

# Characteristic Rheological Features of High Concentration PVA Solutions in Water with Different Degrees of Polymerization

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**ABSTRACT:** This work aims to study the impact of the degree of polymerization (Pn) on the rheological behavior of PVA solutions (15 wt %) under steady and oscillatory shear conditions. The values of Pn range from 1300 to 2400. The results show that PVA-13 solution exhibits almost Newtonian flow behavior, whereas high Pn PVA solutions exhibit shear thinning behavior, for which the complex viscosity increases with Pn. However, the shear viscosity of PVA-24 is lower than that of PVA-20 at low shear rate ( $<1 \text{ s}^{-1}$ ). In addition, the storage modulus of PVA solutions increases with increasing degree of polymerization from 1300 to 2000. There is a sharp increase at degrees of polymerization higher than 1300. However, the storage modulus of PVA-24 is lower than that of PVA-17 and PVA-20 at low shear rate ( $<1 \text{ rad/s}$ ). The viscoelastic

exponent of the PVA solutions shows a minimum value at degree of polymerization 2000. Thixotropy is detected by a hysteresis loop of the flow curves. The creep response of PVA solutions has also been investigated, with PVA-24 showing negligible compliance recovery. These facts indicate that increasing Pn produces a corresponding effect in varying the molecular structure and types of hydrogen bonding, including intra- and inter-chain, and polymer-water hydrogen bonding. Rheological parameters ( $G'$ ,  $n$ ,  $\tan\delta$ ,  $J$ , and so on) can be used to evaluate the change in the molecular structure and type of hydrogen bonding. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2734–2741, 2010

**Key words:** polymerization degree; poly(vinyl alcohol); solution rheology; hydrogen bonding

## INTRODUCTION

Polyvinyl alcohol (PVA), a typical synthetic water-soluble polymer possessing one hydroxyl group per monomer, was first synthesized by Herrmann and Haehnel in 1924.<sup>1</sup> Since then, studies of the basic physicochemical properties of PVA, both in the bulk state and in solution, have been widely carried out using various techniques.<sup>2–5</sup> Generally, the physicochemical properties of water-soluble polymers in aqueous or mixed aqueous solution depend greatly on the strength of the interactions between water molecules and hydrophilic moieties in the polymers, such as hydrogen bonds. In the case of PVA solutions, the formation of inter- and intramolecular hydrogen bonds between hydroxyl groups belonging to monomer units also influences their solution properties. Liu et al.<sup>6</sup> repeated a freezing–thawing treatment several times in PVA solutions and claimed the dominance of intramolecular hydrogen bonds in a dilute region. However, after more than five freezing and thawing cycles, PVA solutions not

only formed intramolecular hydrogen bonding but also intermolecular hydrogen bonding. An atomic force microscopic (AFM) observation revealed that the hydrogen bonds govern the elastic properties of PVA and form the multiple-stranded structure of PVA in aqueous solution.<sup>7</sup>

It is likely that the mechanical properties of PVA solutions are highly dependent on the formation of inter- or intra-molecular hydrogen bonds between OH groups. Moreover, inter- or intra-molecular hydrogen bonding may bring about complicated phenomena such as phase separation and gelation, which means the solution properties exhibit time-dependence.<sup>8–11</sup> However, the relationships between the bonding and these phenomena have not yet been discussed in detail.

As the rheological properties of solutions are sensitive to the structure of the polymer, rheological measurements can be used to assess the state of the polymer solution. Choi et al.<sup>12</sup> studied the rheological behavior of dilute and semidilute solutions of HMW PVA. The gelation process of HMW PVA solution was divided into two types depending on the concentration of the solution. The first type is the gelation that took place directly from the sol state to gel states with a clear gel point (GP). This is for the concentration regime higher than the critical

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concentration. The second type of gelation occurred gradually, accompanying the evolution of gel-like properties in the sol state without a definite GP. This was for the lower concentration regime. Lee et al.<sup>13</sup> investigated the time dependent rheological responses of PVA solutions in DMSO. They found that the shear rate had a paramount effect on the gelation behavior. If a strong gel was initially formed by a strong shear, no additional gelation or additional deformation of the gel took place, even by prolonged shearing. Briscoe et al.<sup>14</sup> investigated the rheological properties of PVA solutions as a function of the degree of polymer hydrolysis, temperature, pressure, and so on. It was found that the rheological properties of aqueous PVA solutions were mainly determined by the equilibrium configurations of hydrogen bonding within the polymer chains and between the polymer chains and water molecules. Actually, the exact causes of the typical viscoelasticity of PVA solutions are still a matter of investigation, although they are of particular interest not only because of their direct applications but also because of their fundamental role in our understanding of polymer segment–segment and segment–solvent interactions.

In particular, the Pn is a fundamental factor affecting the physical properties of PVA.<sup>15–17</sup> However, little has been reported on the rheological properties of PVA solutions in terms of Pn, regardless of the practical importance. Also, most of the publications have focussed on low concentration PVA solutions. At the same time, little is known about the thixotropy and creep behavior of PVA solutions from published work.<sup>12–18</sup> This article focuses on linear and nonlinear viscoelasticity including the thixotropy and creep process. We will report on the effect of Pn on the rheological properties of high concentration PVA solutions in relation to the diffusive motion of PVA chains in solutions.

## EXPERIMENTAL

### Materials

The degree of saponification of PVA (Sichuan Vinylon Company, Sichuan, China) was 99% and the average polymerization degree (Pn) was 1300, 1700, 2000, and 2400. To obtain reproducible results, the powder was vacuum dried at 70°C for 24 h before use. Deionized water was used for all procedures.

Specific viscosity and intrinsic viscosity ( $\eta$ ) were measured at 25°C using an Ubbelohde viscometer. The molecular weight distribution (MWD) was determined by gel permeation chromatography (Waters 150C) at 30°C. Table I shows the characteristic feature of PVA.

### Preparation of solutions

PVA was dissolved in water to give a 15 wt % solution by stirring at 110°C for 3 h; it was kept for 2 h

TABLE I  
Characteristics of PVA

Pn	$[\eta]$ (mL/g)	MWD
1300	0.57	3.0
1700	0.62	2.9
2000	0.91	2.9
2400	0.96	2.9

to ensure homogenization. As the conditions used to prepare solutions may affect the rheological response, the dissolution conditions such as temperature and shear rate were strictly controlled so as to be constant for each sample, to obtain good reproducibility of results. An abbreviation, PVA-X, is adopted to characterize the polymer solution, where X represents the polymer Pn. For example, PVA-20 represents a PVA solution with a Pn of 2000.

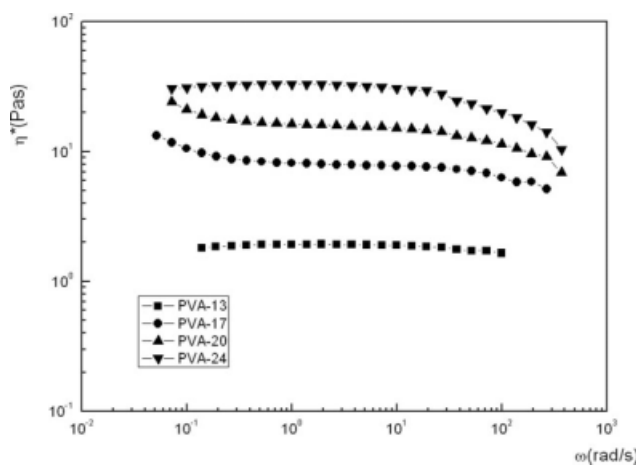
### Rheological measurements

The rheological properties of PVA solutions were measured by a controlled stress rheometer RS 300 (Thermo Haake) at 30°C. A parallel plate geometry was adopted, in which the diameter and gap were 35 and 1 mm, respectively. The rheometer was equipped with a temperature control unit (TC 501) that was calibrated to give a known, constant temperature in the sample chamber. Before testing, the specimens were held for 15 min to eliminate thermal and shear histories. The frequency sweep tests were carried out in an oscillatory mode range from 0.05 to 500 rad/s. The strain level was determined in the strain sweep test so that all measurements were carried out within the linear viscoelastic regime.

The creep and recovery behavior were investigated. A constant stress of 5 Pa was applied, maintained for 50 s, and then suddenly removed. A hysteresis loop test was used to study the thixotropy of the materials. The shear rate was uniformly increased from 0.5 to 100 s<sup>-1</sup> for 1 min and then decreased to 0.5 s<sup>-1</sup> over 1 min. Each measurement was repeated at least two or three times.

## RESULTS AND DISCUSSION

Figure 1 shows the complex viscosity ( $\eta^*$ ) of PVA/water solutions with different values of Pn. The solutions of PVA with higher Pn gave rise to greater values of the complex viscosity at a given frequency. Over the frequency range examined, PVA-17, PVA-20, and PVA-24 solutions show non-Newtonian flow behavior, which may result from the heterogeneity associated with localized gel formation, in which the molecules are arranged along the shear force direction. The complex viscosity of PVA-17 and PVA-20 solutions decreased gradually with



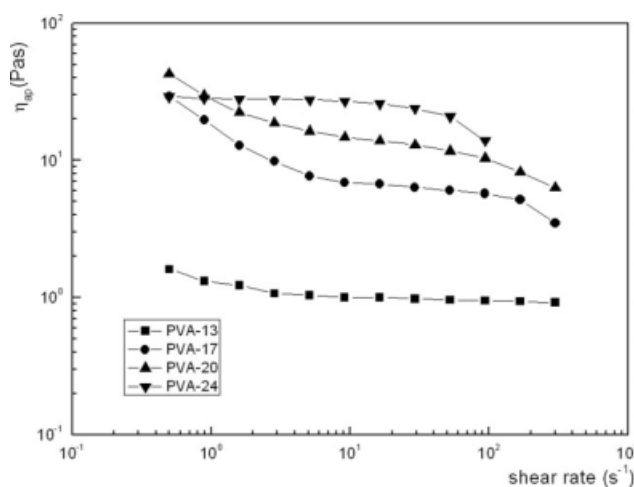
**Figure 1**  $\eta^*$  curves of PVA with different Pn solutions in water at 30°C.

increase of frequency up to 0.5 rad/s. That is, the hydrogels formed are so soft that they are easily destroyed and deformed even by low shear.<sup>19</sup> For the PVA-17, PVA-20, and PVA-24 solutions a rather significant decrease of complex viscosity with increase of frequency was observed above 50 rad/s. This shear thinning behavior observed at high frequency is ascribed to the occurrence of a shear-induced phase separation. The phase separation condition of the polymer solutions were determined by monitoring the sharp drop of measured viscosity during the increase of frequency.<sup>11,14,20</sup> However, a different behavior was observed for the PVA-13 solution, which exhibited almost Newtonian character over the frequency range examined. It may be that the network strand is a Gaussian chain and the number and the lifetime of the crosslink points are not affected by the flow.<sup>21</sup> Comparison of the viscosity curves in Figure 1 indicates two critical values of Pn. One is between 1300 and 1700 and the other one is around 2000–2400. The change in the internal structure of the molecules occurs at these points. This suggests that polar interactions through hydroxyl groups have significant effects on the flow properties of PVA. Thus, PVA solutions in water have been proved to be rheologically heterogeneous.

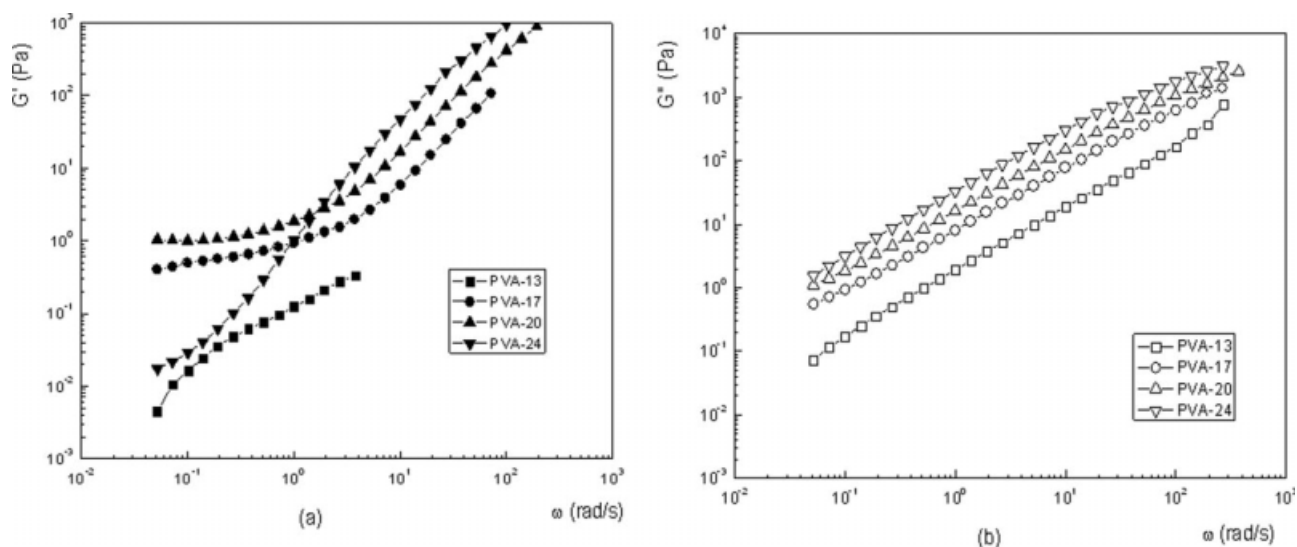
The shear viscosity ( $\eta_{sp}$ ) of PVA/water solutions was also measured, and viscosity curves are shown in Figure 2. PVA-17, PVA-20, and PVA-24 solutions also show non-Newtonian flow behavior. However, PVA-13 shows shear thinning behavior compared with Figure 1. The non-Newtonian behavior might be explained by the fact that orientation of molecular segments is brought about by the flow field. In PVA solutions with a Pn lower than 2400, as the Pn is increased, the extent of shear thinning is increased. This may imply PVA chain with higher Pn develop molecular orientation more easily by shear. Compared with dynamic shearing, a greater extent of

shear thinning of PVA solutions under steady shear is found in Figure 1. Figure 2 reveals that PVA solutions develop molecular orientation more easily by steady shear. It is also worth mentioning that the shear viscosity of PVA-24 is lower than PVA-20 at low frequency, where the crossover of shear viscosity occurs at  $1 \text{ s}^{-1}$ . The results indicate that the value of Pn has a significant influence on the viscoelastic properties of PVA/water solutions.

According to molecular theories, the perfectly homogeneous and isotropic melts and solutions of polymers give a slope of 2 on the logarithmic plot of storage modulus ( $G'$ ) against frequency and a slope of 1 on the logarithmic plot of loss modulus ( $G''$ ) against frequency in the terminal zone.<sup>22</sup> However, PVA solutions do not give theoretically predicted values of the slope but give curves with slopes less than the predicted values at 30°C, as shown in Figure 3. The heterogeneity of the solution systems is responsible for this deviation. This phenomenon can be explained by the physical aggregation of PVA molecules on the molecular level through polar interactions, including hydrogen bonding. All solutions showed increasing values of  $G'$  and  $G''$  with frequency ( $\omega$ ). In Figure 3(a), the value of  $G'$  increases when Pn increases from 1300 to 2000, and an abrupt increase in  $G'$  is found between 1300 and 1700. This increase of  $G'$  is most certainly due to the gradual increase of the inter- and intra-chain hydrogen bonding and hence the increase in interactions and entanglements between the PVA chains. It is generally agreed that the formation of a physical gel from a polymer solution is the result of physical crosslinking of the intermolecules in solution and it is presupposed to be a contact or collision of polymer chains.<sup>6,23</sup> The PVA-24 solution shows very complicated and unusual behavior. In the low-frequency range, the  $G'$  of PVA-24 is only little higher



**Figure 2** Shear viscosity of PVA with different Pn solutions in water at 30°C.



**Figure 3** Storage and loss moduli of PVA solutions with different Pn at 30°C: (a) filled symbols, storage; (b) open symbols, loss.

than PVA-13, but becomes the highest in the high-frequency range. This low value of  $G'$  for PVA-24, is mostly due to the disruption of interchain hydrogen bonding and the consequent decrease of the associations between polymer chains. An increase of hydrogen bonding, both intrachain and between PVA chains and water molecules, is anticipated when the Pn is higher than 2000.

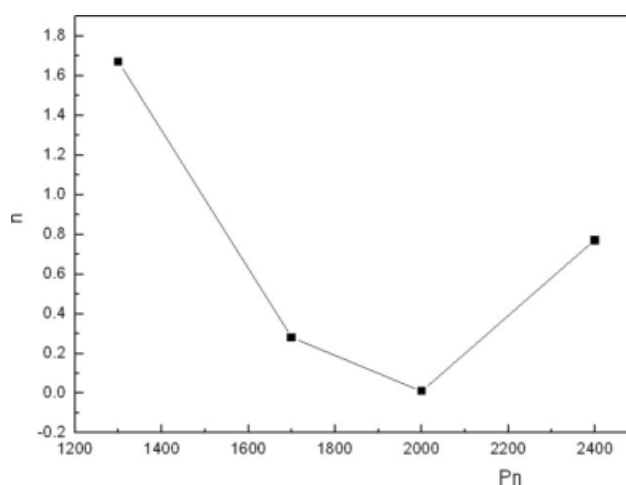
This result showed that the decrease of  $G'$  of the PVA solution with higher Pn can be attributed to the formation of greater intramolecular hydrogen bonding cohesive entanglement. However, a sharp increase of  $G'$  with increase of  $\omega$  was obtained for PVA-24. This is because the shear-induced hydrogel structure formed through hydrogen bonding becomes stronger for PVA-24 solution compared with other PVA solutions. The variation of the extent of hydrogen bonding, for the inter and intrachain and solute-solvent hydrogen bonding, is significantly affected by the value of Pn, and thus the resulting rheological properties of PVA solutions are also influenced.

The slope on the logarithmic plot of  $G'$  against  $\omega$  is called the viscoelastic exponent ( $n$ ).<sup>24–26</sup> The variation of  $n$  for PVA solutions with different values of Pn is shown in Figure 4. The value of  $n$  has been reported to decrease with increasing entanglement density in entangled polymer solution systems. However, in nonentangled systems, the entanglement effect rarely has any influence on  $n$ .<sup>27,28</sup> The value of  $n$  decreases monotonically with increasing Pn from 1300 to 2000 and we observe, especially at low Pn, that  $n$  falls off quickly with increasing Pn. This probably suggests that the entanglement effects reduce the value of  $n$ . However, the value of  $n$  for PVA-24 is much higher than that for PVA-20. It is

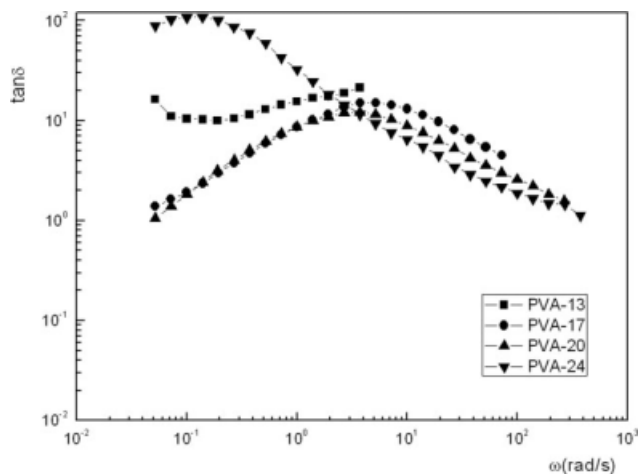
expected that the phase separation becomes pronounced at higher Pn for PVA solutions when the inter hydrogen bonding is reduced and in turn, the solute-solvent hydrogen bonding has increased.

The value of the loss tangent ( $\tan\delta$ ) is a quantitative measure of a solid-like, elastic body or a liquid-like, viscous fluid in a system. In principle, the fluid character is dominant when  $G''$  is greater than  $G'$ , and the solid character is dominant when  $G'$  is greater than  $G''$ .<sup>29</sup> Consequently, plotting  $\tan\delta$  against the frequency offers information on the phase change with the shear rate.

Figure 5 presents a plot of  $\tan\delta$  for PVA solutions in water at 30°C against the frequency. Over the frequency range examined, all the PVA solutions exhibit fluid character. In the low-frequency range (<10 rad/s), PVA-13, PVA-17, and PVA-20 solutions



**Figure 4** Viscoelastic exponent ( $n$ ) of PVA solutions with different Pn at 30°C.



**Figure 5** Loss tangent of PVA with different Pn solutions in water at 30°C.

show an increase in  $\tan\delta$  with frequency; that is the hydrogels formed at rest are so soft that they are easily destroyed and deformed even by low shear. The  $\tan\delta$  of these three PVA solutions then show a decrease with further increase of frequency. For PVA-24 solution, the value of  $\tan\delta$  initially increases with frequency up to 0.1 rad/s, then, in contrast, decreases continuously over the frequency range 0.1–500 rad/s. Shear deformation causes the partial orientation of polymer molecules. The molecular orientation favorably affects polar interactions because of reduced chain mobility. Consequently, the solutions exhibit reduced values of  $\tan\delta$ . Some oriented gel structure would be developed above a critical shear rate, which increases with increasing Pn. This suggests that Pn has a drastic impact on the buildup of aggregated structures formed through shearing.

For polymeric systems, in which some pseudos-structures are involved, the relaxation time ( $\lambda$ ) under dynamic shear can be calculated by eq. (1).<sup>30</sup>

$$J' = G'/([\eta^*]w)^2 = \lambda/[\eta^*] \quad (1)$$

in which,  $J'$  and  $\eta^*$  are the complex compliance and complex viscosity, respectively. If there is some molecular order or physical structure, a much longer relaxation time is expected. Figure 6 shows the variation of the relaxation time of PVA solutions at 30°C for several values of Pn plotted against frequency. As predicted, the relaxation time decreases as the shear rate increases. Like other rheological properties such as modules and loss tangent, the value of Pn has a strong influence on the relaxation time of the PVA solutions for the different states of hydrogen bonding. In the low-frequency range, PVA-17 and PVA-20 have nearly the same values of relaxation time. Also, the relaxation time of PVA-24 is lower than PVA-13. However, the relaxation time

increases with Pn in the high-frequency range. The increase of relaxation time represents the gradual decrease of chain mobility of molecules resulting from restriction between molecules by intermolecular interaction. This also suggests that the shear-induced gelation property of PVA solutions becomes stronger at higher Pn.

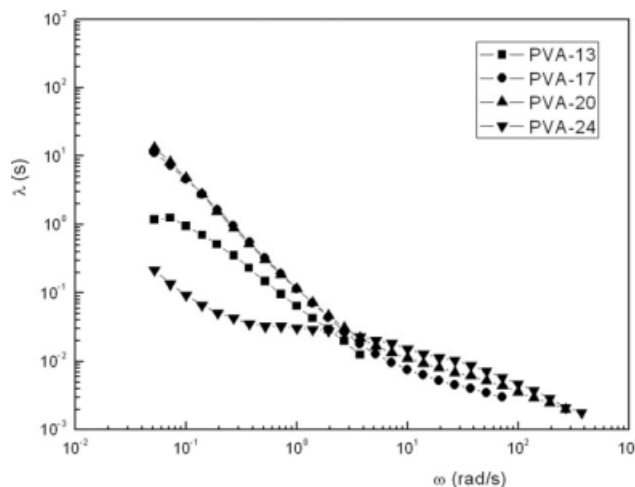
Creep and recovery testing is a good test method for viscoelasticity, it allows one to differentiate well between the viscous and elastic responses of a test specimen. During the creep test of viscoelastic fluids the stress applied will cause a transient response, including elastic and viscous contributions. It is the advantage of the following recovery phase after the release of the applied stress that it separates the total strain into the permanently maintained viscous part and the recovered elastic part.<sup>31,32</sup>

In a creep test a constant stress ( $\tau$ ) is assigned and the time-related strain ( $\gamma$ ) is measured. These are mathematically related by<sup>33</sup>:

$$\gamma(t) = J(t) \cdot \tau \quad (2)$$

where  $J(t)$  is the time-related compliance. Relatively little attention has been paid to the creep response, which can provide insight into the mechanistic origin of the flow of PVA solutions. Figure 7 shows the creep and recovery curves for PVA solutions with different values of Pn.

PVA-13 solution behaves as a purely viscous material, deforming steadily under stress. No recovery takes place after the stress is removed. In contrast, the creep curves of PVA-17 and PVA-20 comprise three parts: the instantaneous compliance, the retardation compliance, and the viscous compliance, followed by a recovery process when the applied stress is removed. The viscoelastic response of the PVA solutions arises from the hydrogel structure in the



**Figure 6** Variation in relaxation time of PVA with different Pn solutions in water at 30°C.

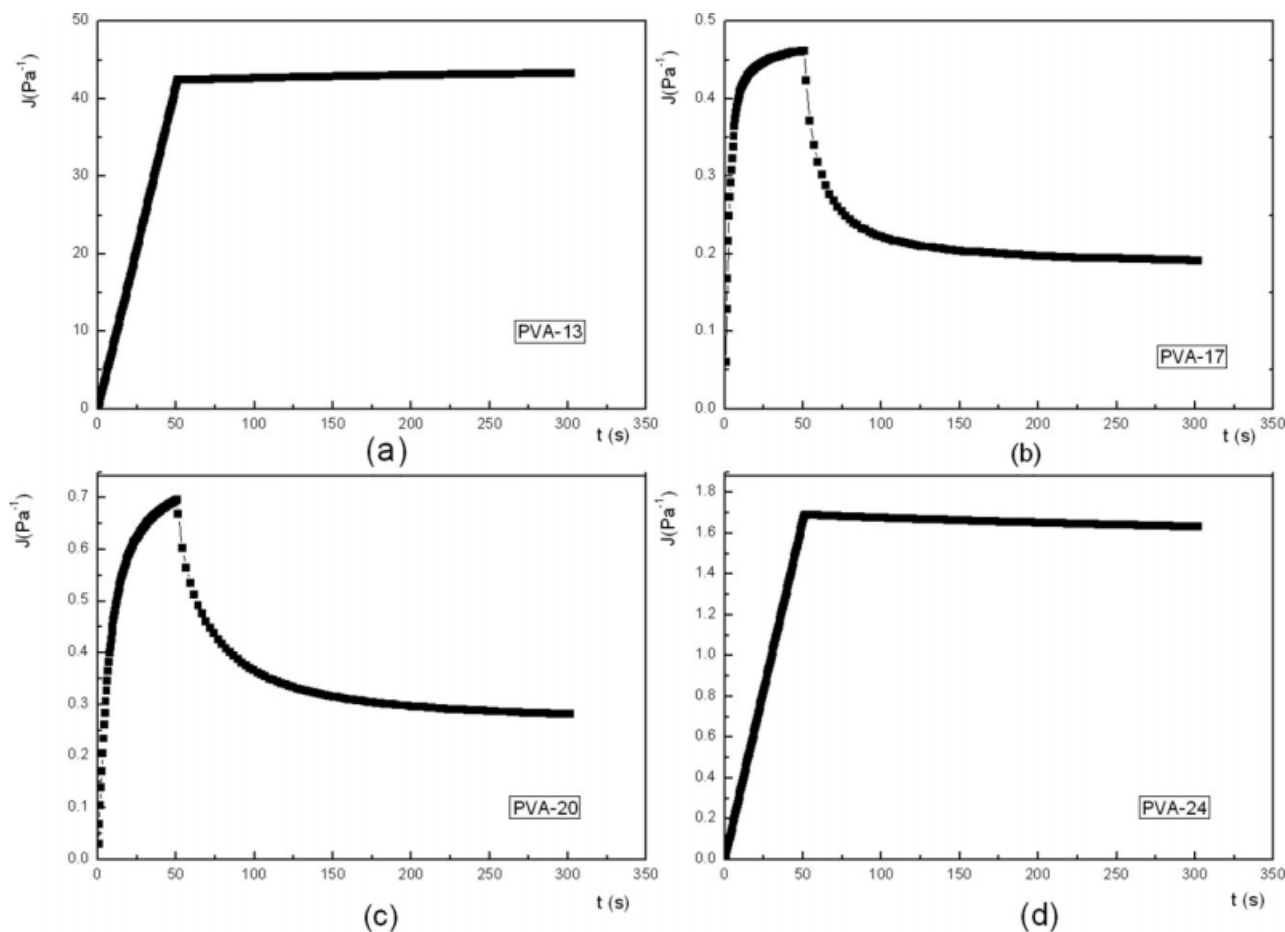


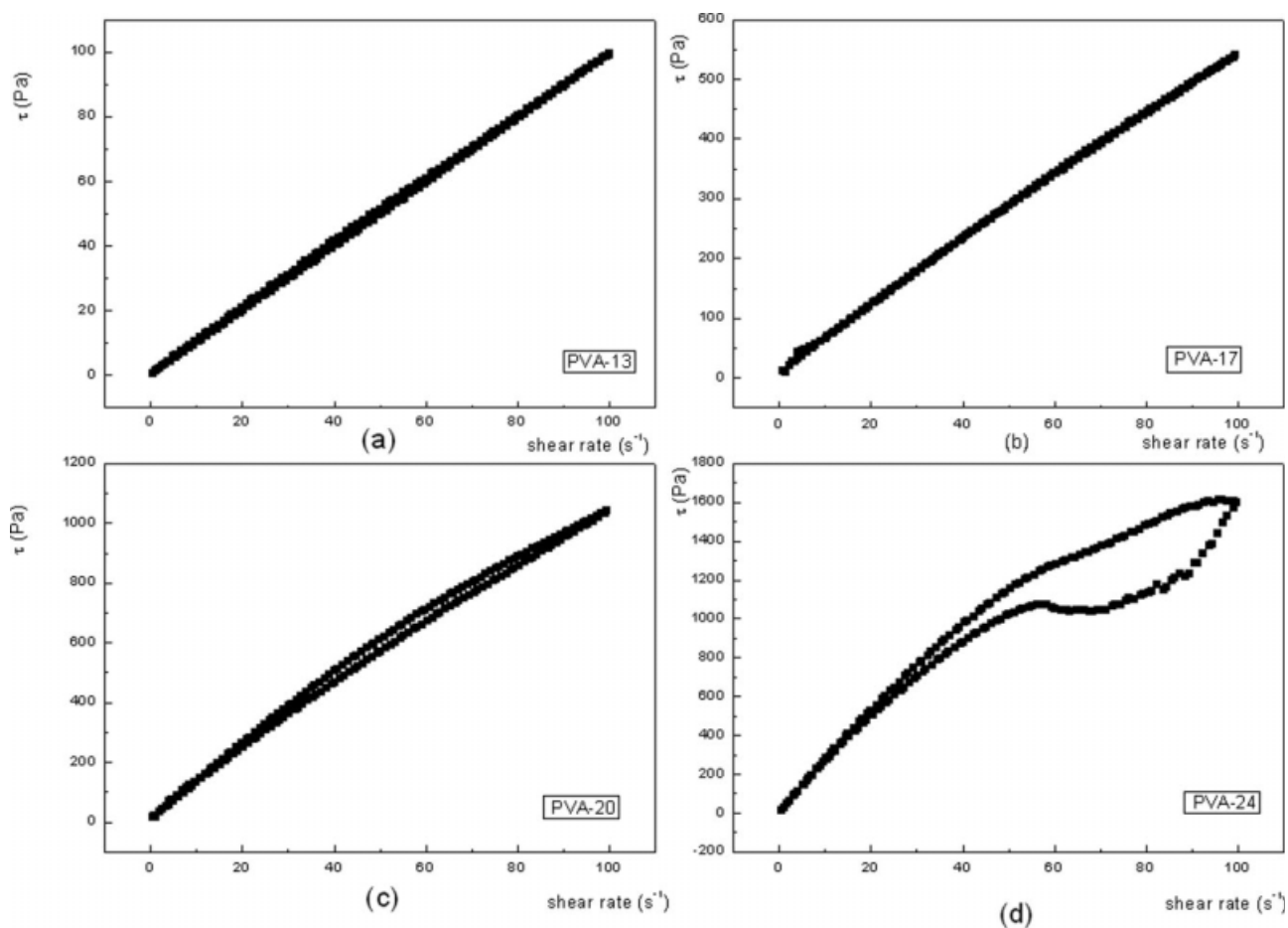
Figure 7 Creep and recovery curves of PVA solutions in water at 30°C at several Pn: (a)-(d).

solutions. From Figure 7(d), we see that the compliance increases linearly with time, and with negligible compliance recovery after removal of the stress. With increasing values of Pn to 2400, the hydrogel structure changes from one configuration to another. Thus the PVA-24 solution shows much less recovery compared with the PVA-20 solution. The results and the data of the creep and recovery testing for PVA solutions are shown in Table II. The results presented earlier also indicate the presence of two critical points, at which even slight changes in Pn could have a significant effect on the compliance recovery, among 1300–1700 and 2000–2400.

The thixotropic profiles of the PVA solutions are shown in Figure 8. These curves are typical of a Bingham pseudoplastic system. The PVA solutions exhibit Bingham plastic behavior and also show thixotropic shear thinning characteristics. The yield values are obtained by extrapolation of the linear portion of the shear stress–shear rate curves to shear rate = 0, which is the critical stress that must be exceeded before the material starts flowing (Table III).<sup>34,35</sup> From Table II, the yield stress substantially increases with increase of Pn to 55.1 Pa for the PVA-24 solution, which is also an indicator of a net structure formed in the PVA solutions.

TABLE II  
The Creep Behavior of PVA Solutions in Water at Several Polymerization

Samples	Total compliance after 50 s of loading ( $\text{Pa}^{-1}$ )	Recoverable compliance after 200 s of unloading ( $\text{Pa}^{-1}$ )	Total compliance after 50 s of loading followed by 200 s of unloading ( $\text{Pa}^{-1}$ )	Compliance recovery percentage after 200 s of unloading (%)
PVA-13	42.43	0	42.43	0
PVA-17	0.462	0.268	0.194	58.0
PVA-20	0.695	0.408	0.287	58.7
PVA-24	1.690	0.049	1.641	2.9



**Figure 8** Thixotropy loop curves of PVA solutions in water at 30°C at several Pn.

The thixotropic area is determined for the PVA solutions (Table III). The area enclosed by the hysteresis loop indicates the degree of structure breakdown due to shearing. The results show an increase in thixotropy with PVA polymerization to 187  $\text{Pa s}^{-1}$  for 1300 and 16,290  $\text{Pa s}^{-1}$  for 2400. These results indicate that the thixotropic property of PVA solutions depends not only on the hydrogel structure but also on the relative strength of the hydrogen bonding existing between the polymer chains and water molecules, compared with that of the inter- and intra-chain hydrogen bonding.

**TABLE III**  
Thixotropy Behavior of PVA solutions in Water at Several Pn

Samples	Thixotropic area ( $\text{Pa s}^{-1}$ )	Yield stresses (Pa)
PVA-13	187	1.5
PVA-17	385	12.0
PVA-20	3117	24.2
PVA-24	16290	55.1

## CONCLUSIONS

Polymerization degree (Pn) proves to have a profound influence on the viscoelastic properties of PVA solutions. Compared with dynamic shearing, a greater degree of shear thinning of PVA solutions under steady shear is found, which reveals that PVA solutions develop molecular orientation more easily by steady shear. A sharp increase of  $\eta^*$  and  $G'$  is found when the value of Pn is higher than 1300. This might be explained by the fact that the higher the Pn, the greater the intermolecular hydrogen bonding in the PVA solutions. The PVA-24 solution exhibited very unusual rheological behavior, showing very low  $G'$  in the low  $\omega$  and the greatest rate of increase of  $G'$  with  $\omega$ , caused by a disruption of the interchain hydrogen bonding and formation of more intrachain and PVA–water hydrogen bonding. The data for the viscoelastic exponent of the PVA solutions also gives the same results. With increase of Pn to 2000 at fixed PVA concentration, the elastic response increases, and greater compliance recovery ensures. For PVA-24 solutions only 3.5% of the

compliance recovery is observed. PVA solutions shows thixotropic shear thinning behavior and high Pn leads to a higher yield stress and shear stress. From the data of the relaxation time of the PVA solutions, we can conclude that PVA solutions with higher Pn develop hydrogel structure more easily by shearing. The rheological properties of aqueous PVA solutions, investigated in this study, are mainly determined by the equilibrium configurations of hydrogen bonding within the polymer chains and between the polymer chains and water molecules. This equilibrium can be varied by changing the molecular weight.

## References

1. Herrmann, W. O.; Heahnel, W. Ger. Pat. 450.286 (1924).
2. Shiomi, T.; Nishioka, S.; Tezuka, Y.; Imai, K. *Polymer* 1985, 26, 429.
3. Pant, R. P.; Rashmi, R. M.; Negi, P. S.; Ravat, K.; Dhawan, U.; Gupta, S. K.; Suri, D. K. *J Magn Magn Mater* 1995, 149, 10.
4. Lewandowska, K.; Staszewska, D. U.; Bohdanecky, M. *Eur Polym J* 2001, 37, 25.
5. Lee, J.; Lee, K. J.; Jang, J. *Polym Test* 2008, 27, 360.
6. Liu, M.; Cheng, R.; Wu, C.; Qian, R. *J Polym Sci Part B: Polym Phys* 1997, 35, 2421.
7. Li, H.; Zhang, W.; Xu, W.; Zhang, X. *Macromolecules* 2000, 33, 465.
8. Lyoo, W. S.; Kim, B. C.; Ha, W. S. *Polym J* 1998, 30, 424.
9. Choi, J. H.; Kim, B. C.; Blackwell, J.; Lyoo, W. S. *Macromolecules* 2001, 34, 2964.
10. Takigawa, T.; Urayama, K.; Masuda, T. *J Chem Phys* 1990, 93, 7310.
11. Shibayama, M.; Uesake, M.; Inamoto, S.; Mihara, H.; Nomura, S. *Macromolecules* 1996, 29, 885.
12. Choi, J. H.; Ko, S. W.; Kim, B. C.; Blackwell, J.; Lyoo, W. S. *Macromolecules* 2001, 34, 2964.
13. Lee, E. J.; Dan, K. S.; Kim, B. C. *J Appl Polym Sci* 2006, 101, 465.
14. Briscoe, B.; Luckham, P.; Zhu, S. *Polymer* 2000, 41, 3851.
15. Lyoo, W. S.; Kim, J. H.; Choi, J. H.; Kim, B. C.; Blackwell, J. *Macromolecules* 2001, 34, 3982.
16. Lyoo, W. S.; Kim, J. H.; Koo, K.; Lee, J. S.; Kim, S. S.; Yoon, W. S.; Ji, B. C.; Kwon, I. C.; Lee, C. J. *J Polym Sci Part B: Polym Phys* 2001, 39, 1263.
17. Abd El-Kader, K. M.; Oradi, A. S. *Polym Test* 2002, 21, 591.
18. Lee, S. J.; Kwak, J. W.; Kim, H. D.; Jeon, H. Y.; Kim, J. H.; Yoon, W. S.; Lyoo, W. S. *Polym Compos* 2004, 12, 561.
19. Lyoo, W. S.; Seo, I. S.; Yeum, J. H.; Yoon, W. S.; Ji, B. C.; Kim, B. S.; Lee, S. S.; Ki, B. C. *J Appl Polym Sci* 2002, 86, 463.
20. Tam, K.; Wu, R.; Pelton, R. *Polymer* 1992, 33, 436.
21. Inoue, T.; Osaki, K. *Rheol Acta* 1993, 32, 550.
22. Song, S. I.; Kim, B. C. *Polymer* 2004, 45, 2381.
23. Liu, M.; Cheng, R.; Qian, R. *Acta Polym Sinica* 1996, 2, 121.
24. Muthukumar, M. *Macromolecules* 1989, 22, 4656.
25. Scanlan, J. C.; Winter, H. H. *Macromolecules* 1991, 24, 47.
26. Izuka, A.; Winter, H. H.; Hashimoto, T. *Macromolecules* 1992, 25, 2422.
27. Nijenhuis, Kt.; Winter, H. H. *Macromolecules* 1989, 22, 411.
28. Hodgson, D. F.; Amis, E. J. *J Non-Cryst Solids* 1991, 131, 913.
29. Winter, H. H.; Chambon, F. J. *J Rheol* 1986, 30, 367.
30. Wissburn, K. F.; Griffin, A. C. *J Polym Sci Polym Phys Ed* 1982, 20, 1835.
31. Gnip, I. Y.; Vaitkus, S.; Kersulis, V.; Vejelis, S. *Polym Test* 2008, 27, 378.
32. Chotpattananont, D.; Sirivat, A.; Jamieson, A. M. *Polymer* 2006, 47, 3568.
33. Schramm, G. *A Practical Approach to Rheology and Rheometry*, 1st ed.; Hakke Press: Germany, 1994; pp 93–206.
34. Kattige, A.; Rowley, G. *Int J Pharm* 2006, 316, 74.
35. Duraigaj, R.; Ekere, N. N.; Salam, B. *J Mater Sci Mater Electron* 2004, 15, 677.