adjacent hydroxyl groups in two different chains.[13–17,22–23]

SPG is a neutral polysaccharide produced by the fungus *Schizophyllum commune*.[27,28] Its chemical structure consists of linearly linked β-(1→3)-D-glucose residues with one β-(1→6)-D-glucose side group for every three main chain residues. SPG exists as a triple helix in water with a quite large persistence length ranging from 100 to 180 nm.[29–31] Grisel and Muller[32–34] reported that SPG aqueous solution also could be gelled by addition of Borax, in which the hydroxyl groups located on the C4 and C6 of the glucose side groups participated the complexation with borate ions (shown in Figure 1). The formation of the monodiol complex introduces a negative charge into the SPG chains, while the formation of the didiol complex leads to cross-linking. Here, we try to quantitatively investigate the effects of Borax content, SPG concentration, salt concentration, salt type, temperature, and strain on gelation kinetics, as well as on the elasticity of the resultant gels.

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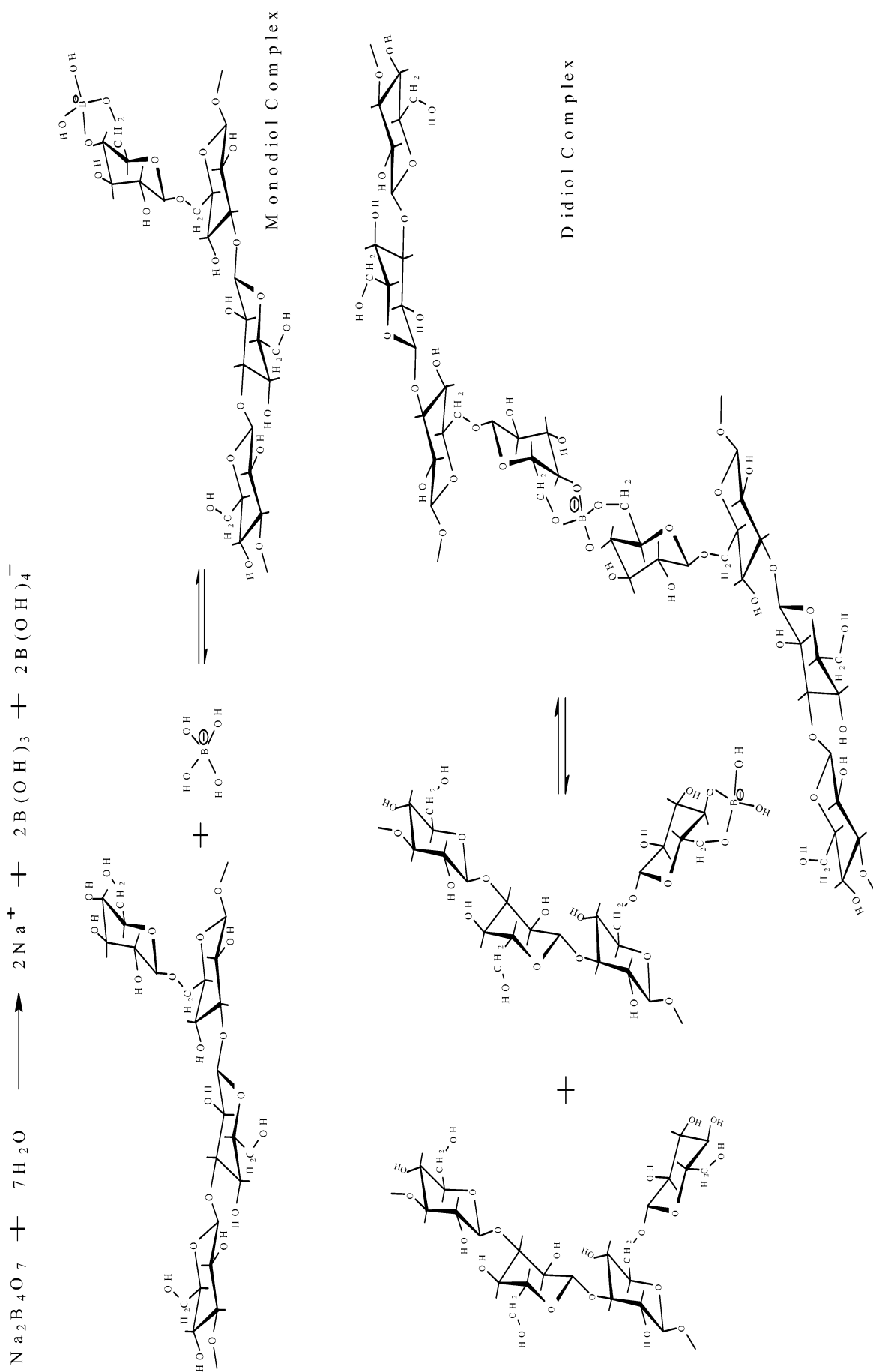
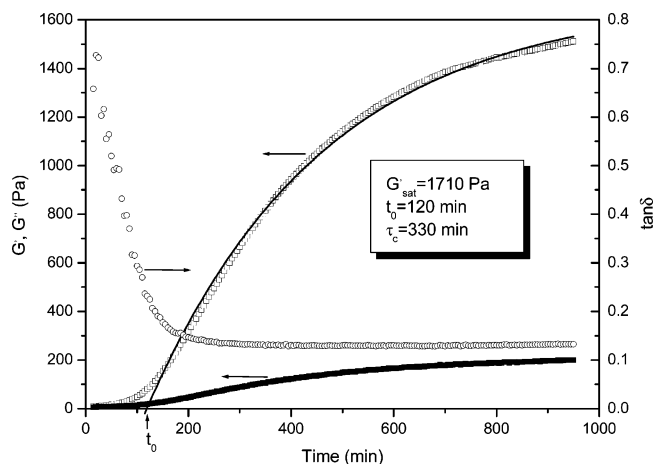**Figure 1.** Complexation of borate ion with SPG.

Figure 2. Time dependence of the storage modulus G' ($\square$), loss modulus G'' ($\blacksquare$), and tan δ ($\bigcirc$) during the gelation of the SPG–Borax system. C_p = 6 g/L; C_b = 32 mM; [NaCl] = 1 M, T = 20 °C; frequency = 1 rad/s; strain = 1%. The solid line represents the curve fitting results to G' by the first-order kinetic model.

2. Material and Methods

2.1. Materials. Schizophyllan (SPG) with a molecular weight of 2 500 000 was kindly offered by Taito Co. Ltd. (Japan). Its intrinsic viscosity in water at 25 °C was determined to be 4550 cm³/g by a rotating cylinder viscometer of Zimm–Crothers type. Borax ($Na_2B_4O_7 \cdot H_2O$) and the other used salts (LiCl, NaCl, KCl, CsCl, $CaCl_2$, and $BaCl_2$) of analytical grade were purchased from Wako Pure Chemical Industries, Ltd. (Japan).

2.2. Preparation of Gel. SPG aqueous solution and Borax aqueous solution at the same NaCl concentration were prepared separately and thermally equilibrated in water bath to the desired experimental temperature. Then equal volumes of each solution were mixed under vigorous stirring to prevent precipitation due to local overconcentration. Thus the final concentrations of SPG (C_p) and Borax (C_b) are half of those before mixing. The SPG–Borax mixture was loaded onto rheometer to examine the time dependence of viscoelastic properties. Note that the time when mixing is started is set as t = 0, and the mixture is self-buffered at pH = 9.2 by Borax.

2.3. Rheological Measurements. Dynamic time sweep measurements were carried out on a Fluids spectrometer RFSII with parallel plate geometry of 25 mm in diameter and 0.5 mm in gap. The equipped transducer has a sensitivity limit of 0.002 g cm in torque. A strain of 1% was applied in all measurements, otherwise specified. The exposed surfaces of samples are coated with a layer of light silicon oil to avoid dehydration. Experimental temperature was controlled within ±0.1 °C by a refrigerated circulator (Julabo, Germany).

3. Results and Discussion

3.1. Gelation Process. Figure 2 shows the evolution of storage modulus (G'), loss modulus (G''), and tan δ with time during the gelation of SPG–Borax system with C_p = 6 g/L and C_b = 32 mM. At the early stage, G' and G'' increase slowly with time, while tan δ decreases rapidly. This is attributed to the branching of macromolecular chains or
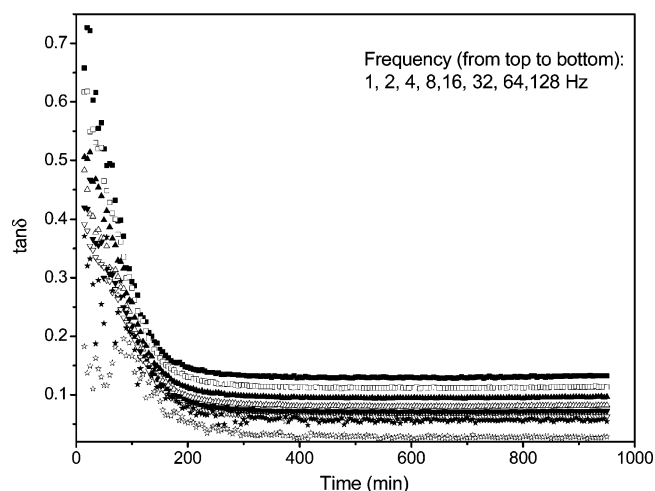

Figure 3. Time dependence of tan δ at different frequencies during the gelation of the SPG–Borax system. C_p = 6 g/L; C_b = 32 mM; [NaCl] = 1 M; T = 20 °C; frequency = 1 rad/s; strain = 1%.

formation of local clusters by cross-linking reaction or both.[35,36] After a certain period of induction time (t_0), G' and G'' start to increase abruptly, suggesting that these branched macromolecules or clusters have just been connected into a three-dimensional network percolating into the entire space. At the late stage, G' and G'' increase steadily and hardly reach the saturated values. Meanwhile, tan δ tends to level off. This is a stage where the three-dimensional network further develops. It is worthy of noting that, in the case of poly(vinyl alcohol)[14,15] or galactomannan,[26] gel forms immediately after addition of Borax and no induction time is observed. This could be due to the different chain natures between poly(vinyl alcohol), galactomannan, and SPG. Because both poly(vinyl alcohol) and galactomannan chains are far more flexible than the rigid wormlike SPG chains, they can easily change their conformations to achieve the favorable position for complexation with borate ions.[33] Thus their gelations take place almost instantaneously when mixed with Borax. In contrast, rigid SPG chains adjust their positions relatively slowly, and an induction time is necessary before gelation.

Grisel and Muller used the Winter–Chambon criterion to determine the critical gelation time for SPG–Borax systems.[34] However, the problem is that even without Borax, SPG solution easily shows weak gel behavior ($G' > G''$) in the examined frequency range due to the high entangling of macromolecular chains. Additionally, as can be seen in Figure 3, tan δ values at various frequencies have no one-pointed crossover during gelation of SPG–Borax. These mean that the Winter–Chambon criterion is not powerful in determining the critical gelation point of the SPG–Borax system.[37–39] Therefore, we try to seek a simpler and more informative model that can describe the growth of the SPG–Borax network.

The first-order kinetic model[40] is often used to fit the gelation processes of biopolymers such as glycinin,[41] β-conglycinin,[41] casein,[42] and konjac glucomannan,[43] which is written as follows:

$$G'(t) = G'_{sat}[1 - \exp(-(t - t_0)/\tau_c)] \quad (1)$$

where t_0 is induction time, τ_c is a characteristic time the reciprocal of which reflects the gelation rate, and G'_{sat} is the saturated storage modulus after infinitely long time. In Figure 2, the solid line is the fitting curve to G' by the first-order kinetics. As can been seen, the time dependence of G' can be well approximated by the first-order kinetic model with $t_0 = 120$ min, $\tau_c = 330$ min, and $G'_{sat} = 1710$ Pa. Note that by curve fitting, we can obtain the saturated value of G', which can never be achieved in actual observation.

Let's turn back to the complexation shown in Figure 1. Because the available complexing sites on SPG chains are much fewer than borate ions and the monodiol complexes are also quite few,[22,23] the two-step complexation can be approximately regarded as a first-order series reaction: SPG $\rightleftarrows$ monodiol complex $\rightleftarrows$ didiol complex. Moreover, because the establishment of the first equilibrium is appreciably faster than that of the second one, the second one is the rate-determining step. In this situation, the overall kinetics is approximately first-order but with a short different initial stage.[60] Therefore, it is readily understandable that the gelation process is well fitted by eq 1.

3.2. Effect of Borax Content (C_b). The time dependences of G' for SPG–Borax systems with various Borax contents are shown in Figure 4a,b. For the purpose of comparison, the data for $C_b = 20$ mM is repeated in Figure 4b. For $C_b = 12$, 14, and 18 mM, G' first increases markedly and then slowly. This process could result from the increase of viscosity caused by the branching of SPG chains or formation of clusters or both.[32,33] However, in these systems, the amount of cross-linking agent is insufficient for extending the network to the whole space, and thus, no gelation occurs. This is unlike in the cases of $C_b \geq 20$ mM, in which G' shows a sudden increase when gelation occurs.

Figure 4b also includes the fitting curves of G' by the first-order kinetic model. In the examined Borax content range, all of the gelation processes are well depicted by the first-order kinetic model, from which t_0, τ_c, and G'_{sat} are obtained. Figure 5 shows the variation of t_0 and $1/\tau_c$ with Borax content. Obviously, induction time t_0 becomes shorter with increasing Borax content, which is consistent with the report by Grisel and Muller.[32,34] Additionally, the gelation rate, $1/\tau_c$, increases with increasing Borax content. It has been widely accepted that gelation proceeds more rapidly at higher cross-linking agent content or coagulant content.[10-11,40-42]

Figure 6 plots saturated storage modulus G'_{sat} as a function of Borax content. A good linearity is observed between G'_{sat} and C_b. Borax solution is a good buffer, and at low concentration, it is totally disassociated into equal quantities of boric acid and borate ion[22] (see Figure 1). On the other hand, it has been proved that in poly(hydroxyl)–Borax gels the number of formed cross-links is proportional to the amount of free borate ion in solution when complexation equilibrium is reached.[23] Similarly at fixed SPG concentration, the amount of added Borax proportionally determines the number of cross-links in SPG–Borax gel. Therefore, the linear relationship between G'_{sat} and C_b suggests that for SPG–Borax gel G'_{sat} increases linearly with increasing cross-link concentration. Similar results were
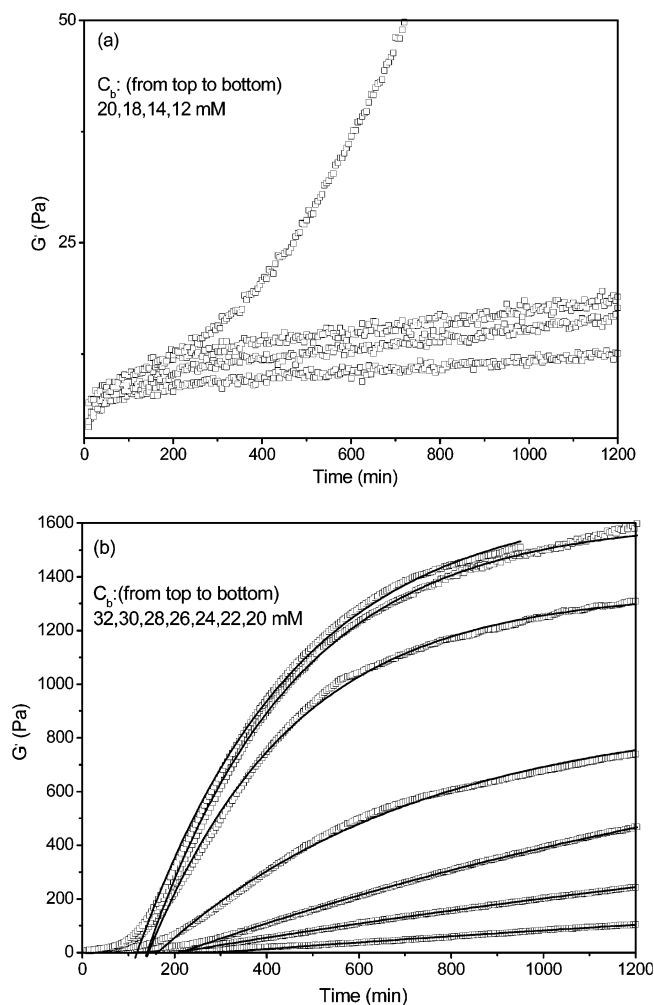

Figure 4. Time dependence of the storage modulus G' for SPG–Borax systems with various Borax contents (C_b). The solid line represents the curve fitting results to G' by the first-order kinetic model. $C_p = 6$ g/L; $T = 20$ °C; [NaCl] = 1 M; frequency = 1 rad/s; strain = 1%; (a) $12 \leq C_b \leq 20$ mM; (b) $20 \leq C_b \leq 32$ mM. For the purpose of comparison, the data for $C_b = 20$ mM is displayed in both panels.

also observed for poly(vinyl alcohol)–Borax and galactomannan–Borax gels.[14-15,26]

For an ideal rubber, the static equilibrium storage modulus is related to the cross-link concentration, c_c, or the number of network chains per unit volume, n, by eq 2.[44] Because

$$G'_{sat} \approx G_e = 2c_c RT = nkT \qquad (2)$$

the storage modulus of SPG–Borax gel has little dependence on frequency, we can use G'_{sat} obtained at $\omega = 1$ rad/s to approximate G_e when discussing network elasticity. Because most gel networks are not ideal rubbers, a front factor α must be introduced into eq 2 to take into account the presence of ineffective cross-links. In the case of poly(vinyl alcohol)–Borax gel, α was reported to be 0.1, indicating that only one-tenth of the cross-links are effective cross-links.[14] If we assume that the SPG–Borax system has the same equilibrium constant as poly(vinyl alcohol)–Borax,[14,47] we can work out $\alpha \approx 0.01$ for the SPG–Borax gel. Actually, α is expected to be even smaller than 0.01 if we consider that the SPG–Borax system has a weaker tendency to react backward. The more considerable front factor for the SPG–Borax gel could be attributed to the rigid nature of the SPG chain.
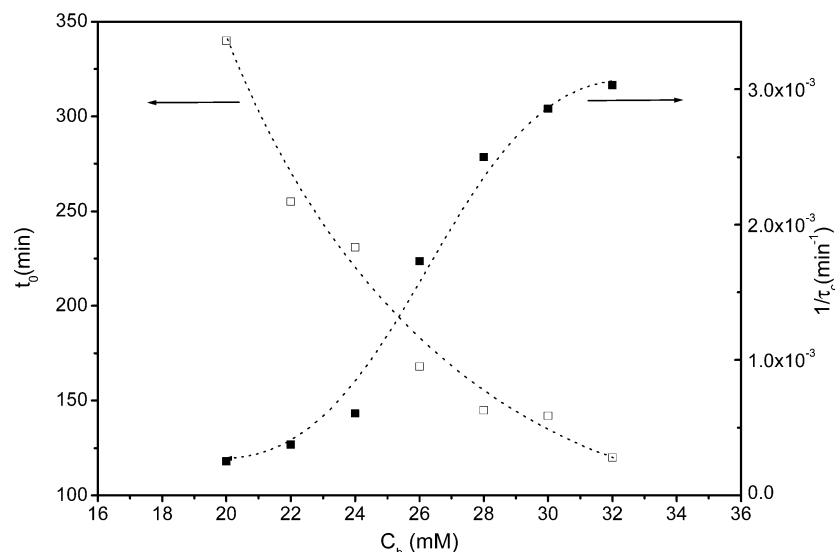
Figure 5. Plots of t_0 and $1/\tau_c$ against Borax content (C_b). t_0 and τ_c are obtained through curve fitting of data in Figure 4b.
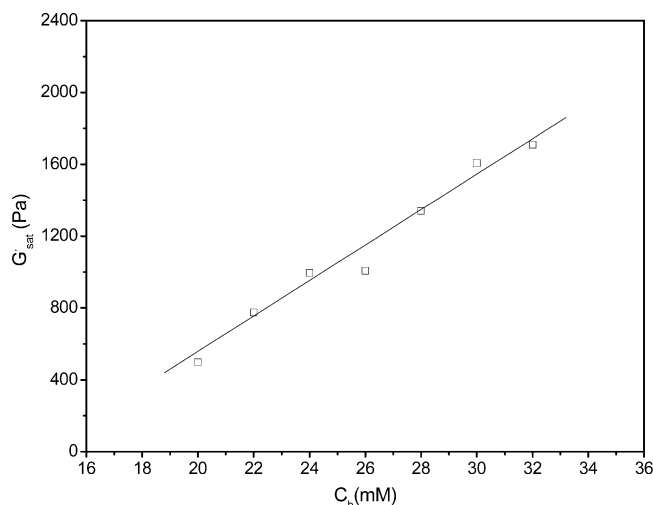

Figure 6. Plot of G'_{sat} against Borax content (C_b). G'_{sat} is obtained through curve fitting of data in Figure 4b.

Figure 7. Time dependence of the storage modulus G' during the gelation of SPG−Borax systems with various SPG concentrations (C_p). C_b = 24 mM; T = 10 °C; [NaCl] = 1 M; frequency = 1 rad/s; strain = 1%. The solid line represents the curve fitting results to G' by the first-order kinetic model.

One of the utmost important assumptions when deriving eq 2 is that the network is composed of randomly jointed Gaussian chains. For poly(vinyl alcohol) and galactomannan in water, they adopt relatively flexible conformations (persistence length $L_p \leq 10$ nm)[45,46] and thus can be regarded as Gaussian chains. However, for SPG chains in water, they are rigid wormlike triple helices with a quite large persistence length from 100 to 180 nm,[29−31] which should be treated as non-Gaussian chains with limiting extensibility. The elasticity for a non-Gaussian network is a function of not only cross-link concentration but also strain. However in small strain range, it is almost strain-independent and can be reduced to the same form as that of the Gaussian chain network.[44] In our measurements, G'_{sat} was obtained with a small strain of 1%; therefore, eq 2 modified with a front factor α is also applicable. However, we will show later that when strain is >10% the elasticity of the SPG−Borax gel depends markedly on strain.

3.3. Effect of Schizophyllan Concentration (C_p). The effect of SPG concentration on gelations of SPG−Borax systems is shown in Figure 7. The corresponding fitting curves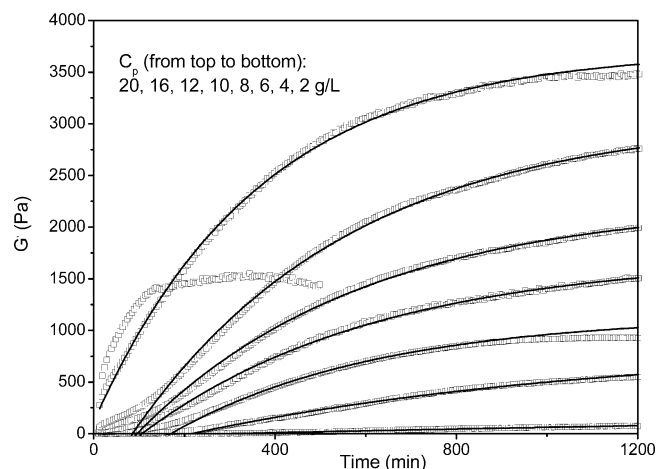 of G' are also included. With increasing SPG concentration, the gelation proceeds more rapidly, which agrees with most reports on the effect of polymer concentration on gelation.[10−11,40−41,43] For C_p = 16 and 20 g/L, the gelation occurs almost instantaneously when Borax is added, and no induction time is observed. As for the SPG−Borax system, the gelation rate is dominated by the rate of formation of didiol complex. With increasing SPG concentration, the possibility for two chains to contact and attain the favorable positions for complexation increases,[26,33] which results in faster gelation. Additionally in the case of C_p = 20 g/L, the gelation becomes so fast that syneresis occurs, which is often encountered in the gelations of poly(hydroxyl) compounds with Borax.[23,34] The occurrence of syneresis makes it impossible to examine the effect of concentration above C_p = 20 g/L by rheological measurements.

Figure 8 gives the plots of t_0 and $1/\tau_c$ versus SPG concentration, C_p. It is clear that induction time, t_0, becomes shorter as C_p is increased. The gelation rate, $1/\tau_c$, increases rapidly at lower concentrations and gradually at higher concentrations.
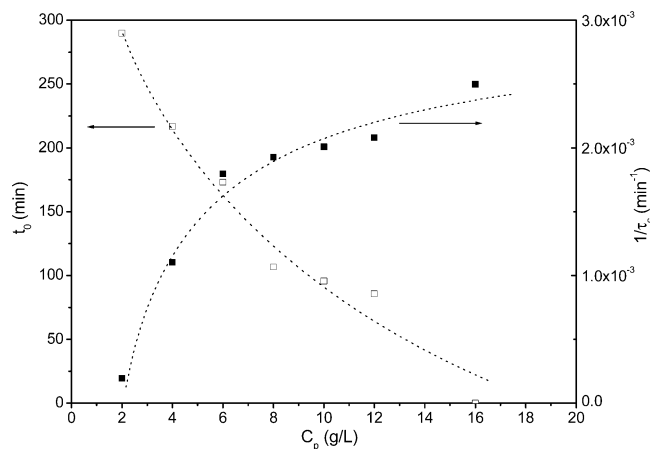
Figure 8. Plots of t_0 and $1/\tau_c$ against SPG concentration (C_p). t_0 and τ_c are obtained through curve fitting in Figure 7.
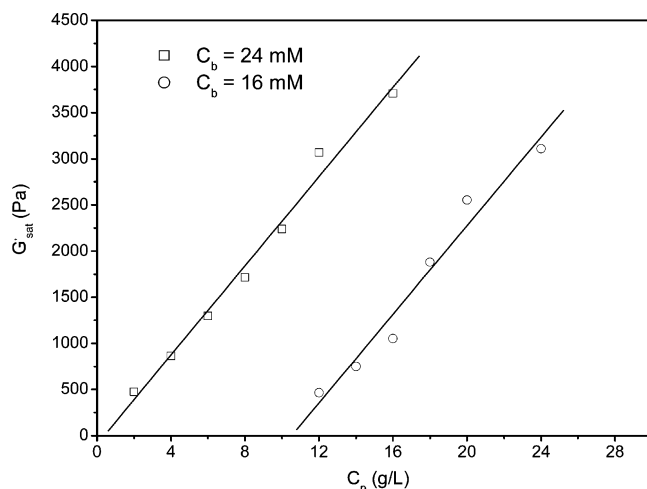

Figure 9. Plot of G'_{sat} against SPG concentration (C_p). C_b = 24 mM ($\square$), and C_b = 16 mM ($\bigcirc$).

Figure 10. Time dependence of the storage modulus G' during the gelation of the SPG−Borax system at different temperatures. C_p = 6 g/L; C_b = 24 mM; [NaCl] = 1 M; frequency = 1 rad/s; strain = 1%. The solid line represents the curve fitting results to G' by the first-order kinetic model.

Figure 9 plots the saturated storage modulus G'_{sat} as a function of SPG concentration, C_p, at C_b = 24 and 16 mM. It is surprising to see that G'_{sat} is almost a linear function of C_p. Such a dependence of storage modulus on concentration is rare for biopolymer gels, for which storage modulus is empirically known to be a power law function of concentration with an exponent of 2 in the concentrated range.[1] Moreover from the intercepts on the C_p-axis, we can estimate the critical gelation concentration to be 0.8 and 10.5 g/L for C_b = 24 and 16 mM, respectively. Obviously gelation at the lower content of Borax can be achieved if SPG concentration is increased.

For poly(vinyl alcohol)−Borax and galactomannan−Borax gels,[15,26] storage moduli were reported to scale, respectively, as $C^{4.7}$ and $C^{2.6}$, which are quite different from the scaling behavior ($C^{1.0}$) of the present SPG−Borax gel. What is the origin of these differences? As was discussed above, these three systems show a linear relationship between storage modulus and cross-link concentration. This suggests that the number of formed cross-links scales as $C^{4.7}$, $C^{2.6}$, and $C^{1.0}$, respectively, at fixed Borax content. Because cross-linking is the reaction involving two macromolecular chains, the interchain contact is quite important. Pezron et al.[23,26] argued that at fixed Borax content the number of formed cross-links should be proportional to the number of interchain contacts,
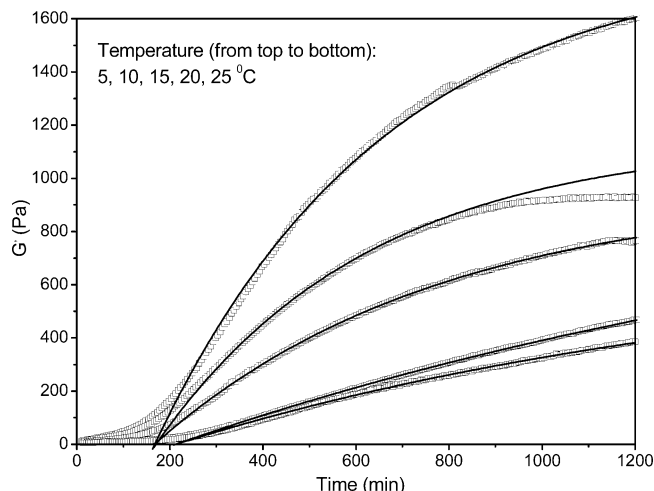
which scales as osmotic pressure (i.e., $C^{3v/(3v-1)}$ where v is an excluded volume coefficient relating the radius of gyration of a macromolecule, R_G, to its polymerization degree N by $R_G = N^v$).[48] In comparison with compact and flexible chain, rigid chain has a larger value of v and thus a smaller exponent $3v/(3v-1)$. As chain-extendedness increases in the order poly(vinyl alcohol) < galactomannan < SPG,[26,29,49] v increases and the scaling exponent decreases successively. Note that if we assume that $v = 1$ for rodlike SPG, the exponent $3v/(3v-1)$ should be 1.5, which is comparable to the experimental value of 1.0.

3.4. Effect of Temperature. Because the cross-linking mechanism of the gelation of SPG−Borax is governed by an exothermic complexation equilibrium[13−26,33] (see Figure 1), temperature should be an important factor influencing the gelation process. Figure 10 shows the evolution of G' for the SPG−Borax system gelled at different temperatures, along with the fitting curves by the first-order kinetic model. The gelation proceeds more rapidly and tends to approach a larger saturated storage modulus at lower temperatures. With respect to the induction time, t_0, it is also shortened by decreasing temperature, but its dependence on temperature is not as remarkable as that on Borax content and SPG concentration (see Figures 4 and 7).

Figure 11 shows the Arrhenius treatment for gelation rate, $1/\tau_c$. The apparent activation energy, E_a, is calculated to be −74.5 kJ/mol from the slope of the straight line. The Arrhenius relationship was widely used to describe the temperature dependence of the gelation process for biopolymers such as methylcellulose,[8b] β-lactoglobulin,[50] κ-carrageenan,[51] and konjac glucomannan.[11] The sign of the apparent activation energy is related to the temperature dependence of the cross-linking reaction or the intermolecular forces that are involved in the formation of junction zones. For the present system, the cross-linking reaction is an exothermic equilibrium complexation, implying that the formed cross-links are less stable at higher temperature. Therefore, the formation of a three-dimensional percolating network is more difficult and slower at higher temperature. This leads to the
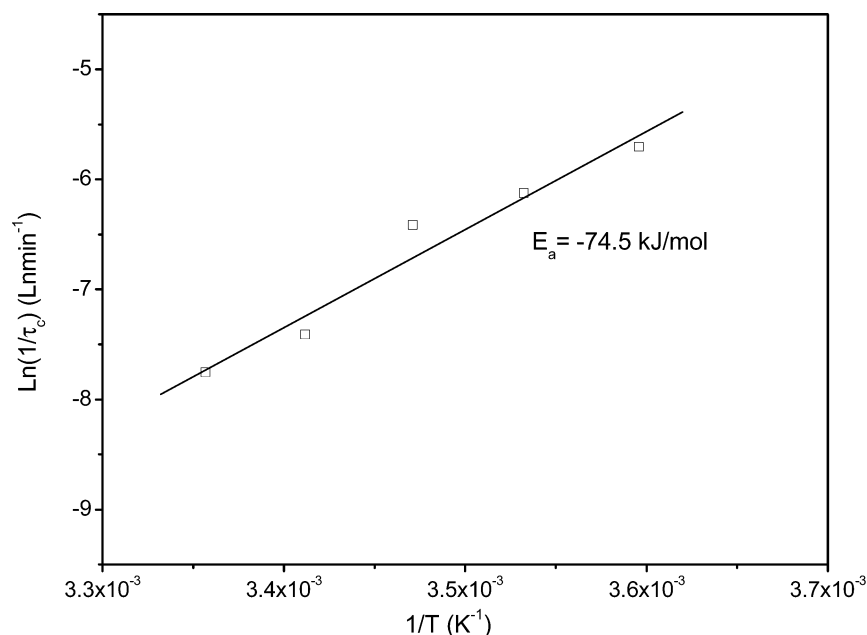
Figure 11. Arrhenius plot of the gelation rate, $1/\tau_c$, against $1/T$. τ_c values are obtained through curve fitting of data in Figure 10.
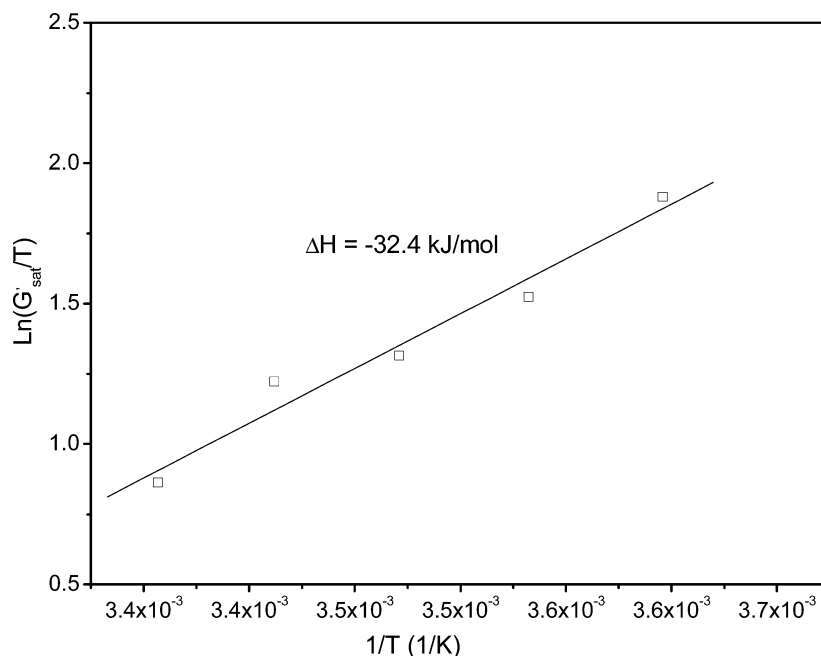

Figure 12. Plot of $\ln(G'_{sat}/T)$ against $1/T$. G'_{sat} is obtained through curve fitting of data in Figure 10.

negative apparent activation energy for gelation of the SPG–Borax system.

As for the temperature dependence of the saturated storage modulus, we still can use eq 2 taking into consideration the influence of temperature on the cross-link concentration:[52–55]

$$G = 2c_cRT = 2c'_c \exp\left(\frac{-\Delta H}{RT}\right)RT \qquad (3)$$

Therein ΔH is the cross-linking enthalpy and c'_c is a reference cross-link concentration. Equation 3 can be recast into the following form:

$$\ln\left(\frac{G}{T}\right) = \frac{-\Delta H}{RT} + k \qquad (4)$$

where k is a constant. Figure 12 plots $\ln(G/T)$ as a function of $1/T$. A fairly good linear relationship is observed, from the slope of which the cross-link enthalpy is determined as -32.4 kJ/mol. This value is larger than those found for poly-(vinyl alcohol)–Borax gel (-11 kJ/mol)[13] and galactoman-nan–Borax gel (-14 kJ/mol),[26] suggesting that borate ions form relatively more stable cross-links with SPG than with poly(vinyl alcohol) or galactomannan. It is emphasized that the lower gelation speed of borate with SPG should be attributed to the larger activation energy, which is not in discrepancy with the larger cross-linking enthalpy.

The cross-linking enthalpy determines the dynamic nature of cross-links, the larger enthalpy meaning less-dynamic cross-links. For poly(vinyl alcohol)–Borax gel[14] and galac-tomannan–Borax gel,[26] both of them were found to exhibit liquidlike behaviors at lower frequencies (up to 1 rad/s),
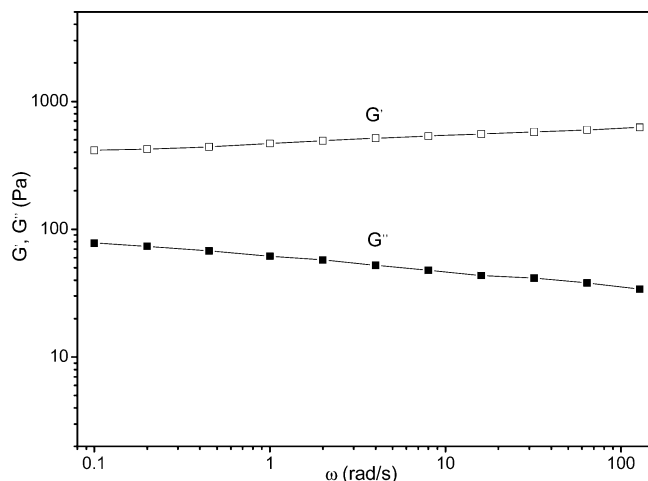
Figure 13. Frequency dependence of G' (□) and G'' (■) for the SPG−Borax system gelled for 24 h. C_p = 6 g/L; C_b = 24 mM; [NaCl] = 1 M; T = 20 °C; strain = 1%.

Figure 15. Plot of G'_{sat} against the NaCl concentration. G'_{sat} is obtained through curve fitting of data in Figure 14.
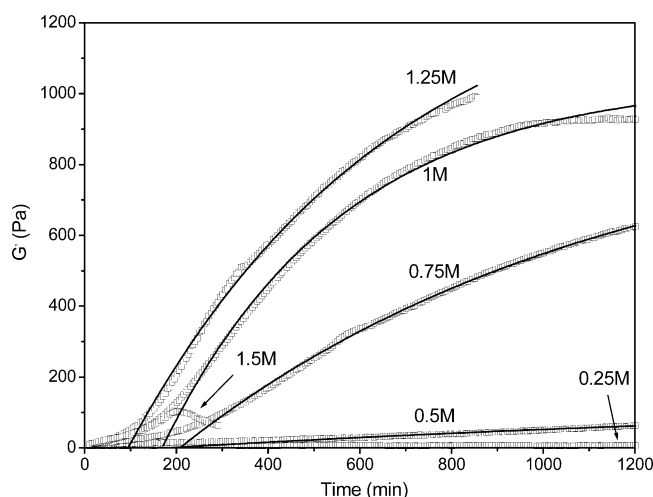

Figure 14. Time dependence of the storage modulus G' during the gelation of the SPG−Borax system with various NaCl concentrations (indicated beside the curves). C_p = 6 g/L; C_b = 24 mM; T = 10 °C; frequency = 1 rad/s; strain = 1%. The solid line represents the curve fitting results to G' by the first-order kinetic model.

Figure 16. Plots of t_0 and $1/\tau_c$ against the NaCl concentration. t_0 and τ_c are obtained through curve fitting of data in Figure 14.

which were attributed to the equilibrium reactions with small cross-linking enthalpies.[13] Additionally, these two gels were reported to be self-healing after cut. Figure 13 shows a typical example of the dynamic mechanical spectra for the SPG−Borax gel. G' is almost independent of frequency, and G'' decreases with increasing frequency, typical of rubber-like behavior. It should be noted that even scanning to the low frequency of 0.1 rad/s we are still not able to observe the liquidlike behavior. This may be due to the less-dynamic nature of the cross-links compared with those in poly(vinyl alcohol)−Borax and galactomannan−Borax gels. Of course, the long relaxation time network constituted by rigid SPG triple helices should also contribute to such dynamic mechanical behavior. Moreover, we tested the self-healing ability for SPG−Borax gel. It was found that the gel cannot recover even for 24 h after destruction, which is also due to the less-dynamic nature of the cross-links in SPG−Borax gels.

3.5. Effect of Salt Concentration and Salt Type. As shown in Figure 1, the gelation of SPG−Borax involves the formation of the charged monodiol complex, which confers
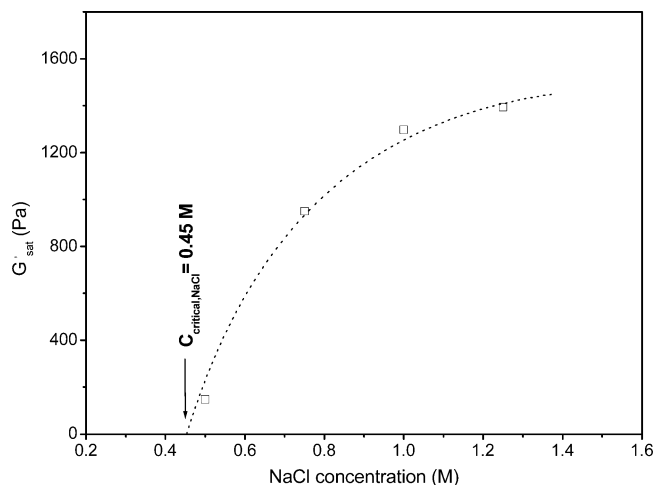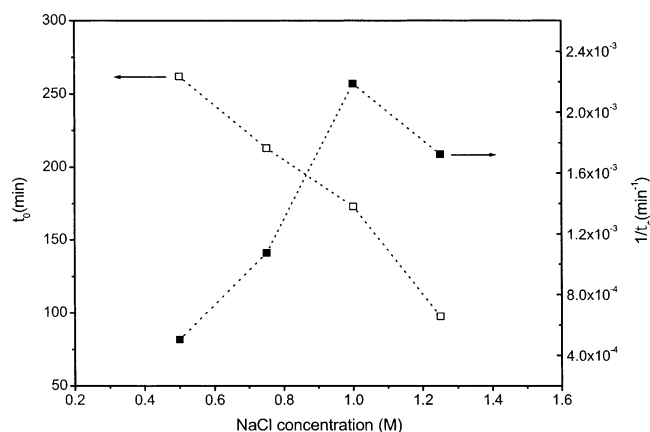
SPG polyelectrolyte property. As a result, gelation is only observed after sufficiently screening the electrostatic repulsion between SPG chains. In fact, the addition of some amount of salt is a prerequisite for the gelation of SPG−Borax.[34] Figure 14 clearly shows that the kinetics of the gelation of SPG−Borax is largely influenced by the added NaCl concentration, higher NaCl concentration producing a faster gelation process. For NaCl concentration of 0.25 M, the gelation is not observed, while for NaCl concentration of 1.5 M, the gelation proceeds so rapidly that syneresis occurs, which results in the decrease of G' after an increase. The effect of added salt concentration is consistent with that reported by Grisel and Muller.[32−34]

In Figure 14 are also shown the fitting curves to G' by the first-order kinetic model, and the plot of G'_{sat} as a function of NaCl concentration is reported in Figure 15. G'_{sat} increases with increasing NaCl concentration, which can be interpreted by the fact that the number of formed cross-links is larger at higher NaCl concentration because of more sufficient screening of the electrostatic repulsion. Moreover, we can estimate a critical NaCl concentration of $C_{critical,NaCl}$ = 0.45 M for the occurrence of gelation. Figure 16 shows the variation of t_0 and $1/\tau_c$ versus NaCl concentration. On the whole, induction time, t_0, becomes shorter with increasing NaCl concentration, and gelation rate, $1/\tau_c$, increases with increasing NaCl concentration. The gelation
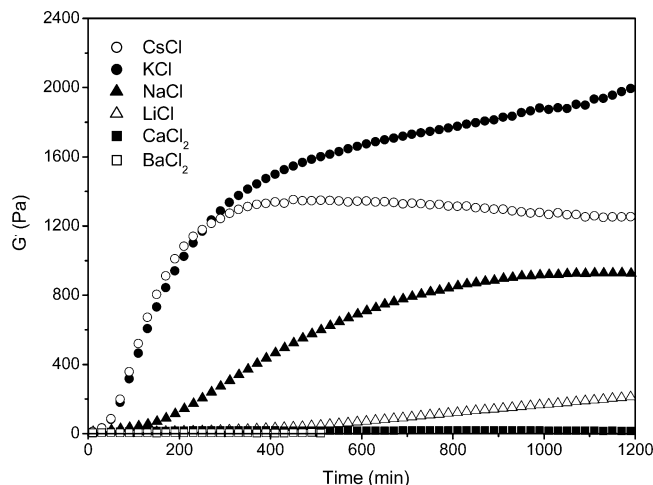
Figure 17. Effects of the different types of salts on the gelation of the SPG−Borax system. C_p = 6 g/L; C_b = 24 mM; T = 10 °C; frequency = 1 rad/s; strain = 1%. The ionic strength is fixed as I = 1 mol/L.

Figure 18. Effects of the applied strain on the gelation of the SPG− Borax system. C_p = 6 g/L; C_b = 28 mM; [NaCl] = 1 M; T = 20 °C; frequency = 1 rad/s. The solid line represents the curve fitting results to G' by the first-order kinetic model.

rate at high NaCl concentration seems to fall off, which may be caused by the occurrence of syneresis during measurement. The addition of NaCl shields electrostatic repulsion and makes the formation of both monodiol complex and didiol complex easier, which leads to the faster gelation.

The effects of different types of salts are compared in Figure 17. For the monovalent cations, the gelation is accelerated when cation size increases (Li$^+$ < Na$^+$ < K$^+$ < Cs$^+$). Additionally the obtained storage modulus G' also increases with increasing cation size. This means that a larger cation is more favorable for the gelation of the SPG−Borax system. This effect could be related to the different binding extents for different cations:[34,56] the binding extent increases with decreasing cation size, and as a result, the negatively charged monodiol complex is better stabilized when a smaller cation is used, which delays the formation of the didiol complex and thus the gelation. Moreover, it was reported that a larger cation has a more remarkable role in screening electrostatic repulsion[57] and thus is more favorable for gelation.

When divalent cation (Ca^{2+} or Ba^{2+}) is added, gelation is not observed, indicating the salt-type selectivity of the gelation of SPG−Borax. The presence of Ca^{2+} or Ba^{2+} leads to formation of calcium borate or barium borate with less solubility, which greatly decreases the number of free borate ions available for the cross-linking reaction. Therefore SPG− Borax solution does not gel in the presence of Ca^{2+} or Ba^{2+}. In fact when BaCl$_2$ is added, the formation of a white precipitate was observed, which may be barium borate.

3.6. Effect of the Strain Used. As mentioned above, the gelation of SPG in the presence of Borax is governed by two complexation equilibria, and the formed cross-links have a dynamic nature. Therefore, it is expected that the applied strain when measuring G' may affect the gelation process. Figure 18 displays the G' curves monitored at strain = 1%, 5%, and 10%. Note that all of these strains lie in the linear viscoelastic region. The G' curve tends to reach a higher saturated value when smaller strain is used. This suggests that the number of formed cross-links increase with decreasing strain. Because the formed cross-link is susceptible to
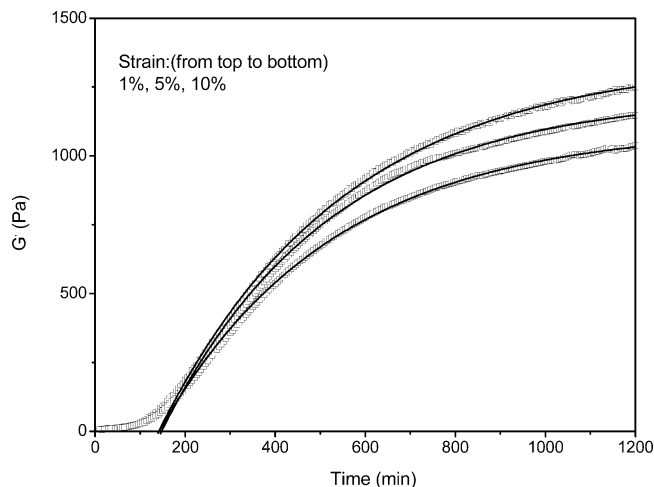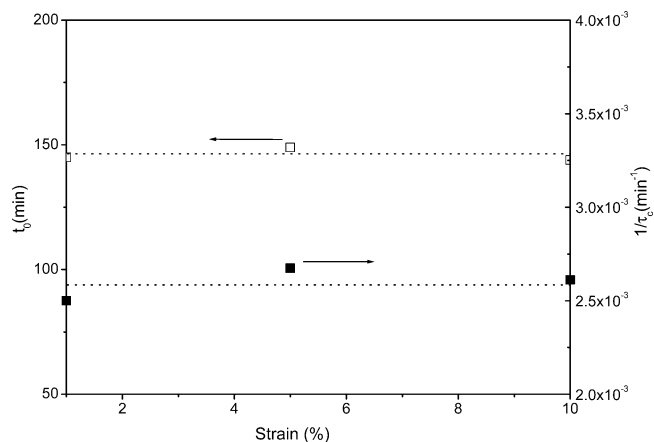

Figure 19. Plots of t_0 and $1/\tau_c$ against strain. t_0 and τ_c are obtained through curve fitting of data in Figure 18.

the larger deformation, increasing strain makes the cross-links less-stable, which results in a network containing fewer cross-links.

Figure 19 plots the curve-fitting parameters, t_0 and $1/\tau_c$, as a function of strain. Both induction time, t_0, and gelation rate, $1/\tau_c$, are almost independent of strain. This implies that the kinetics of the formation of cross-links is not influenced by strain, no matter that the cross-links are less stable at larger strains.

3.7. Strain Dependence of Network Elasticity. In the preceding part, we discussed the elasticity of SPG−Borax gels at relatively small deformation where the elasticity is just a function of cross-link concentration and is independent of strain. Because the SPG chain is a rigid wormlike triple helix and has non-Gaussian chain features, the network elasticity is expected to depend on strain at large deformations.[44] Figure 20 shows the dynamic strain sweep measurement for the SPG−Borax gel. Below the strain of 10%, G' is independent of strain. Within this small strain range, the SPG chain has the ability to be extended, and the network elasticity is mainly entropic and contributed by the conformation change during deformation.[44] In the strain range from 10% to 30%, a strain-hardening phenomenon, that is, G' and G'' increase with increasing strain whereas tan δ decreases,
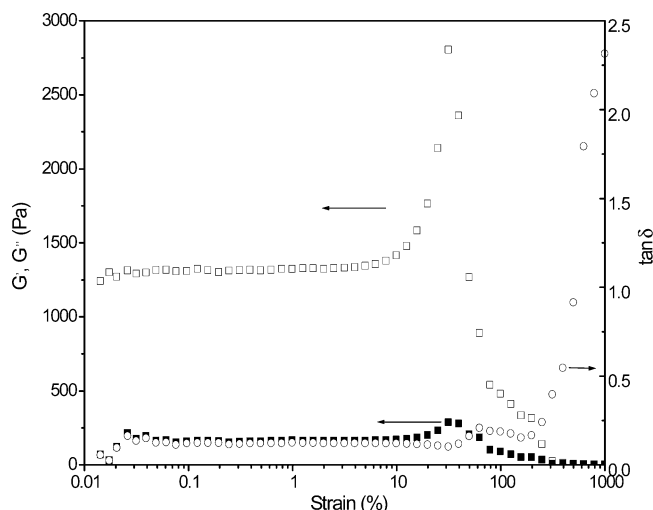
Figure 20. Dynamic strain sweep measurement for the SPG−Borax system gelled for 24 h: G' (□); G'' (■); tan δ (○); C_p = 6 g/L; C_b = 28 mM; frequency = 1 rad/s; T = 20 °C.

occurs. Such phenomenon is not often observed for other systems and indicates that the deformation has been approaching the limiting extensibility of the SPG chain. SPG chain within this strain range is typical of a non-Gaussian chain,[44] and the enthalpic term of elasticity originating from the bending of network chains becomes predominant.[58,59] For a flexible chain, non-Gaussian chain behavior becomes important when it is extended between $^1/_3$ and $^1/_2$ of the fully extended chain length.[44] For the present SPG−Borax network, this behavior starts to occur at far smaller deformations (strain = 10%), which could be interpreted by the poor extensibility of rigid SPG chains. When strain is above 30%, the gel first reaches a maximum G' of 3000 Pa and then ruptures. The rupture at such a low strain and not so low storage modulus indicates the brittleness and hardness of the network.

4. Conclusion

Dynamic viscoelastic measurements have been done to investigate the gelation of a rigid-chain polysaccharide, schizophyllan (SPG), with Borax as cross-linker. The gelation process of this system can be well described by the first-order kinetic model, from which induction time, t_0, gelation rate, $1/\tau_c$, and saturated storage modulus, G'_{sat}, are obtained. Six factors, Borax content, SPG concentration, temperature, salinity, salt type, and strain, are found to affect the gelation of SPG−Borax. The gelation proceeds more rapidly at higher Borax content, and no gelation is observed below a critical Borax content. The storage modulus is a linear function of the Borax content, as expressed by the modified ideal rubber elasticity theory. To our surprise, a linear relationship also exists between storage modulus and SPG concentration. Such a concentration dependence of storage modulus is quite scarce and could be understood by considering that the number of the formed cross-links is linearly related to the number of interchain contacts, which scales as $\sim C^1$ for rigid SPG chains. Because of the exothermic nature of the cross-linking reaction, lower temperature is favorable to the gelation. From the temperature dependences of gelation rate

and storage modulus, the apparent activation energy, E_a, and the cross-linking enthalpy, ΔH, are determined to be −74.5 and −32.4 kJ/mol, respectively. Compared with poly(vinyl alcohol)−Borax and galactomannan−Borax gels, the determined cross-linking enthalpy of SPG−Borax is relatively larger and the formed cross-links are more stable, which is further confirmed from dynamic mechanical spectra. Only after screening interchain electrostatic repulsion by adding alkaline metal salt, the gelation occurs, and gelation rate increases with increasing salt concentration. The stimulating effect of monovalent cations is in the following order: $Li^+ < Na^+ < K^+ < Cs^+$, which is due to the higher binding extent for smaller cations. However when the divalent cations Ca^{2+} or Ba^{2+} are added, the gelation does not occur, which is attributed to the formation of less-soluble calcium borate or barium borate. The magnitude of applied strain influences the strength of the obtained gels, while it does not change induction time and gelation rate.

Because the network of the SPG−Borax gel is constituted by rigid SPG chains with limited extensibility, the elasticity behavior is observed to deviate from Gaussian chain network when strain is larger than 10%. The gel is relatively brittle and ruptures at a small strain of 30%.

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