Viscosity Behavior of Poly(vinylamine) and Swelling-Contraction Phenomenon of Its Gel

Shiro KOBAYASHI,* Kyung-Do SUH, Yukio SHIROKURA,
and Tomochika FUJIOKA

*Department of Molecular Chemistry and Engineering,
Faculty of Engineering, Tohoku University,
Aoba, Sendai 980, Japan*

(Received March 28, 1989)

ABSTRACT: The reduced viscosity of high molecular weight poly(vinylamine) (PVAm) depends greatly on pH, ionic strength, and heavy-metal ion concentration. The reduced viscosity of PVAm shows a maximum at $\text{pH} \approx 3$ in the case of the ionic strength $\mu = 0$ (KCl); in the region of $\text{pH} < 3$ the viscosity decreased abruptly and the change of pH to the basic region also brought about a decrease of the viscosity. A similar tendency was observed in the presence of a salt KCl ($\mu = 0.01, 0.1$ and 1.0). A PVAm gel was prepared to apply these behaviors for a chemo-mechanical material. The gel shows a good response with respect to the changes of pH, ionic strength, and cupric ion concentration. In addition, a phenomenon of phase transition is observed in PVAm gel under certain conditions.

KEY WORDS Poly(vinylamine) / Viscosity Behavior / Poly(vinylamine) Gel / Swelling-Contraction Behavior / Chemo-mechanical Material / Phase Transition /

Recently, we have investigated the chelating properties of polyamines having different micro-structures.¹⁻³ Polyamines examined are poly(vinylamine) (PVAm),³ poly(allylamine) (PAAm),¹ linear and branched poly(ethylenimines) (LPEI and BPEI, respectively),² which provide a full set of primarily different micro-structures for amine functional groups.² During the course of these studies we have

the polyamines in connection with the effects of the polymers' conformation on the chelating abilities.¹⁻³ Now, we have found a dramatic viscosity change of PVAm, which is due to the specific micro-structure of PVAm having the primary amino group linked directly to the main chain. This viscosity behavior has explored us to develop a new gel derived from PVAm for a chemo-mechanical material. The PVAm gel swells and contracts in a very large extent with respect to changes of pH, ionic strength of a neutral salt (KCl), and cupric ion concentration. The gel has a cation-forming group, which constitutes a sharp contrast to the well-known gels having an anion-forming group such as poly(acrylic acid) and poly(methacrylic acid).^{4,5}

PVAm

PAAm

LPEI

BPEI

paid attention on the viscosity behaviors of

EXPERIMENTAL

Materials

Two PVAmHCl samples prepared by radi-

cal polymerization of *N*-vinylformamide followed by acidic hydrolysis⁶ were supplied from Mitsubishi Kasei Co., Tokyo. The ¹H NMR spectrum of PVAmHCl showed no signal due to formyl proton (δ 8.1); the amount of *N*-formyl group in PVAmHCl was less than 1%, if any. The η_{sp}/c values of the two samples were 0.33 and 3.23, respectively, measured in 1 *N* NaCl aqueous solution with $c=0.1$ g dl⁻¹ and the number-average molecular weights of these samples are estimated as 1.0×10^4 (PVAm-1) and 8.0×10^5 (PVAm-80), respectively, according to the literature.⁷

Preparation of Gel

The gels were prepared by using 3.5 g of PVAm and 1.0 g of a bis-epoxide, nonaethylene glycol diglycidyl ether^{1,8} as a crosslinking agent. The 3.5 ml of 2.11 mol l⁻¹ PVAm solution was mixed with the 0.7 ml of the bis-epoxide (0.164 mol l⁻¹), and then transferred to a glass mold, which was allowed to stand for 48 h at room temperature to give 2 mm thick of the transparent gel. The plate thus prepared was immersed in the distilled water at room temperature for several days and cut into strips

10 × 10 × 2 mm in size. All the gel samples used in this study was prepared by using PVAm-80.

Measurements

The reduced viscosity of polymer solutions was measured with an Ubbelohde viscometer at various pH values at 25°C with varying the ionic strength of a neutral salt KCl. The pH was adjusted by using aqueous HCl and NaOH solutions. All measurements were performed under CO₂-free conditions.

RESULTS AND DISCUSSION

Viscosity Behavior of PVAm

Figure 1 shows the relationship between the reduced viscosity (η_{sp}/c) and pH for aqueous solutions of PVAmHCl-1 (Figure 1(a)) and PVAmHCl-80 (Figure 1(b)) with the various ionic strength ($\mu=0, 0.01, 0.1$, and 1.0 mol l⁻¹ with KCl). A relatively steep peak appears for the PVAmHCl-1 sample at pH ≈ 3 in all cases of ionic strength, except $\mu=1.0$ mol l⁻¹ (KCl). For the PVAm sample, the degree of ionization is 100 percent around pH 3, *i.e.*, all the amino groups attached to the polymer chain

Figure 1. (a) η_{sp}/c -pH relationships of PVAm-1 at 25°C in water: $c=1.0$ g dl⁻¹; (1) $\mu=0$, (2) 0.01, (3) 0.1, and (4) 1.0 mol l⁻¹ (KCl). (b) η_{sp}/c -pH relationships of PVAm-80 at 25°C in water: $c=0.2$ g dl⁻¹; (1) $\mu=0$, (2) 0.01, (3) 0.1, and (4) 1.0 mol l⁻¹ (KCl).

are protonated.³ Thus, polymer chains take the most stretched structure in this pH region because of the electrostatic repulsion among neighboring ammonium groups. On the other hand, in regions of $\text{pH} > 3$ and $\text{pH} < 3$, the value of the reduced viscosity decreased dramatically since the repulsion is relaxed and the flexibility of chain is enhanced due to the neutralization of ammonium groups (at $\text{pH} > 3$) and to the increasing of the counterion (Cl^-) concentrations (at $\text{pH} < 3$). The viscosity behaviors of PVAmHCl-80 are almost similar to those of PVAmHCl-1 over the wide range of pH 2–12 in all cases of ionic strength. However, the value of the viscosity for PVAmHCl-80 at $\text{pH} \approx 3$ in the case of $\mu = 0$ is approximately 90 times larger than that of PVAmHCl-1. For PVAmHCl-80, the value of the viscosity at $\text{pH} \approx 3$, at which the degree of ionization reaches 100%, is nearly 100 times larger than that at pH 10–11. The similar behavior was also observed in the presence of a salt KCl with $\mu = 0.01$, 0.1, and 1.0, respectively.

Figure 2 indicates the effects of a heavy-metal ion (Cu^{2+}) on the viscosity. Cupric ion clearly brought about the viscosity decrease, which is explained by the conformation change due to the chelate formation of Cu^{2+} with the amino group of PVAm.

Swelling-Contraction Behavior of PVAm Gel

In order to take advantage of this large viscosity change due to the different chain conformation depending on the changes of pH, neutral salt concentration, and heavy-metal ions, a PVAm gel has been prepared and its swelling-contraction behaviors have been investigated under various conditions to apply it for a chemo-mechanical material. The PVAm gel has been obtained by crosslinking PVAm with a bis-epoxide, nonaethylene glycol diglycidyl ether.^{1,8}

The degree of volume swelling Q of the gel is defined as following:

$$Q = \{(V/V_0) - 1\} \times 100 [\%] \quad (1)$$

Figure 2. η_{sp}/c -pH relationships of PVAm-80 at 25°C in water in the presence of Cu^{2+} (CuCl_2): $C = 0.2 \text{ g dl}^{-1}$; (1) $[\text{Cu}^{2+}] = 0$, (2) $[\text{Cu}^{2+}] = 4.0 \times 10^{-4} \text{ mol l}^{-1}$, and (3) $[\text{Cu}^{2+}] = 1.0 \times 10^{-3} \text{ mol l}^{-1}$.

where, V_0 and V are the volume of the gel before and after swelling, respectively. The term of V/V_0 can be expressed as $(A/A_0)(V/V_0)^{1/3}$ under the conditions of isotropic swelling, where A_0 and A are the areas of the plate-like gel before and after swelling, respectively. Thus, eq 1 is rewritten as follows

$$Q = \{(A/A_0)^{3/2} - 1\} \times 100 [\%] \quad (2)$$

In this study, the degree of volume swelling of the gel under various conditions was calculated from eq 2.

Figure 3 shows the dependency of the volume swelling Q on pH for PVAm gel. The respective Q value was determined after the gel volume reached constant in a freshly prepared solution of a certain pH value (normally, several hours), and then, the pH value was recorded. When pH changes from the base to acid region (from pH 12 to 1), the gel takes the most swollen state at around pH 3. In this pH region, the degree of volume swelling Q is about 2000%. In the range of pH below 3, however, the gel began to contract and reached the Q value of 350% around pH 1. The above

Figure 3. Dependency of the volume swelling Q on pH for PVAm gel.

results are nearly similar to the viscosity behavior for PVAm solution (see Figure 1).

With the pH change from pH 1 to 12, the swelling-contraction behaviors of the gel are reversible in the regions of $\text{pH} < 3$ and $\text{pH} > 10$. In the range between pH 3 and 10, however, the gel showed an irreversible behavior and a phase transition occurred at pH 10 (Figure 3). It was reported that a phase transition phenomenon is observed in some gels.⁹⁻¹² Tanaka *et al.*¹³⁻¹⁵ reported that the polymer network of certain acrylamide gels undergoes a discrete transition in equilibrium volume with changes of solvent composition and/or of temperature. They also demonstrated by using an acrylamide gel containing a portion of carboxylic acid group that the ionization of the acid in the polymer gel plays an essential role in the phase transition.¹⁶ As mentioned in the viscosity behavior for a PVAm sample, the degree of ionization of amino groups attached to the main chain is 100% around pH 3 reached zero at pH 10-11. Therefore, it is reasonable to assume that the difference in the degree of neutralization between the acidic and basic regions affects significantly on the hysteresis behavior of the swelling-contraction of the gel, that is, charged groups attached to the network play an essen-

Figure 4. Swelling-Contraction behaviors of PVAm gel in 0.01 *N* NaOH (region I) and in 0.01 *N* HCl (region II). The sign $\times$ means breaking of the gel.

tial role in this behavior. The reasonable explanation for this complicated behavior of the present cationic type gels needs further studies.

The swelling-contraction behaviors of PVAm gel in 0.01 *N* NaOH and 0.01 *N* HCl solutions are shown in Figure 4. At the first stage, the gel was immersed in 0.01 *N* HCl solution, and then after equilibrium was reached, the swollen gel was transferred into 0.01 *N* NaOH solution (region I). In the region I, the swollen gel began to shrink and the equilibrium state was attained after 15 h. This contracted gel was immersed again in 0.01 *N* HCl solution (region II), and then the gel began to swell until 2500% in Q value. The swelling-contraction behavior in pH change could not be repeated because of the occurrence of phase transition as observed in Figure 3.

Figure 5 shows the dependency of the volume contraction ratio Q_A/Q_B on the concentration of neutral salt (KCl) solution at pH 3 for PVAm gel, where Q_A and Q_B are the degree of volume swelling of the gel after and before immersing in various concentrations of the KCl solution. All of the gel was swollen in 0.01 *N* HCl solution prior to the experiment. The gel began to contract at the KCl concentration of $10^{-4} \text{ mol l}^{-1}$ and the striking shrinkage was achieved at the concentration

Figure 5. Dependency of the swelling-contraction ratio Q_A/Q_B on the concentration of KCl at pH 3 for PVAm gel.

Figure 6. Effect of salt on swelling-contraction behaviors of PVAm gel in 1.0 mol l^{-1} KCl (region I) and in 0.01 N HCl (region II).

around 1.0 mol l^{-1} . Thus, in Figure 6, the effect of salt on swelling-contraction behaviors of the PVAm gel was investigated in 1.0 mol l^{-1} KCl solution. In region I, the gel swollen in 0.01 N HCl solution was immersed in a 1.0 mol l^{-1} KCl solution. In this case, the equilibrium was reached after 1 h; as can be seen from Figures 5 and 6, the gel in a KCl solution reached to equilibrium more rapidly than in a basic solution. The shrunk gel was again immersed in 0.01 N HCl solution to swelling (region II). This swelling-contraction cycle can be repeated several times without the destruction of the gel.

Figure 7 shows the effect of chelation on

Figure 7. Effect of chelation on swelling-contraction behaviors of PVAm gels in Cu^{2+} (CuCl_2) solutions of 0.005 mol l^{-1} (pH 5.0) ($\blacktriangle$) and 0.01 mol l^{-1} ($\square$) (region I), and in 0.01 N HCl (region II).

swelling-contraction behaviors of PVAm gels in 0.005 and 0.01 mol l^{-1} Cu^{2+} solutions. The experimental method was similar to those of Figures 5 and 6. A relatively fast response was attained by using the Cu^{2+} solution and the difference of concentration in the metal ion was observed in swelling-contraction behavior of PVAm gel. In the region I, the gel contracts due to the chelate-formation with Cu^{2+} ions. In 0.01 N HCl solution, the Cu^{2+} ions are liberated and the gel swells again by the protonation of amino groups. In these cases, the swelling-contraction behavior was repeated several times.

Acknowledgments. S. K. is indebted to Grant-in-Aid for Scientific Research on Priority Area of "Macromolecular Complex" (No. 62612502 and 63612502) from the Ministry of Education, Science, and Culture of Japan for partial support of this study. We acknowledge the gift of two PVAm samples from Mitsubishi Kasei Co., Tokyo.

REFERENCES

1. S. Kobayashi, M. Tokunoh, T. Saegusa, and F. Mashio, *Macromolecules*, **18**, 2357 (1985).
2. S. Kobayashi, K. Hiroishi, M. Tokunoh, and T. Saegusa, *Macromolecules*, **20**, 1469 (1987).

3. S. Kobayashi, K-D. Su, and Y. Shirokura, *Macromolecules*, **22**, 2363 (1989).
4. W. Kuhn and A. Katchalsky, *Bull. Soc. Belg.*, **57**, 421 (1948); *Helv. Chim. Acta.*, **31**, 1994 (1948).
5. W. Kuhn, *Experimentia*, **5**, 318 (1949); A. Katchalsky, *Experimentia*, **5**, 319 (1949).
6. K. Itagaki, T. Ito, K. Ando, and J. Watanabe, Jpn. Kokai 61-51007 (March 13, 1986) (to the Mitsubishi Kasei Co., Tokyo).
7. C. J. Bloys van Treslong and C. F. Morra, *J. Royal Netherlands Chem. Soc.*, **94**, 101 (1975).
8. S. Kobayashi, T. Tanabe, T. Saegusa, and F. Mashio, *Polym. Bull.*, **15**, 7 (1986).
9. T. Tanaka, *Phys. Rev. Lett.*, **40**, 820 (1978).
10. H. L. Frisch and S. Fesciyan, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 309 (1979).
11. C. B. Post and B. H. Zimm, *Biopolymers*, **18**, 1487 (1979).
12. G. Swislow S.-T. Sun, I. Nishio, and T. Tanaka, *Phys. Rev. Lett.*, **44**, 796 (1980).
13. T. Tanaka, S. Ishiwata, and C. Ishimoto, *Phys. Rev. Lett.*, **38**, 771 (1977).
14. T. Tanaka, L. O. Hocker, and G. B. Benedek, *J. Chem. Phys.*, **59**, 5151 (1973).
15. T. Tanaka, D. Fillmore, S-T. Sun, I. Nishio, G. Swislow, and A. Shah, *Phys. Rev. Lett.*, **45**, 1636 (1980).
16. D. Nicoli, C. Young, T. Tanaka, A. Pollak, and G. Whitesides, *Macromolecules*, **16**, 887 (1983).