Viscometric Investigation of Intramolecular Hydrogen Bonding Cohesional Entanglement in Extremely Dilute Aqueous Solution of Poly Vinyl Alcohol

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ABSTRACT: An investigation of influence of cryogenic treatment on extremely dilute aqueous solution of poly(vinyl alcohol) (PVA) was performed by viscometry. The solution was frozen in liquid nitrogen or in a freezer at −25°C, then thawed at ambient temperature and concentrated by evacuation. The viscosity of the solution was measured using the dilute method. The experimental results indicated that the viscosity of the solution is related to *N,* the times of the freezing and thawing cycle, and the temperature for freezing. Undergoing a treatment of freezing and thawing, the viscosity of the solution is decreased, while it can be recovered the value of before the treatment as the solution had been heated at a high temperature. Thus, a conclusion may be obtained; that is, for an extremely dilute aqueous solution of PVA, which concentration is below C_{gel}, threshold concentration for gelation, an intramolecular hydrogen bonding cohesional entanglement can be formed by freezing as $N < 5$. However, in the case of $N > 5$, it not only formed an intramolecular hydrogen bonding but also produced an intermolecular hydrogen bonding. At the same time, the abnormal behavior of reduced viscosity of the solution in extremely dilute concentration region has been explained.
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INTRODUCTION

Studies on intermolecular hydrogen bonding crosslinking and physical gel of PVA have been extensively performed.[1–3] However, experimental and theorietical studies on intramolecular hydrogen bonding crosslinking and the critical behavior of viscosity of the polymer are few, although they are of particular interest not only because of their direct application but also because of their fundamental role in our understanding on polymer segment–segment and segment–solvent interactions. Cutler[4] et al. briefly studied the effect of adsorption on measurement of viscosity of very dilute solutions of PVA in the early 1950s. They found there was a definite decrease in the reduced viscosity at small value of circa 6×10^{-4} g/mL. Intramolecular chemical crosslinking of PVA was first treated by Kuhn[5] and co-workers. They obtained an expression for the decrease in the intrinsic viscosity as a function of the crosslinking

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number. Lately, Braun,[6] Arbogast,[7] and Gebben[8] also studied the subject successively and the obtained results are similar to that of Kuhn's. Several years ago, Takigawa[9,10] et al. examined the critical behavior of viscosity of the solution from PVA in a dimethyl sulfoide and water mixture solvent near the gelation point. According to the variation of viscosity of cooled solution and noncooled solution, they considered that PVA molecules will shrink, due to the formation of intramolecular hydrogen bonding, and the formation of PVA cluster by intermolecular hydrogen bonding is small in the low concentration region, although cluster formation by intermolecular hydrogen bonding is dominate in the high concentration region. However, systematic reports about intra- and intermolecular physical crosslinking of PVA are still lacking. In the previous article,[11] we reported the cryogenic gelation for PVA aqueous solution and found that for the gelation process there were three distinct regions of concentration bounded by two threshold concentrations. C_{gel} and C^*_{gel}; their values are 5×10^{-5} and 6×10^{-2} g/mL, respectively. C_{gel} and C^*_{gel} were defined as the concentration started to form a gel, and the entire solution was gelatinized as a whole, respectively. No visible gel could be detected even upon repeated freezing and thawing for the extremely dilute solution of $C < 5 \times 10^{-5}$ g/mL, while the entire solution was gelatinized as a whole in the high concentration region of $C = 6 \times 10^{-2}$ g/mL. To explore the influnce of cryogenic treatment on concentrated solution of PVA, recently, we studied the intermolecular hydrogen bonding cohesional entanglement and physical gels from cryogenic aqueous solution of PVA.[12] It is generally agreed that the formation of a physical gel from a polymer solution is the result of the physical crosslinking of the intermolecules in solution and it is presupposed to be a contact or collision of polymer chains. Although no visible gel could be detected for the cryogenic aqueous PVA solution whose concentration was below C_{gel}, the macromolecular coils will contract because of freezing, so the some groups or pendents on the chain will be close to each other; thus, it may be concluded that the intramolecular hydrogen bonding will be formed in extremely dilute solution and its structure should be similar to that of intermolecular hydrogen bonding. We may also infer that the degree of forming intramolecular hydrogen bonding should be related to the temperature for freezing, as well as times of the freezing and thawing cycle. Macromolecular size will change if intramolecular hydrogen bonding was formed; at the same time, it reflects certainly property of solution, such as viscosity of solution. In this article we will try to explore the influnce of cryogenic treatment on the structure of the PVA chains and the property of the solution.

EXPERIMENTAL

Material

Poly(vinyl alcohol) (PVA) sample employed in this work was a commerical product. The degree of polymerization (DP) of PVA range is from 2400 to 2500, and the degree of saponifaction (DS) is from 98.0 to 99.0 mol %. The molecular weight of the sample is 1.14×10^5 g/mol, determined by static light scattering.

Solution Preperation

A known amount of PVA was dissolved in distilled water under reflux for 2.5 h and prepared in a soulution of 1×10^{-2} g/mL, then prepared in a solution of 1000 mL with 3×10^{-5} g/mL and transfered into a flask of 1000 mL. The flask was immersed into liquid nitrogen for 30 min or placed in a freezer at -25°C for 24 h. The flask was taken out of the liquid nitrogen container or freezer and thawed for 24 h at 25°C. This process was called a one-time freezing and thawing cycle, namely $N = 1$.

The experimental result show that the variation of viscosity of the solution with 3×10^{-5} g/mL for nonfrozen and frozen was very small. To accurately observe the effect of the freezing treatment on the viscosity of the solution, we exploried, for the first time, a method for concentrating, that is, a solution underwent a treatment of freezing and thawing that was concentrated by evacuation at ambient temperature until it came to the desired concentration.

Viscosity Measurement

The viscosity of the concentrated solution whose concentration was calculated from the amount of the removed water measured at 30 ± 0.03°C using a Ubbelohde type capillary viscometer. The measured concentration range was from 2×10^{-5} g/mL to 1.4×10^{-3} g/mL. The relative viscosity was from 1.001 to 1.14. The elution time of distilled water for the clean viscometer was 310.78 s at

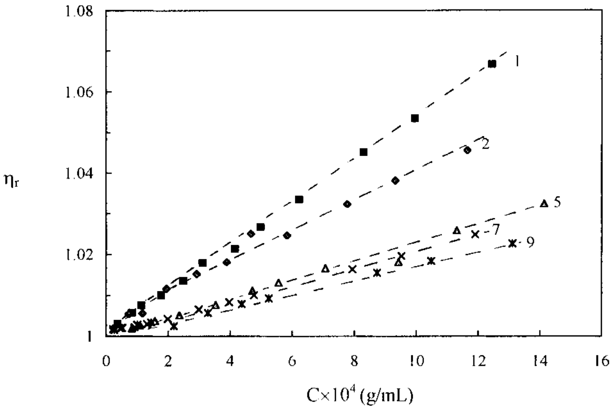

Figure 1. The variation viscosity of aqueous solution of PVA with the times of freezing and thawing cycle. The numbers denote the times of freezing and thawing cycle. Dotted lines, calculated according to the equation (4).

30°C, while it was 311.43 s for the viscometer cleaned with distilled water at ambient temperature after it contacted the solution of the PVA. The correction for kinetic energy and drainage was neglected because the viscometer has much longer elution time.

Laser Light Scattering Measurement

Nonfrozen and frozen PVA solutions of C = 1 × 10^{-6} and 1 × 10^{-4} g/mL were used for laser light scattering. All solutions were filtered by using a 0.5 μm Millipore filter to remove dust. A commercial LLS spectrometer (ALV/SP-150 equipped with an ALV- 5000 muti-τ digited correlator) was used with a solid-state laser (ADLAS DPY425 II, output power ≈ 400 MW at $\lambda = 532$ nm) as the light source. By placing a polarizer in front of the detector, we measured only the vertically polarized scattering light. The scattering angle for the solution of $C = 1 \times 10^{-6}$ and 1×10^{-4} g/mL is 15° and 30°, respectively. All experiments were done at 25.0 ± 0.1°C.

RESULTS AND DISCUSSION

According to the common definition,[10,13] relative viscosity η_r, specific viscosity η_{sp}, and reduced viscosity η_{sp}/C of a solution are expressed as follows,

$$\eta_r = \eta/\eta_o \tag{1}$$

$$\eta_{sp} = (\eta - \eta_o)/\eta_o \tag{2}$$

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C \tag{3}$$

where η and η_o are viscosity of solution and solvent, respectively. $[\eta]$, k' and C are intrinsic viscosity, Huggins the constant and concentration of solution, respectively.

Figures 1 and Figure 2 show the variation of relative viscosity as well as reduced viscosity with times of the freezing and thawing cycle. As can be seen from these figures, the viscosity of the PVA solution that underwent cryogenic is lower than that of the nonfrozen solution. We also noticed that the more times of freezing and thawing, the lower the viscosity will be. On the other hand, the variation of viscosity with the times of freezing and thawing is smaller; $N > 5$. This is identical with that of the property of swelling and dissolution for PVA physical gels.[12] The viscosity decreases with increasing the times. This may be caused by the following two aspects: (1) as mentioned above, we did not observe intermolecular hydrogen bonding to PVA aqueous solution with the concentration of a below-gelation threshold C_{gel} as $N < 5$; however, it is probable that the intramolecular hydrogen bonding can be formed even at that concentration because the macromolecular chains may be became contracted or in a crumpled compact state from an extended coil. In other words, the conformation of the macromolecules in solution will be changed by a cryogenic treatment. Thus, the intramolecular hydrogen bonding between pendent hydroxyl groups on the macromolecular chain might be produced, and it decreases size of the molecules. Consequently,

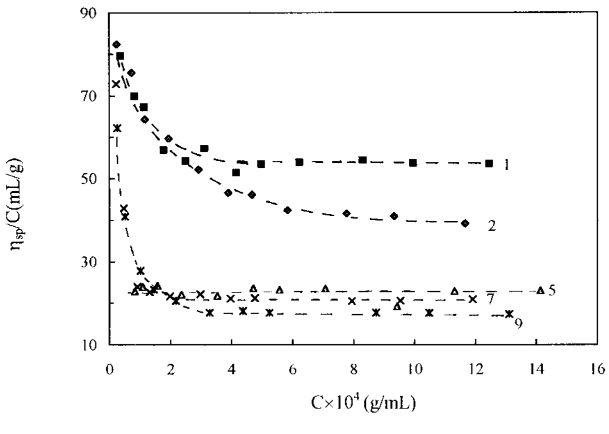

Figure 2. The variation of reduced viscosity of aqueous soution of PVA with the times of freezing and thawing cycle. The numbers as Figure 1. Dotted lines: calculated according to the equation (5).

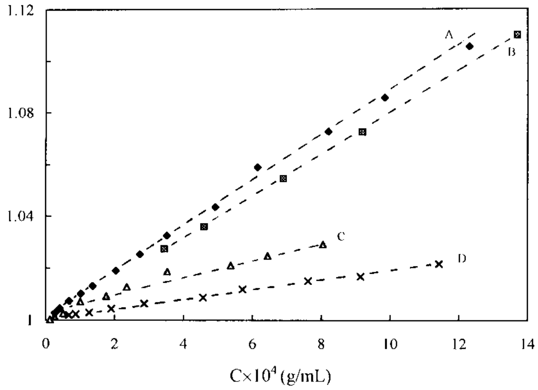

Figure 3. The variation of relative viscosity of aqueous solution of PVA with the temperature of freezing. A: Non-frozen solution; B: Heated for 2.5 h at 90 ~ 100°C after frozen 2 times in liquid nitrogen; C: Frozen 3 times at −25°C; D: Frozen 3 times in liquid nitrogen. Dotted lines: as Figure 1.

the viscosity of the solution is decreased. (2) Abbas et al. studied the effect of cryogenic treatment on the polystyrene solution and claimed that the long-chain macromolecules will suffer from degradation by freezing. This conclusion was reached from the results of viscometric and size exclusion chromatographic (SEC) measurements.[14,15] They considered that decreasing the solution viscosity and increasing the retention volume of SEC was the result of degradation of the macromolecular chain. Similarly, the viscosity of the PVA solution was decreased when it suffered from a cryogenic treatment, whether this is also caused by the degradation of PVA chain is unsure. To clarify this question, we heated the PVA solution that was frozen two times in liquid nitrogen for 2.5 h at 95–100°C, then concentrated it by evacuation at ambient temperature and measured its viscosity. The result showed that the viscosity was very close to that of the nonfrozen solution (see Fig. 3). This result showed that the decrease of the viscosity of the PVA solution after cryogenic treatment is only attributed to the formation of intramolecular hydrogen bonding cohesional entanglement instead of degradation of the PVA chains. Zimm and Stockmayer[16] calculated the dimension of a macromolecular coil. They found that the value of $(R_c/R_1)^3$ was 0.354, where R_c and R_1 was the mean square radius of gyration of a freely jointed cyclic chain having intramolecular cross-linkages and a linear chain, respectively. While the value of $[\eta]_N/[\eta]_o$ is from 0.532 to 0.167, corresponding to N from 1 to 9, where $[\eta]_o$ and $[\eta]_N$ is the intrinsic viscosity of the PVA solution nonfrozen and frozen N times, respectively. As we can see, the value estimated from the intrinsic viscosity of our work is close to that predicted by Zimm and Stockmayer in line with the mean square radius of gyration, at the same time, taking account R^3 and $[\eta]$ having the same of dimension; thus, it may confirm the above conclusion in other aspect.

To examine the stability of the intramolecular cohesional entanglement, the following experiments were done. First, determining the viscosity of the solution ($C = 1.4 \times 10^{-3}$ g/mL) that remained 1 month at ambient temperature after being frozen, the result showed that the viscosity is almost identical with that of the just-frozen and concentrated solution. Besides, the measurements of laser light scattering for the solution that remained for 4.5 h and 58 h at ambient temperature after being frozen were conducted; the results indicated the shape and position of the peaks for the sample remaining at different time is very close.

The above results demonstrated that the intramolecular cohesional entanglement structure formed by cryogenic treatment is stable at ambient temperature. However, it will be destroyed and back to the extended coil state at high temperature because of the destruction of intramolecular hydrogen bonding cohesional entanglement. That is the reason why the viscosity of the solution can recover the value from before the cryogenic treament when it was heated at a high temperature.

To reconfirm the results obtained by viscometric, laser light-scattering analysis was conducted. Figure 4 shows a line-width distribution Γ of PVA solution of $C = 1 \times 10^{-6}$ g/mL. As we can see from Figure 4, there exists only one peak either for the frozen or nonfrozen sample. However, the peak

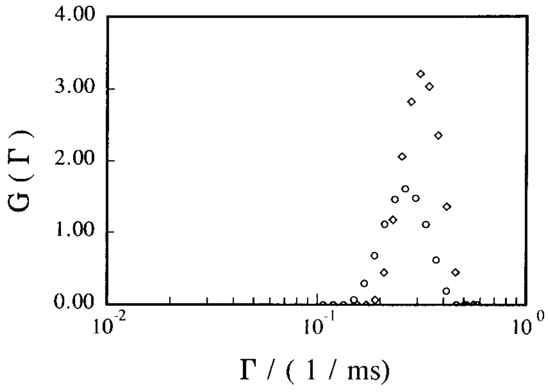

Figure 4. Line-width distribution of solution of $C = 1 \times 10^{-6}$ g/mL. Before freezing (○), freezing 1 time at −23°C (◇).

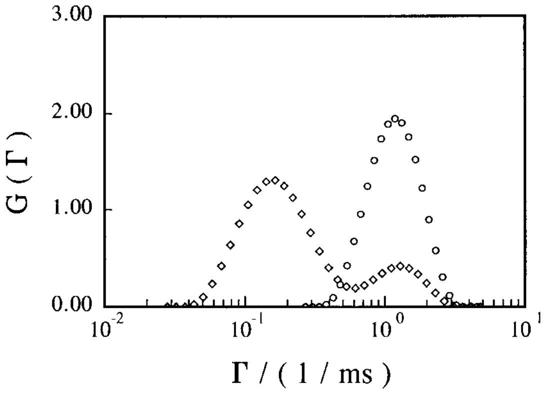

Figure 5. Line-width distribution of solution of C $= 1 \times 10^{-4}$ g/mL. Before freezing (○), freezing 3 times at −23°C (◇).

of the frozen sample is shifting at a higher Γ. The hydrodynamic radius, R_h is 15.0 nm and 13.3 nm for nonfrozen sample and frozen sample, respectively. This is attributed to the transition of macromolecular conformation from an extended coil to a collapsed state resulting from a formation of intramolecular hydrogen bonding cohesional entanglement. Figure 5 indicates a line-width distribution of PVA solution of $C = 1 \times 10^{-4}$ g/mL. In Figure 5 there exists only one peak for nonfrozen sample, while there appears two peaks for the frozen sample, and their position and shape are different from the nonfrozen one. The peak with a lower Γ is related to the intermolecular aggregates and entanglements; the other peak with a higher Γ may be caused by the intramolecular cohesional entanglements. The above results showed that only intramolecular cohesional entanglement will be formed and only single molecules exist for the extremely dilute solution. However, not only intramolecular but also intermolecular cohesional entanglement will be produced for the solution of $C > C_{gel}$ subjected to a cryogenic treatment. This is in agreement with the results of viscometric and gelation of the PVA solution performed by us before.[11]

Figure 6 shows variation of the intrinsic viscosity [η] with times of the freezing and thawing cycle. [η] was obtained on the basis of the method for data treatment in our previous article. The curve of [η] dropped off with increasing N at the early stage; however, [η] is almost independent of N as $N > 5$ (see Fig. 6). It is due to increasing of the numbers of intramolecular hydrogen bonding cohesional entanglement in the process of freezing and thawing; thus, the more numbers of intramolecular hydrogen bonding, the conformation of macromolecular chains will be more compact. As a result, the lower [η] will be. The numbers that are capable of forming intramolecular hydrogen bonding cohesional entanglement reach a limit value as $N = 5$, in this case, [η] does not vary even further freezing and thawing. The coil of PVA became a loose globular structure containing solvent inside of a coil after more freezing and thawing. Yet, This solvated globular structure is different with a real solid globule; of course, its hydrodynamic property is also different with a solid globule. Its size and viscosity of the solution should be larger than that of a solid globule because of the interaction of macromolecular chains and solvents inside the coil. The above results indicate that the number of intramolecular hydrogen bonding in the PVA solution subjected to a cryogenic treatment are related to the times of freezing and thawing. Mealwhile, it should also relate to the temperature for freezing. We may predict the lower the temperature of the crumpler coil, the lower viscosity will be. Figure 3 shows the variation of the relative viscosity with temperature for freezing. As we can see from Figure 3, the relative viscosity of solution frozen at −25°C is lower than that of the nonfrozen, while the relative viscosity of the solution frozen in liquid nitrogen is lower than that of the solution frozen at −25°C. This result is consistent with the above prediction.

We found that the PVA solution is a transparent liquid as $N < 5$, while small suspended particles can be observed as $N > 7$. However, these suspended particles disappear as the solution was heated. This phenomenon tells us that both compact conformation of polymer chains and the polymer aggregates formed by intermolecular hydrogen bonding occurs simultaneously even at C

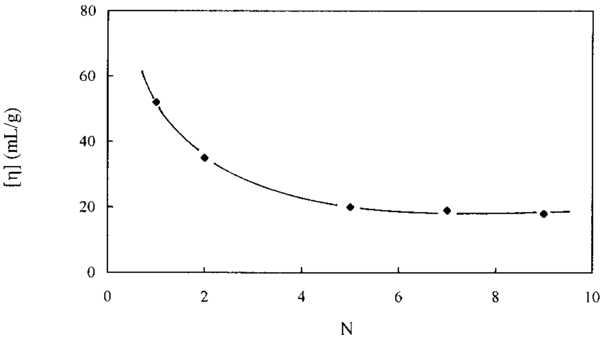

Figure 6. The variation of intrinsic viscosity of aqueous solution of PVA with the times of freezing and thawing cycle.

$< C_{\text{gel}}$ when the times of freezing and thawing is larger, for example $N > 5$; however, it is still predominant that intramolecular hydrogen bonds cohesional entanglement even in this case. To avoid effect of the suspended particles existing in solution on measurement of elution time, it is necessary that the frozen solution be filtrated before measurement of viscosity. The effect of filtration is negligible for the gel particles on the concentration because the number of gel particles observed as $N > 7$ is very small.

On the other hand, the concentration of PVA in the liquid phase will increase during the freezing process; that is to say, when water forms ice, the local concentration of PVA in the liquid phase will increase until the eutectic point is reached. However, our experimental results show that the fact that rapid freezing, for example, in liquid nitrogen, results in more intramolecular interactions than slow cooling suggests that this is not important for PVA solutions.

We have noticed that the variation of reduced viscosity with the concentration was not a strictly linear down to extremely dilute solution, while all of curves of reduced viscosity plotted against concentration are turned upward in an extremely dilute concentration region in Figure 2. As mentioned above, if the viscometer-measured PVA solution was cleaned only by repeating with distilled water at ambient temperature, the elution time of distilled water increased about 0.21% compared with that of cleaning by boiling water. On the other hand, the wettability of the inner wall surface of viscometer to water was different. If the viscometer was cleaned by boiling water, the elution time of distilled water and wettability can recover to its original state. We considered there was a positive connection between the above phenomenon and characteristic of curves in Figure 2; that is, polymer chains were firmly adsorbed on the viscometer wall surface in the process of measurement for the solution and may have formed a polymer layer; thus, elution time of the solvent was decreased. Consequently, the reduced viscosity of the solution shows abnormal behavior. The relationship between reduced viscosity and the concentration of solution is not strictly a linear down to extremely dilute solution, with either an upward or downward turn. This phenomenon was noticed by many investigators in the early 1950s.[4,17–21] Most of them considered that the concentration occurred as a turning of the critical concentration at which the physical contact of the polymer chain starts. However, the other held a contrary opinion-they believed the measurement of viscosity for extremely dilute solution demanded a rather high accuracy.[22,23] Furthermore, the reduction in radius of viscometer capillary and actual concentration of solution due to absorption of polymer from the solution may also influnce the result of measurement.[24–28] To explain abnormal behavior of reduced viscosity, someone proposed a hypothesis of adsorption, yet, it was short of a quantitative description. Lately, we explained systematic effect of adsorption on viscosity of extremely dilute solution of polymer. On the bases of a correction for adsorption, we derived equations for relative viscosity and reduced viscosity as follows:

$$\eta_r = (1 + [\eta]\,C)\,(1 + k\,C/(C_a + C)) \quad (4)$$

$$\eta_{sp}/C = [\eta]\,(1 + k\,C/(C_a + C)) + C/(C_a + C) \quad (5)$$

where $[\eta]$ is intrinsic viscosity. $k = (t_o(1) - t_o(0))/t_o(0)$, where $t_o(1)$ and $t_o(0)$ are elution time of solvent corresponding to $\theta = 1$ and $\theta = 0$. θ is the fraction of viscometer capillary wall surface covered by macromolecules. C_a is the concentration of solution as $\theta = 1/2$. The viscosities calculated by the above equations were shown by dotted lines in Figures 1 and 2. The result shows the value calculated is in good agreement with that of those measured. Thus, we considered that the abnormal behavior of reduced viscosity of the polymer solution in an extremely dilute concentration region is solely due to the adsorption of polymer chains on the viscometer surface.

CONCLUSIONS

The decreasing of viscosity and hydrodynamic radius R_h for extremely dilute aqueous PVA solution subjected to a cryogenic treatment is attributed to the transition of macromolecular conformation from an extended coil to a collapsed compact state resulting from a formation of intramolecular hydrogen bonding cohesional entanglement. This transition may be considered as a relaxation. It depends mainly on system temperature at other fixed conditions. The abnormal behavior of reduced viscosity of the PVA solution in an extremely dilute concentration region is due to absorption of macromolecules on the viscometer capillary wall.

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