

Effect of Emulsion Polymerization Conditions of Vinyl Acetate on the Viscosity Fluctuation and Gelation Behavior of Aqueous Poly(vinyl alcohol) Solution

WON SEOK LYOO,¹ SUNG MIN LEE,¹ KANG KOO,¹ JOON-SEOK LEE,¹ HAN DO GHIM,² JAE PIL KIM,² JINWON LEE,³

¹ School of Textiles and Regional Research Center, Yeungnam University, Kyongsan 712-749, South Korea

² School of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea

³ Department of Chemical Engineering, Seoul 139-701, South Korea

Received 1 August 2000; accepted 2 December 2000

ABSTRACT: Poly(vinyl alcohol) (PVA) was prepared by emulsion polymerization of vinyl acetate (VAc) at 40, 50, and 60°C. PVAs of various molecular parameters were dissolved in water at concentrations of 3, 5, and 7% (g/dL) and aged at 30 and 60°C. The effects of the molecular weight and polymerization temperature on the viscosity fluctuation and gelation behavior of aqueous PVA solutions were investigated. Viscosity was increased with increasing molecular weight when other parameters were held the same. PVA of superior molecular regularity due to the lower polymerization temperature of VAc had higher relative viscosity. Viscosity and its fluctuation of PVAs with aging time varied with the polymerization temperature of the precursors, concentration of the aqueous solutions, and aging time. For PVA with a number-average degree of polymerization of 2800 prepared from poly(vinyl acetate) polymerized at 40°C, a sharp increase in viscosity was observed after 500 min of aging at a concentration of 7%. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1897–1902, 2001

Key words: PVA; molecular parameters; viscosity; gelation; aging

INTRODUCTION

Poly(vinyl alcohol) (PVA) has been used mainly in aqueous solutions for its particular water solubility with high chemical stability. PVA is one of the first synthetic polymers to be produced on a large scale commercially and has been developed and utilized in various industrial applications, including as an emulsifier and stabilizer for colloid suspensions, a sizing agent and coating in the textile and paper industry, and an adhesive.¹ Moreover, PVA hydrogel has been paid attention to for its

good biocompatibility and usability in various biomedical applications^{2–5} such as in embolic materials, artificial kidney membranes, skin replacement materials, and drug-delivery systems. The control and rationalization of the origins of the viscosity of aqueous PVA solutions are naturally important in these applications.⁴ Hydrogels can be obtained from aqueous PVA solutions by adopting several methods such as photocrosslinking,^{6–8} freezing and thawing,^{9–12} irradiation,^{13–15} chemical crosslinking,¹⁶ and aging. Among these techniques, aging is most largely dependent on the molecular parameters of PVA, such as molecular weight, stereoregularity, 1,2-glycol contents, and degree of saponification.

PVA cannot be prepared from its structural monomer, vinyl alcohol (VA), for the instability of

Correspondence to: W. S. Lyoo (wslyoo@yu.ac.kr).
Contract grant sponsor: Yeungnam University.

Journal of Applied Polymer Science, Vol. 82, 1897–1902 (2001)
© 2001 John Wiley & Sons, Inc.

VA. Therefore, saponification of precursors, such as poly(vinyl acetate) (PVAc), is an unavoidable process. Molecular parameters of PVA can be effectively controlled due to these separated preparation methods: polymerization and saponification.^{17–23} Complete saponification of the precursor possibly results in PVA of a linear molecular structure with a hydroxyl group for each repeating unit. The many hydroxyl groups cause it to have a high affinity to water, with strong hydrogen bonding between the inter- and intramolecular hydrogen bonding of adjoining hydroxyl groups. It is well known that with an increase in the number of acetate groups the negative heat of dissolution increases, the critical temperature of the phase separations is lowered, and the solubility at high temperatures decreases gradually.¹

Generally, the viscosity of aqueous PVA solutions is considered as function of the molecular weight and concentration of PVA. But the effects of structural regularity cannot be ignored. Molecular irregularities, including the 1,2-glycol structure, are determined mainly by the polymerization temperature of the precursor. PVAc polymerized at higher temperature has more chance of forming head-to-head linkages for abundant activation energy.¹ But its effects on the physicochemical behavior of aqueous PVA solutions have not fully appreciated yet.

The hydrophilicity of PVA is an advantage for its applications, but a limiting factor in its characterization, because PVA molecules are likely to aggregate through hydrogen bonding due to its polyhydroxy groups. Therefore, despite a number of studies that dealt with the crosslinking and hydrogel formation of PVA in an aqueous solution, there have been few studies on the polymer chain conformation during these processes.

The object of our present study was to examine the gelation process of PVA by aging and the effects of polymerization temperature. To achieve these purposes, completely saponified PVAs of similar molecular weights were prepared from various PVAc's polymerized at 40, 50, and 60°C. PVAs, having gradually differentiated molecular weights, were also prepared at the same polymerization temperature.

EXPERIMENTAL

Materials

Vinyl acetate (VAc), purchased from Shin-Etsu, was washed with an aqueous solution of NaHSO₃

Table I Parameters for Emulsion Polymerization of VAc

Amount of Water	80 mL
Amount of VAc	40 mL
LWZ	0.01 L/L of water
	0.02 L/L of water
KPS	0.0005 mol/L of water
	0.001 mol/L of water
Temperature	40, 50, 60°C
Agitating speed	250 rpm

and water and dried over anhydrous CaCl₂, followed by distillation under a reduced pressure of nitrogen. The other materials were used without further purification.

Emulsion polymerizations were carried out in a three-necked round-bottom stirred reactor. Polyoxyethylene nonylphenyl ether sodium sulfate (LWZ, Cao Co.) and potassium peroxydisulfate (KPS) were used as an emulsifier and initiator, respectively. The agitation was conducted at 250 rpm using a Teflon half-moon-shaped impeller blade mounted on a glass shaft and inserted into a glass adapter (Top, TOA Co., Japan). The flask was purged with nitrogen for 30 min at room temperature and then heated. Once the polymerization temperature was attained, LWZ and VAc were added to the reactor. After 15 min, KPS was added. The reaction product was purified by reprecipitating three times into water and then dried in a vacuum at 50°C. The polymerization conditions are summarized in Table I. To a solution of 2 g of PVAc in 100 mL of methanol, 2.5 mL of a 40% NaOH aqueous solution was added, and the mixture was stirred for 5 h at room temperature to yield PVA. The PVA produced was filtered and washed well with methanol. PVA samples showed the number-averaged degree of polymerization (P_n) of 2300–3300 and indicated a degree of saponification of over 99%. Table II shows the specification of PVAs used in this study.

Viscosity Measurement

PVA1–5 were dissolved in water at 80°C to form stable aqueous PVA “sol” solutions without turbidity. Concentrations were varied at 3, 5, and 7% (g/dL) for all specimens. A Ubbelohde-type capillary viscometer was rinsed thoroughly many times with distilled water and dried with acetone initially as well as after each run. A constant temperature water bath with an error range of $\pm 0.01^\circ\text{C}$ was used. A clamp was set up so that the

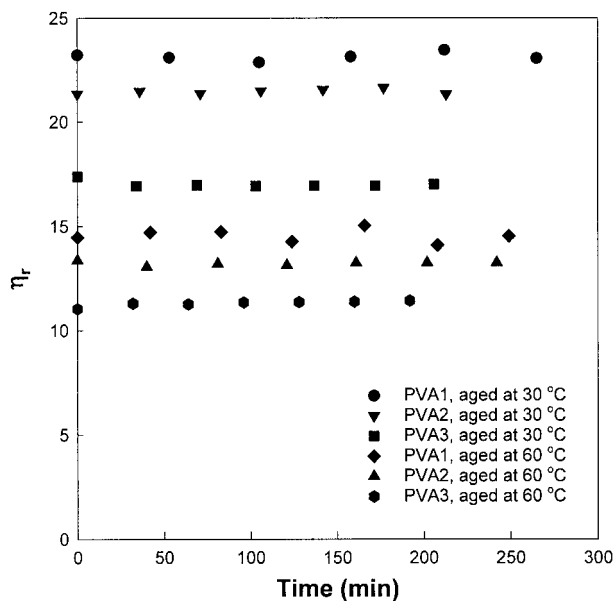


Figure 1 Relative viscosities of 3% aqueous solutions of PVA1, -2, and -3 with aging time.

viscometer is placed inside the water bath, with the fiducial masks visible below the water level. The relative viscosity (η_r) of the aqueous PVA solution was determined at 30 ± 0.01 and $60 \pm 0.01^\circ\text{C}$ with a predetermined time interval at 30 and 60°C , respectively.

RESULTS AND DISCUSSION

It has been widely accepted that the viscosity of the polymer solution depends on the molecular weight of the polymer or that viscosity increases with increasing molecular weight. Gelation of a polymer solution is also considered to be achieved by controlling the polymer concentration and temperature. However, this concept is somewhat ambiguous. When polymers are chemically or physically crosslinked, one should first obtain branched polymers before the formation of the gel phase. This soluble crosslinked polymer makes it possible to measure the molecular weight or polymer size, which is directly related to the properties of the gel structure.⁵ Therefore, the gel structure derived from the molecular parameters is more important.

Effects of Molecular Weight

Determining the molecular structures of PVA is not an easy job. But it is well known that the

molecular structure depends mainly on the polymerization temperature. Therefore, in this study, PVAs prepared from PVAc's polymerized at the same temperature and different initiator concentrations were adopted as PVAs of the "the same molecular structure" and different molecular weight.

In this study, PVAs having P_n 's of 3300, 2800, and 2300 were each prepared from PVAc's emulsion polymerized at 60°C . These PVAs were dissolved in water with concentrations of 3, 5, and 7%, respectively, and aged for a time.

Figure 1 shows the viscosity changes of 3% aqueous solutions of PVA1, PVA2, and PVA3 aged at 30 and 60°C with the aging time. From the fact that there is no significant fluctuation in the viscosity, these solutions can be assumed to maintain a stable sol phase during aging. The viscosities of the PVA solutions increased with increase in the molecular weight, which was in good agreement with the generally accepted tendency. This tendency was repeated in 5% solutions aged at 30 and 60°C and in 7% solutions aged at 60°C , proved in Figures 2 and 3. But in the case of a 7% solution aged at 30°C , as shown in Figure 3, there is an increase in the viscosity between P_n of 3300 and 2800. From these results, it can be deduced that PVAs obtained from PVAc's polymerized at 60°C proceed to the gelation process between 30 and 60°C in the case of P_n between 3300 and 2800. Therefore, it can be concluded that the ge-

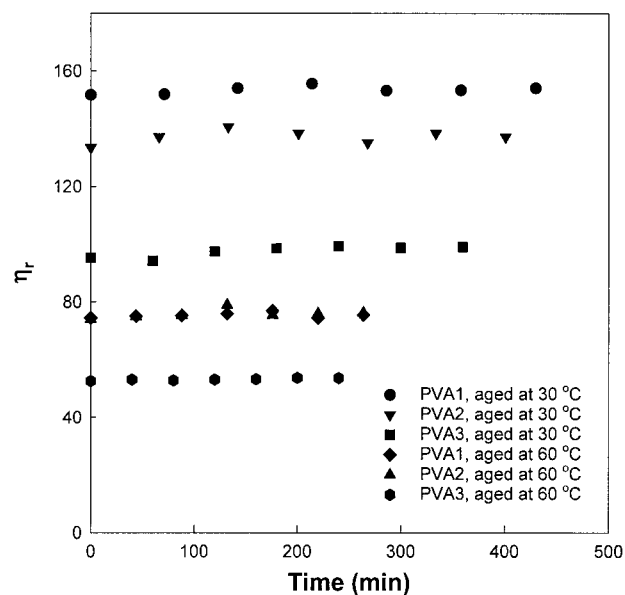


Figure 2 Relative viscosities of 5% aqueous solutions of PVA1, -2, and -3 with aging time.

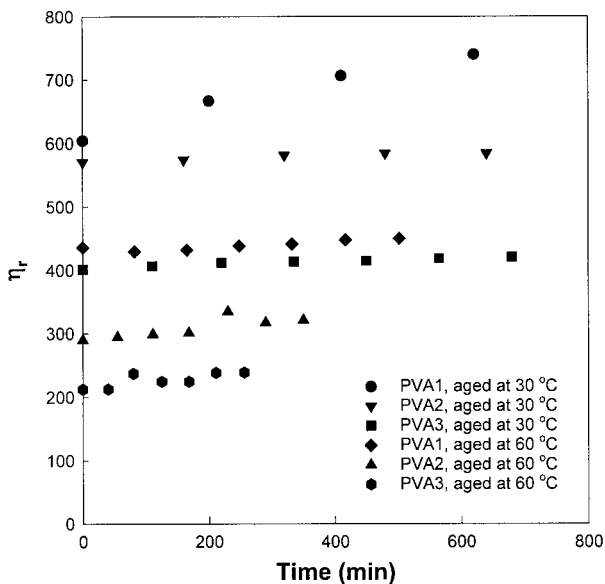


Figure 3 Relative viscosities of 7% aqueous solutions of PVA1, -2, and -3 with aging time.

lation behavior of PVAs of the same molecular structure follows the generally accepted tendency: Gelation is accelerated with increasing molecular weight and decreasing aging temperature.¹

Effects of Polymerization Temperature

Lower polymerization temperature reduces the irregularities of PVAc such as branching and the 1,2-glycol structure.^{1,18–20} From Table II, it can be found that PVA2, PVA4, and PVA5 have the same P_n but different P_n 's of PVAc's. This means that the possibility of irregularity including branching increases at a higher polymerization temperature.

Figure 4 shows the viscosity changes of 3% aqueous solutions of PVA2, PVA4, and PVA5 aged

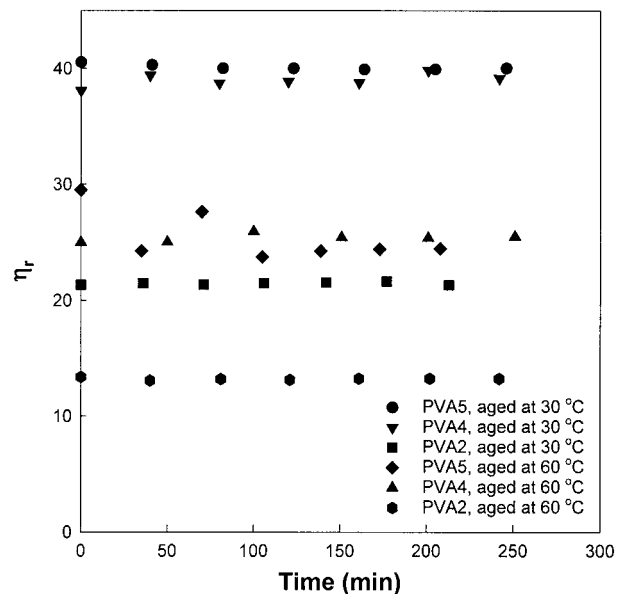


Figure 4 Relative viscosities of 3% aqueous solutions of PVA2, -3, and -5 with aging time.

at 30 and 60°C with the aging time. The viscosities of PVA2, PVA4, and PVA5 maintain constant values. This value, however, for PVA2 is relatively low compared with those of PVA4 and PVA5. The viscosity of PVA2 aged at 30°C is even lower than those of PVA4 and PVA5 aged at 60°C. This cannot be explained by classical theory solely; depending on the molecular weight and gel structure derived from molecular parameters, it can be considered as a new candidate. The viscosity of the PVA solution may be affected by the crosslinkability of the polymer chains because there is no difference in molecular weights. It is well known that polymer chains having superior regularity easily form physical crosslinking. Therefore, PVA4 and PVA5, which have a more regular chain structure due to lower polymerization temperatures of PVAc's, may be suspected of having higher values of the crosslinked molecular size than that of PVA2. A difference of viscosities in PVA4 and PVA5 cannot be detected by the aging of the 3% solution.

Viscosity fluctuations for PVA2, PVA4, and PVA5 dissolved at 5% with the aging time are represented in Figure 5. An aqueous PVA solution experienced a gradual viscosity increase at certain concentrations.¹ PVA2 and PVA4 solutions showed plateau-shaped viscosity curves. In contrast, the viscosity of the PVA5 solution increased gradually with the aging time. This dif-

Table II (PVA)s Used in Viscometric Experiment

Sample No.	P_n	Polymerization Temperature (°C)
	PVA (PVAc)	
PVA1	3300 (18,000)	60
PVA2	2800 (17,000)	60
PVA3	2300 (8800)	60
PVA4	2800 (8000)	50
PVA5	2800 (6700)	40

ference was enlarged in the 7% case as shown in Figure 6. The viscosity of the 7% PVA5 aqueous solution underwent a steep increase and could not be detected after 500 min of aging. From these results, it can be assumed that there is a difference between the molecular structures (or molecular regularities) of PVA4 and PVA5.

CONCLUSIONS

In the gelation of aqueous PVA solutions by aging, the crosslinked molecular size seemed to play an important role in the gelation behavior. The crosslinked molecular size is considered to increase with increasing molecular regularity. The dependence of the gelation behavior on the molecular weight, which has been widely accepted, is proved only when other molecular parameters, especially structural regularity, are maintained. Molecular regularity and the resulting cross-linked molecular size changed enormously according to the polymerization temperatures of the PVAc's. Conclusively, the viscosity and gelation conditions of PVA can be explained effectively not only by the molecular weight but also by the molecular structure. In the near future, we will report on the quantitative structural differences of PVAs arising from the different polymerization temperatures of PVAc's.

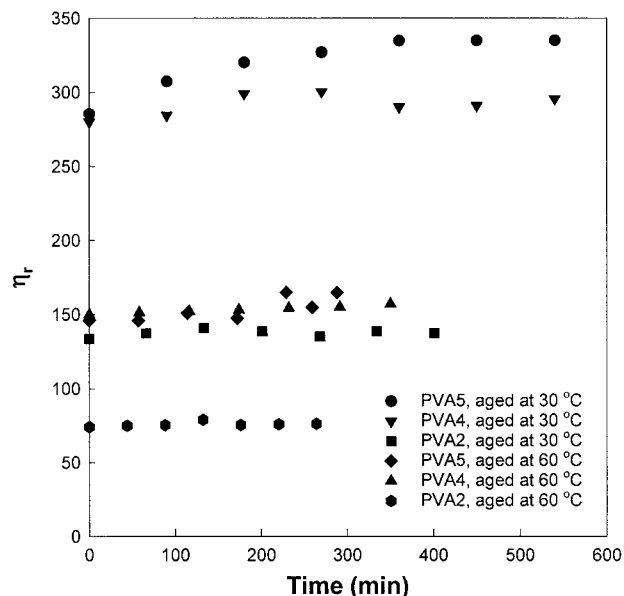


Figure 5 Relative viscosities of 5% aqueous solutions of PVA2, -3, and -5 with aging time.

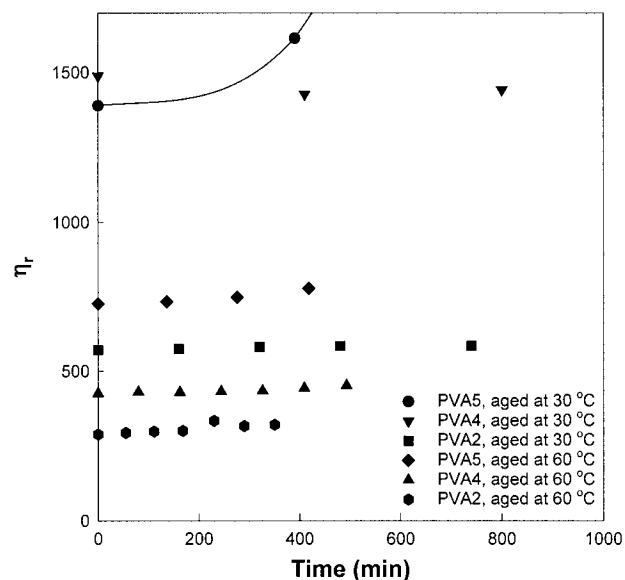


Figure 6 Relative viscosities of 7% aqueous solutions of PVA2, -3, and -5 with aging time.

This research was supported by Yeungnam University research grants in 1999.

REFERENCES

1. Polyvinyl Alcohol—Development; Finch, C. A., Ed.; Wiley: West Sussex, 1992.
2. Mongia, N. K.; Anseth, K. S.; Peppas, N. A. *J Biomater Sci Polym Ed* 1996, 7, 1055.
3. Gimenez, V.; Reina, J. A.; Mantecon, A.; Cadiz, V. *Polymer* 1999, 40, 2759.
4. Briscoe, B.; Luckham, P.; Whu, S. *Polymer* 2000, 41, 3851.
5. Wang, B.; Mukataka, S.; Kokufuta, E.; Ogiso, M.; Kodama, M. *J Polym Sci Polym Phys* 2000, 38, 214.
6. Sohn, B. K.; Cho, B. W.; Kim, C. S.; Kwon, D. H. *Sens Actu Chem* 1997, 41, 7.
7. Leca, B.; Morelis, R. M.; Coulet, P. R. *Mikrochem Acta* 1995, 121, 147.
8. Hertzberg, S.; Moen, E.; Vogelsang, C.; Ostgaard, K. *Appl Microbiol Biotech* 1995, 43, 10.
9. Mori, Y.; Tokura, H.; Yoshikawa, M. *J Mater Sci* 1997, 32, 491.
10. Liu, M. Z.; Cheng, R. S.; Qian, R. Y. *J Polym Sci Polym Phys* 1997, 35, 2421.
11. Hickey, A. S.; Peppas, N. A. *Polymer* 1997, 38, 5931.
12. Nagura, M.; Saitoh, N.; Gotoh, Y.; Ohkoshi, Y. *Polymer* 1996, 37, 5649.
13. Chen, W.; Bao, H.; Zhang, M. *Radiat Phys Chem* 1985, 26, 43.

14. Ulanski, P.; Bothe, E.; Rosiak, J. M.; Sonntag, C. *Macromol Chem Phys* 1994, 195, 1443.
15. Muhlebach, A.; Muller, B.; Pharisa, C.; Hofmann, M.; Seiferling, B.; Gueny, D. *J Polym Sci Polym Chem* 1997, 35, 3603.
16. Brasch, U.; Burchard, W. *Macromol Chem Phys* 1996, 197, 223.
17. Lyoo, W. S.; Ha, W. S. *J. Polym Sci Polym Chem* 1997, 35, 55.
18. Lyoo, W. S.; Kim, B. C.; Lee, C. J.; Ha, W. S. *Eur Polym J Short Commun* 1997, 33, 785.
19. Lyoo, W. S.; Blackwell, J.; Ghim, H. D. *Macromolecules* 1998, 31, 4253.
20. Lyoo, W. S.; Lee, S. G.; Kim, J. P.; Han, S. S.; Lee, C. J. *Colloid Polym Sci* 1998, 276, 951.
21. Lyoo, W. S.; Ha, W. S. *J Korean Fiber Soc* 1996, 33, 321.
22. Lyoo, W. S.; Kim, B. J.; Ha, W. S. *J Korean Fiber Soc* 1996, 33, 231.
23. Lyoo, W. S.; Yeum, J. H.; Ghim, H. D.; Ji, B. C.; Yoon, W. S.; Kim, J. P. *J Korean Fiber Soc* 2000, 37, 487.