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ORIGINAL CONTRIBUTION

Salt-induced thickening and gelation of a poly(carboxylate) having three kinds of hydroxyl groups

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Abstract A salt-induced physical gelation was found for the aqueous solution of poly(carboxylate)s having three kinds of hydroxyl groups, i.e., primary, tertiary and one on a hemiacetal ring. The gelation point (critical salt concentration) was positively correlated with the content of the hemiacetal component, while the previously confirmed hydrogen bond between the hemiacetal OH and –COO$^-$ group does not seem to essentially contribute to the physical gelation. Above a critical polymer concentration, the solution viscosity was first decreased and then increased with increasing NaCl concentration, leading to gelation. However, below the critical polymer concentration, the viscosity decreased. These different behaviors of the solution viscosity depending on the polymer concentration were ascribed to a preferential promotion of intermolecular or intramolecular hydrogen bonds among the hemiacetal OH groups above and below the critical polymer concentration, respectively.

Keywords Physical gelation · Thickening · Intermolecular hydrogen bond · Poly(carboxylic acid) · Viscosity

Introduction

Intermolecular and intramolecular hydrogen bond (HB) of hydrophilic polymers in aqueous systems is crucial for determining the solution properties. For example, rheological properties of aqueous poly(vinyl alcohol) (PVA) solution are mainly determined by the relative strength of the intra- and intermolecular HBs and ones with water (i.e., hydration) [1]. Carboxyl group (–COOH) is also an effective HB donor for interpolymer complex formation [2]. Further, the intermolecular HB, as well as cross-linking via counterions, plays an essential role in the sol–gel transition of polysaccharides. [3–5] Needless to say, gelation of PVA by repeating “freeze-thaw” process is also a result of enhanced and stabilized intermolecular HBs between the OH groups. [6, 7] Thus, hydroxyl and carboxyl groups are key HB donors for producing interpolymer complexes, supra-molecular polymers and physical gels, and so on.

In this context, a hydrophilic polymer that contains three kinds of OH groups: primary OH on α-hydroxyallyl alcohol component, hemiacetal OH on cyclic hemiacetal component, and tertiary OH on α-hydroxyacrylate component, may be interesting [8]. This polymer is prepared by a simple reduction of a polylactone (PLAC; see Fig. 1 of [10]). Yamazawa et al. [9] have studied molecular structures of reduced PLAC (red-PLAC) samples having different degrees of reduction and found various intra- and intermolecular HBs between the three kinds of OH groups and –COOH group. Especially, the hemiacetal OH group forms a stable HB with –COO$^-$ group, which is interrupted by the allyl alcohol OH. Sunohara and Satoh [10] also suggested that –COO$^-$ group in the red-PLAC is stabilized by intramolecular HB with hemiacetal OH group on the basis of significantly low p*K*a values and more marked infrared shifts observed for red-PLAC samples of more hemiacetal contents. Thus, aqueous solution of red-PLAC, which has different kinds of OH groups as HB donor and acceptor as well as –COO$^-$ group as a HB acceptor, seems to be an intriguing system where intra- and intermolecular HB must

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be essentially involved with the rheological behaviors. In the present study, we have investigated solution viscosity of the red-PLAC as functions of salt concentration, polymer concentration, temperature, and polymer constitution (contents of hemiacetal, allyl alcohol, and α-hydroxy acrylic acid components).

Experimentals

Sample preparation

PLAC (M_w=5.0×10^5) was kindly supplied by Nippon Peroxide. The PLAC sample, which composed of approximately 70 mol% of lactone ring component and approximately 30 mol% free carboxyl group, was washed by methanol (MeOH) for 30 min under stirring and air-dried before use. With this pretreatment, the free carboxyl group in PLAC was partly converted to methyl carboxylate group [11]. All the solvents and $NaBH_4$ were of analytical grade (Tokyo Kasei) and used without further treatment. Water was deionized and distilled before use.

Reduction of PLAC was performed with two types of procedures (I and II) to obtain red-PLACs with various compositions. The details were given in our previous papers [8–10]. Bare outlines for the procedures are as follows:

Procedure I (same as procedure A of [9]); PLAC was dissolved in DMSO/MeOH or DMF/MeOH mixed solvent. The polymer solution was slowly added into methanol containing desired amounts of $NaBH_4$. The reduction reaction was continued for 5 h under stirring at 0 °C. This procedure is adequate for obtaining hemiacetal-rich red-PLAC samples.

Procedure II (same as procedure C of [9]); Re-reduction of the red-PLAC samples obtained with procedure I was performed by adding desired amounts of $NaBH_4$ into an aqueous solution of the red-PLAC. The reaction was continued for 5 h under stirring at 25 °C. With this procedure, one can transform hemiacetal component in the "parent" red-PLAC sample to allyl alcohol without significant change in the carboxyl group content.

The solution proton nuclear magnetic resonance (^{1}H NMR) spectra for all the reduced samples were obtained to estimate the polymer composition. Experimental conditions for the NMR measurement and the detailed procedures for the composition estimation are given elsewhere [9]. Polymer compositions thus estimated are shown in Table 1. As seen from the table, red-PLAC (named as RP) samples of various composition were obtained. RP1 and RP2 series, which were obtained by re-reduction (procedure II), composed of the allyl alcohol and hemiacetal components in various ratios with keeping almost constant carboxyl group contents (~60% for RP1 series and ~40% for RP2 series). Although all the RP samples prepared by procedure I should have a similar composition, the hemiacetal component varied from 32 to 75%, and the carboxyl group ranged from 10 to 60%. Especially RP6 and RP7 samples had much less carboxyl group and significantly higher amounts of hemiacetal component compared with the others. Such an unsteady result for those two sample preparations may be partly ascribed to some possible different contents of the $–COOCH_3$ group, which were converted from the free –COOH group during pretreatment of PLAC with methanol; methyl carboxylate must be easily reduced by $NaBH_4$ compared with the free carboxyl counterpart.

Viscometry

Solution viscosities of the red-PLAC samples were measured with a vibration-type viscometer (Viscomate 10A, CBC Materials) as functions of salt concentration (0–0.3 mol/kg), polymer concentration (0.1–3 wt%), and temperature (6, 25, or 30 °C). The salt concentration was changed by adding required amount of NaCl sequentially

Table 1 The reduction condition and the composition (%) of red-PLAC samples

Sample name	Procedure	PLAC/$NaBH_4$	Allyl alcohol	hemiacetal	–COOH
RP1	I	1:8	6	34	60
RP1-0.5	II	1:0.5	16	28	56
RP1-10	II	1:10	27	15	58
RP2	I	1:8	12	49	39
RP2-1	II	1:1	31	35	34
RP2-5	II	1:5	33	27	40
RP2-10	II	1:10	43	20	37
RP3	I	1:8	5	38	57
RP4	I	1:8	14	40	46
RP5	I	1:8	13	32	55
RP6	I	1:8	15	75	10
RP7	I	1:8	13	60	27

into the polymer solution. LiCl, KCl, CsCl, and NaF were also used as added salts. With this salt addition, the polymer concentration was decreased by about 5% at most. In most systems, salt addition resulted in a macro-gel formation. The confirmation of the gelation was performed by the so-called "sample inversion" method.

Viscoelasticity measurements were performed for RP1 and RP5 samples which contained NaCl or CsCl with a rheometer (Reosol-G3000, UBM) to obtain the storage and loss elastic modulus (*G*′ and *G*″) as a function of temperature (20–60 °C) at 1 Hz.

Freeze-thaw test

Effects of freezing on the RP sample viscosity were investigated. Two RP7 samples (3.0 wt%), which contained no NaCl and 0.1 mol/kg NaCl, respectively, and one RP6 sample in the absence of NaCl were frozen at −20 °C for 1 h and then thawed at 25 °C. Solution viscosities of RP7 samples were measured after 1 and 5 h since the start of thawing.

Fourier transform infrared spectroscopy

To see if HB of the $–COO^-$ group is responsible for the gelation of red-PLAC aqueous solutions or not, attenuated total reflection Fourier transform infrared (FT-IR) spectra (FT-IR8200 PC equipped with ATR-8200H, Shimadzu) were obtained for RP2 and RP2-5, both of which contain approximately 40 mol% of $–COO^-$ group.

Results and discussion

Salt-induced gelation

Solution viscosities of RP2 series, which were measured as a function of NaCl concentration at 6 °C, were shown in Fig. 1. Viscosities of all the RPs initially decreased with increasing the NaCl concentration and then showed a significant upturn except for RP2-10 system. At the endpoints of the upturn, the respective sample solutions formed a macro-gel. The viscosity data at the end point (gelation point) of the respective systems should be taken as a rough measure of solution viscosity just before the gelation because the vibration-type viscometer measures the viscosity of "solution" just around the probe even when the sample became a macro-gel.

The initial decrease in the viscosity is to be ascribed to a contraction of the polymer chain caused by the screening of the electrostatic repulsion among the carboxylate groups upon addition of NaCl, a normal behavior for polyelectrolyte solution. On the other hand, the upturn in the viscosity with increasing the salt concentration is an extraordinary behavior as observed for aqueous polyelectrolyte solutions.

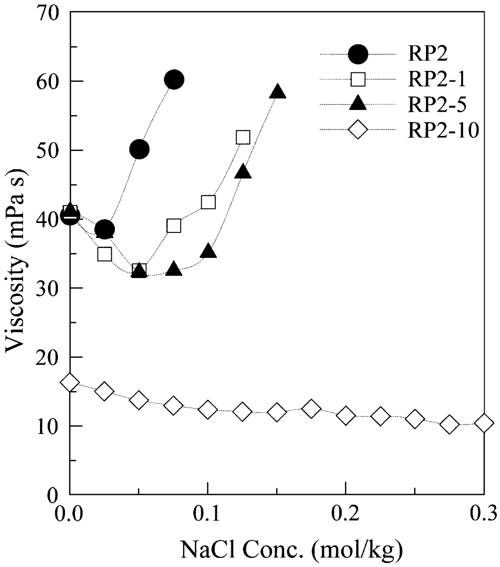

Fig. 1 Salt-induced thinning and thickening behavior of RP2 series samples (C_p=3.0 wt%)

The thickening behavior and/or resultant physical gelation of aqueous polyelectrolyte solutions have been reported for many systems [2, 12–14]. However, in most cases, the driving force for the thickening or the responsible intermolecular interaction is the hydrophobic interaction. For example, Li and Kwak [15] ascribed a significant pH-dependent thickening observed for aqueous solutions of acrylic acid–acrylamide copolymers, the latter of which was hydrophobically modified with alkyl chains (C10, C12, or C14) mainly to hydrophobic interaction among the hydrophobic chains and partly to hydrogen bond between –COOH and $–COO^-$ groups. In some cases, intermolecular HB has been assigned a main driving force for thickening behaviors observed for polyelectrolyte solutions. Sotiropoulou et al. [16] reported a first example of a polyelectrolyte solution system showing a thickening behavior through pure hydrogen bonding interactions; mixtures of poly(acrylic acid) (PAA) and poly(acrylic acid-co-2-acrylamido-2-methylpropane sulfonic acid)-graft-poly(*N*,*N*-dimethyl acryl amide) (P(AA-co-AMPSA)-g-PDMAM) showed a significant viscosity increase, or even a physical gelation, in the lower pH region (<3.75) due to the hydrogen bonding association between PAA and PDMAM side chains.

In these two examples, a pH decrement induced the observed thickening effects through decreasing the electrostatic repulsion among the polymer chains; otherwise, the hydrophobic and the hydrogen bonding interactions would not be able to effect the viscosity enhancement. On the other hand, another simple method must be also effective to reduce the electrostatic repulsion among the polyelectrolyte chains, i.e., salt addition. In fact, it has been well known that polysaccharides such as carrageenan show physical gelation in the presence of alkali metal salt [3–5, 17]. For example, a typical mechanism for the gelation of kappa-carrageenan has been believed to be through cation (counterion) mediation between charged groups on the helix (single or double) polymer chains. [5] Although such a gelation mechanism has been extensively studied, main concerns of the researchers were to investigate and elucidate the gel properties as functions of temperature, polymer concentration, and cationic (counterion) species, much less attention being paid on the thickening behavior leading to gelation with increasing added salt concentration. Thus, the present finding that aqueous solutions of a synthetic polycarboxylic acid show those remarkable viscosity increases preceded by an initial viscosity decrement with increasing the salt concentration seems to be a first example, at least to our best knowledge.

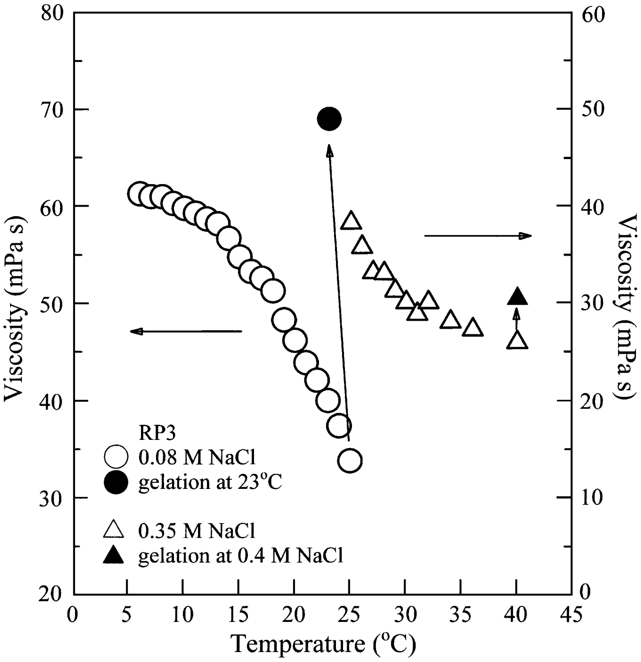

Fig. 2 Temperature effects on the viscosity of RP3 samples. (C_p=3.0 wt%). The *open symbols* were viscosity data that were obtained by increasing the temperature. The *filled circle* was obtained by decreasing the temperature down to 23 °C from 25 °C. The *filled triangle* was obtained by adding NaCl

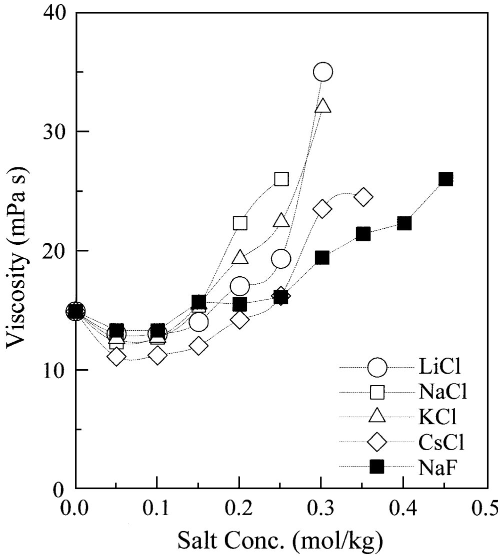

Fig. 3 Dependence of the solution viscosity of RP5 sample on the salt species added

As referred above, the hydrophobic interaction, HB, and/or the counterion-mediated polymer association may also be nominated as the main cause for the observed thickening and gelation behavior. However, experimental results shown in Figs. 2, 3, and 4 seem to safely exclude the possibility of the first and the third ones as a main mechanism. Figure 2 shows the temperature dependence of the viscosity for the two RP3 systems, which once formed physical gel at 6 and 25 °C by adding 0.08 and 0.35 mol/kg, respectively. The significant decrease in the viscosity with increasing the temperature is inconsistent with the hydrophobic interaction, suggesting that some exothermal interaction is responsible for the gel formation. Figure 3 shows the salt-induced thickening and gelation behavior of RP5 for several kinds of salts systems. The cation effects are appreciable as $Cs^+ < K^+$, $Li^+ < Na^+$, namely, in this order, the gelation occurred in the lower salt concentration. This ion specificity seems to be consistent with the well-known counterion specificity for carboxyl anion [18]. However, the observed counterion specificity for the gelation is much less significant compared with those found for the carrageenan systems [5], suggesting that the counterion-mediated polymer association mechanism is unlikely as a main one for the gelation of the present RP systems. Another and stronger support for excluding the

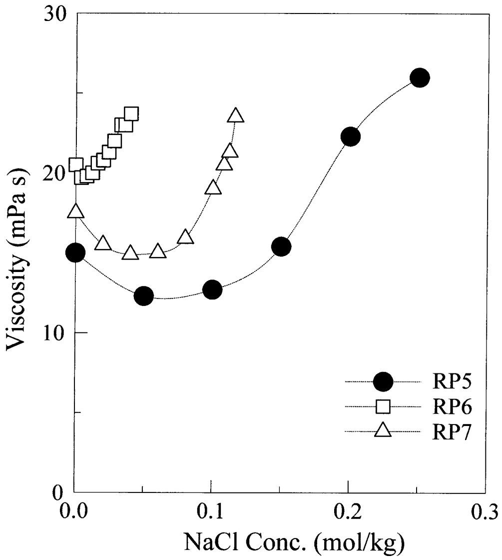

Fig. 4 Dependence of the solution viscosity on the sample composition. Allyl alcohol/Hemiacetal/–COOH=13:32:55 for RP5, 15:75:10 for RP6, 13:60:27 for RP7

counterion-mediated mechanism may be obtained from the results shown in Fig. 4 where the viscosity behaviors among three RP samples of different compositions are compared; RP6 system showed a physical gelation by adding 0.04 mol/kg of NaCl, the lowest concentration for gelation among those found for the RP samples. This means that the carboxyl group, and hence the counterions, are not essentially involved with the gel formation, as the RP6 sample contains only 10 mol% of carboxyl group, the lowest among the RP samples used here.

Thus, the second one, i.e., the hydrogen bonding interaction, seems to be most likely as the main cause for the observed gelation. There are many candidates for the responsible hydrogen bonding interaction; those among the three kinds of OH groups and –COO$^-$ amount to 9. On the basis of the gelation behavior of RP6 sample (Fig. 4), however, one may safely deduce that the intermolecular HB between hemiacetal OH groups should essentially contribute to the thickening and the physical gelation. Namely, the higher the hemiacetal composition (RP6 > RP7 > RP5), the lower the salt concentration necessary to induce gelation (RP5 > RP7 > RP6).

On the other hand, other candidates may not be essentially responsible for the gelation. For example, HB with –COO$^-$ group would first dropout from the candidates on the basis of the same reasoning as that made for the counterion-mediated mechanism, that is, because of such a low carboxyl group content (10%) of RP6 sample. In addition to the significant dependency of the gelation point on the polymer composition (hemiacetal content), the results shown in Fig. 4 clearly show that the absolute values of viscosity are inversely dependent on the carboxyl content or charge density; the higher the polymer charge density is, the lower the viscosity becomes, as RP6 (10%) > RP7 (27%) > RP5 (55%). This strongly suggests that it is not the polymer chain extension due to the electrostatic repulsion that determines the solution viscosity of the present polyion systems but the intermolecular HB between hemiacetal OH groups.

In our previous studies, on the other hand, we found that the dissociated state of the carboxyl group (–COO$^-$) is largely stabilized by the HB formation with the hemiacetal OH group [10, 11]. This apparent inconsistency between the previous conclusion, which was obtained by a pH titration study and the present gelation behavior, may be ascribed to the difference in the polymer concentration. Namely, in such a low polymer concentration employed in the previous study (approximately 0.03 mol/l, 0.3%) [10], only the intramolecular HB must be available. Therefore, the stabilization of the dissociated carboxyl group (or significantly low p*K*a values of red-PLAC with higher hemiacetal contents) can be attributed to the intramolecular HB formation between the carboxyl anion and the hemiacetal OH, but not to the intermolecular one. In fact, Fig. 5 shows that the gelation of RP2 sample was accompanied by no significant shift for the –COO$^-$ peak at 1,585 cm^{-1}. On the other hand, the corresponding peak for the aqueous solution sample of RP2-5 that contains less hemiacetal OH group appeared at a slightly lower wavenumber (1,578 cm^{-1}). This may be ascribed to the lower degree of intramolecular HB formation between the carboxyl anion and the hemiacetal OH. Thus, it is not unreasonable to suppose that the HB between –COO$^-$ and hemiacetal OH was not a main cause for the salt-induced gelation of the pertinent polymer samples.

α-OH and allyl alcohol OH groups still remain as possible contributors for the physical gelation. However, both would also fail; for the former, the content is the lowest for the RP6 sample (25%), suggesting that the OH group is not essentially involved with the gelation. For the latter, our previous studies seem to deny the possibility as a contributor to the gelation; the ^{13}C NMR [11] and the pH titration [10] studies suggested that the allyl alcohol OH groups intramolecularly form HBs with the hemiacetal OH groups. In fact, this is consistent with the present finding that RP2-10 sample, the allyl alcohol content of which is the highest (43%) among the samples, showed no gelation with increasing NaCl concentration (Fig. 1).

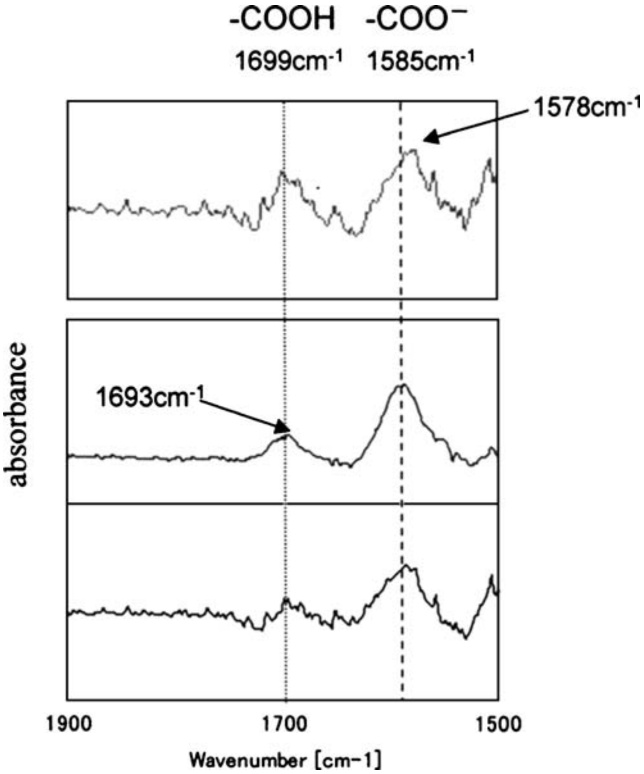

Fig. 5 ATR-FTIR spectra for COO$^-$ and COOH groups in RP2 and RP2-5 samples. The upper spectrum is for RP2-5 in aqueous solution. The middle and the lower spectra are RP2 in aqueous solution and in gel state, respectively

After all the above discussion, we may safely conclude that the intermolecular HB formation between the hemiacetal OH groups is mainly responsible for the salt-induced physical gelation of aqueous solutions of the red-PLAC samples.

Freeze-thaw effect

It has been well known that the freeze-thaw (F-T) processing on aqueous solution of hydrophilic polymers such as PVA may promote the gelation by forming intermolecular HB, which serves as a physical cross-linking [6, 7]. Thus, it seemed to be interesting to see how the F-T processing affects the solution viscosity and if it can cause a gelation of the red-PLAC samples or not. The latter was actually confirmed to be the case. RP6 and RP7 samples (3% aqueous solutions) gelated after one cycle of F-T processing. Both samples remained at a gel state after 1 h since the thawing, although they returned to a sol during standing at 25 °C for 3 h. The latter fact indicates that the produced gel was only temporary, and the formed HB cross-linking was rather weak. However, the intermolecular HB was further strengthened by freezing in the presence of 0.1 M NaCl. In fact, the viscosity in the presence of 0.1 M NaCl after 5 h slightly increased with repeating the F-T cycle (data not shown) and finally remained the gel state at the 6th F-T cycle. These results suggest that the increase in the ionic strength effectively screened the electrostatic repulsion among the polymer charges to favor the intermolecular HB.

Viscoelasticity measurement

As suggested by the freeze-thaw test, the salt-induced physical gels of the red-PLACs may also be rather weak, or consist of weak intermolecular HBs. The viscoelasticity measurement in fact demonstrated it is the case. Figure 6 shows the temperature dependence of G' and G'' values for 3% RP1 aqueous solution that contained 0.2 mol/kg NaCl and 3% RP5 solutions that contained 0.27 mol/kg NaCl and 0.45 kg/mol CsCl. The continuous decrease in the G' values with increasing the temperature means that the intermolecular HBs are broken or become weak. The initial increase in the G'' values is also corresponding to the temperature effect on the gel network, while the subsequent decrease in the G'' is to be ascribed to the decrease in the absolute G values. Here, one should note that the G' values are rather low (~40 Pa) even in the lower temperature region, which may be attributed to the weak intermolecular HB formed in the present polymer systems.

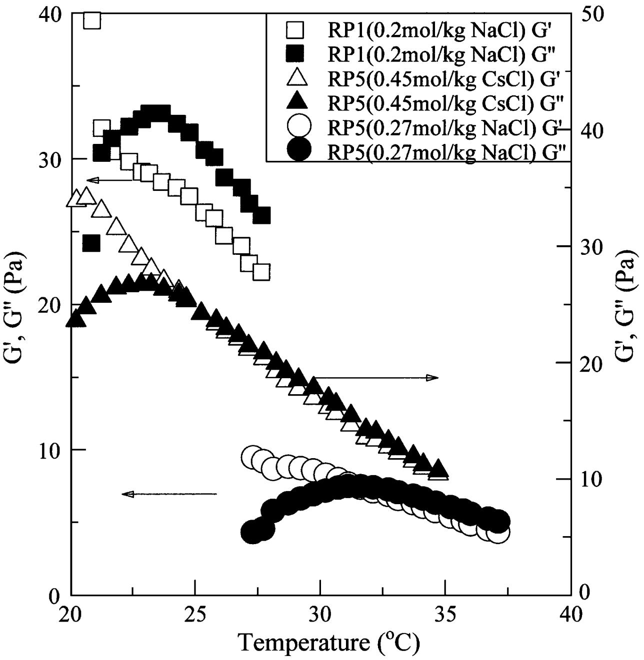

Fig. 6 Rheological behaviors (G' and G'') of RP1 and RP5 samples with increasing temperature

According to a rough criterion, [19] the crossing point of the G' and G'' values may be taken as the gelation point (temperature), below which, the system is to be in a gel state. Namely, the gelation point of the RP1 sample was found around at 21 °C, and those of the RP5 samples containing NaCl and CsCl were approximately 31 and 25 °C, respectively. Here, it may be interesting to compare those gelation points with the critical salt concentrations that were obtained by the viscosity measurements under a constant temperature condition, 0.14 mol/kg NaCl for RP1 at 25 °C, 0.27 mol/kg NaCl for RP5 at 30 °C, 0.35 mol/kg CsCl for RP5 at 30 °C. Among the three systems, the RP5 system which contained 0.27 mol/kg NaCl showed a consistent result between the two kinds of experiments, temperature and salt concentration dependencies of the gelation. However, the other two systems showed a contradictory result; in spite of the higher salt concentrations than those of the salt concentration dependency measurements, the gelation temperatures (21 and 25 °C) are significantly lower than those temperatures (25 and 30 °C, respectively) employed in the static viscosity measurements. This inconsistency may be ascribed to a difference in the experimental procedures of the two kinds of measurements, the viscosity and the viscoelasticity measurements. Namely, in the former, the aqueous polymer solution initially contained no salts; hence, the polymer chains must be extended by the electrostatic repulsion. This polymer extension must be favorable for forming the intermolecular HBs, leading to a lower critical salt concentration or a higher gelation temperature. On the other hand, in the latter experiment, the salt was added before the measurement. Therefore, the electrostatic repulsion was to be screened to allow the polymer chain to take a more compact conformation. This situation must be favorable for the intramolecular HBs rather than the intermolecular ones, resulting in a lower gelation temperature. If this reasoning is the case, then, the apparent coincidence of the gelation point observed for the RP5/0.27 mol/kg NaCl system would in turn become a puzzle to which no answer is given at the present stage. This point will be referred again in the subsequent section.

Polymer concentration dependence of the viscosity

As seen from the experimental results and the discussion above, the intermolecular and the intramolecular HBs seem to compete against each other in aqueous RP solution systems. This competition may be modulated by changing the polymer concentration, C_p, (average distance between the polymer chains) and/or the salt concentration, C_s, (polymer chain extension and electrostatic repulsion). To see the effect of the polymer concentration on the inter- and intramolecular HBs, solution viscosities of RP1, RP1-0.5, and RP1-10 samples measured at different C_ps were plotted against $C_s^{-1/2}$ in Fig. 7. It is well known that viscosities of aqueous polyelectrolyte solutions are linearly correlated with $C_s^{-1/2}$ because the polymer chain size (expansion) inversely increases to the square root of the ionic strength of the medium. [20] Thus, if no specific interactions other than electrostatic one exist, a linear correlation should be obtained. If any attractive interactions (or HB) are intermolecularly effective among the polymer chain, upward deviations from the linear correlation may become apparent with increasing the salt concentration. Further, if the attractive force (HB) is operating intramolecularly, a downward deviation would occur. The expected variation in the dependency of the viscosity on $C_s^{-1/2}$ was actually observed as shown in Fig. 7. For example, in the case of RP1, a linear plot was obtained for C_p=1.6 wt%, above which significant upward deviations and below which slight downward deviations were respectively observed. This polymer concentration dependency of the plot suggests that the intermolecular HBs and intramolecular HBs are competitively operating in the aqueous polymer solution. As a matter of fact, the balance point, namely,

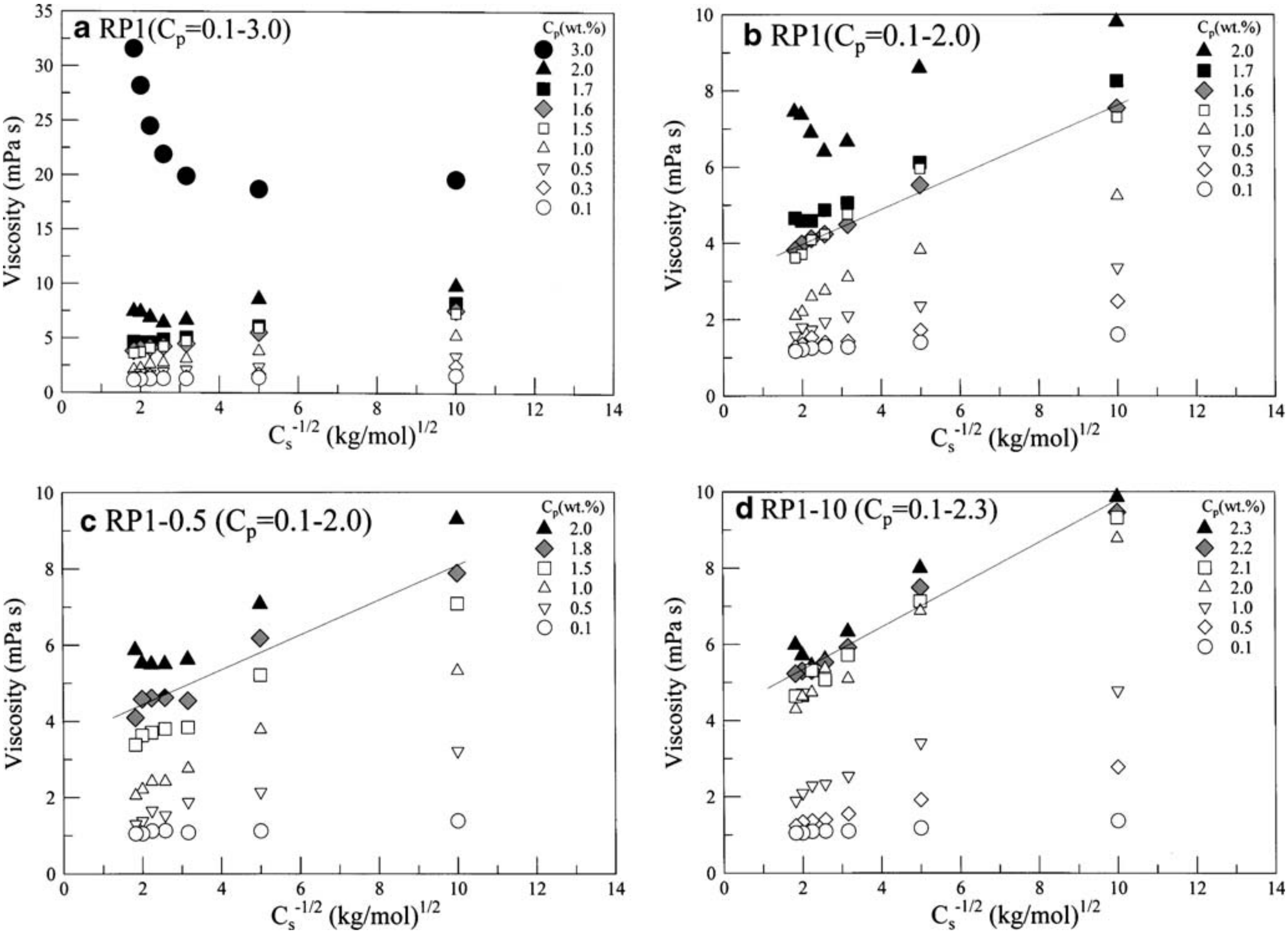

Fig. 7 Effects of polymer concentration (C_p) on the salt concentration dependency of the solution viscosity of RP1 series samples. **a** RP1 (full data), **b** RP1 (C_p=0.1–2.0 wt%), **c** RP1-0.5 (C_p=0.1–2.0 wt%), d:RP1-10 (C_p=0.1–2.3 wt%)

the polymer concentration where the inter- and the intramolecular HBs are balanced and a linear correlation is obtained for the viscosity vs $C_s^{-1/2}$ plot, displaces to more concentrated solutions for RP1-0.5 and RP1-10 systems (1.8 and 2.2 wt%, respectively) containing less hemiacetal OH and more allyl alcohol OH groups than RP1. This trend is consistent with the above conclusion that the hemiacetal OH is essentially involved with the intermolecular HBs and also with the previous one that the allyl alcohol OH forms intramolecularly forms HBs with the hemiacetal OH groups [10, 11]. Here, one may note that the data points at the balance point of RP1-0.5 system are somewhat scattered. A similar trend was also seen for those plots just below the balance point of RP1-0.5 and RP1-10 systems. For example, in the former, a plateau of the viscosity appears before the final drop at the highest C_s. In the latter, instead of a monotonous decrease, the viscosity once increased and then turned to a continuous decrement with increasing C_s (or decreasing $C_s^{-1/2}$). These behaviors seem to suggest that the inter- and the intramolecular HBs are rather subtly competing or balancing each other. This subtle balance between the two hydrogen bonding interactions may in fact be a reason for the apparent agreement and disagreement between the gelation points that were estimated with different experimental procedures as described in the preceding section.

Finally, one may also note that the plots in the lower C_p samples (e.g., 0.5 and 0.1 wt%) are nearly linear, which seems to mean that the intramolecular HBs are not effective in such a low C_p region. However, this is just an apparent observation derived from the low polymer concentrations whose contribution to the solution viscosity should be marginal. In fact, when the reduced viscosity as a measure of the polymer coil size instead of the solution viscosity was plotted against $C_s^{-1/2}$, as exemplified in Fig. 8 for RP1-10, the plots in the relevant lower C_p region clearly show downward deviations. The critical C_p where the contributions from the inter- and the intramolecular HBs are balanced and a linear plot is obtained is of course the same (2.2 wt.%) as one obtained in Fig. 7d.

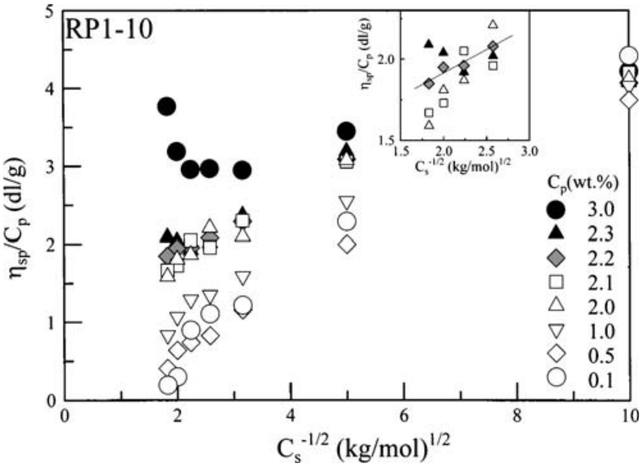

Fig. 8 Effects of polymer concentration (C_p) on the salt concentration dependency of the reduced viscosity of RP1-10 sample

In conclusion, we have found that the red-PLAC samples with various compositions of hemiacetal OH, allyl alcohol OH, and α-OH groups show salt-induced thinning and thickening, mostly followed by a physical gelation. The critical salt concentration for the gelation was well correlated with the hemiacetal content. Thus, the intermolecular HB between the hemiacetal OH groups was assigned to be responsible for the salt-induced thickening and gel formation. Although the intermolecular HB between the carboxyl anion and the hemiacetal OH was detected in our previous studies, and hence nominated as a strong candidate for the gelation, the experimental fact that RP6 which contained as low as 10 mol% of carboxyl group formed a physical gel most easily or at the lowest NaCl concentration definitely withdrawn the nomination.

The most significant finding of the present study may be the salt-induced thinning and thickening behaviors of the aqueous solution systems of the redPLAC samples, which may be caused from a subtle balance of the inter- and intramolecular HBs among the three kinds of OH groups and the carboxyl group, and may also be regulated by the polymer concentration and the temperature. This means that the present red-PLAC samples are able to show a significant thinning or a significant thickening behavior for a given polymer composition by modulating one of the polymer concentration, the salt concentration, and the temperature. However, the present polymeric material may be rather uncommon and indeed of complicated structure; if this unique property could be realized for a more simple polymeric system, it would be of interest in a practical field. For that purpose, we must answer the question "Why is the hemiacetal OH group so effective to form intermolecular HB?" As for an origin of the supposed remarkable ability for the intermolecular HB formation of the hemiacetal OH group, here, we invoke a similarity of the present red-PLAC polymers with polysaccharides. In fact, the hemiacetal ring may be taken as an isomer of deoxyribofranose. According to Uedaira et al. [21], saccharides such as the deoxyribose that have few equatorial OH groups apt to interact each other in water because of the relatively poor hydrophilicity compared with those having many equatorial OH groups. Thus, although the stereochemistry of the present polymer has not been definitely determined, the orientation of the hemiacetal OH group on the ring may be a possible origin for the distinguished ability for gel formation. This means, if the speculation is the case, that one may easily prepare a polymer whose solution viscosity properties are compared to the present ones (i.e., salt-induced thinning, thickening, and physical gelation), e.g., by incorporating relevant saccharide residues at the side chain of poly(carboxylic acid) such as PAA, seemingly a worthwhile attempt.

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