

Viscosity Behaviors and Gel Properties of Linear and Branched Polyethylenimines: Effects of Micro-Structures

Shiro KOBAYASHI,* Hitoshi SHIRASAKA, Kyung-Do SUH,
and Hiroshi UYAMA

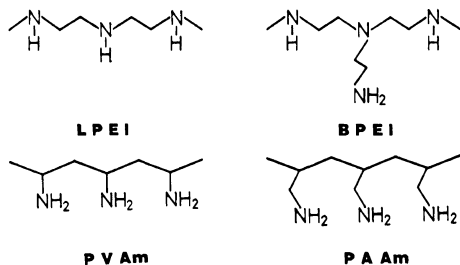
*Department of Molecular Chemistry and Engineering, Faculty of Engineering,
Tohoku University, Aoba, Sendai 980, Japan*

(Received November 30, 1989)

ABSTRACT: The reduced viscosity of linear and branched polyethylenimine (LPEI and BPEI, respectively) was measured at various pH and ionic strength to examine the effects of the micro-structure. The viscosity value of LPEI decreased with increasing pH ($\text{pH} > 2$) in the absence or presence of a salt (NaCl). The larger the ionic strength in the aqueous solution of LPEI, the smaller the viscosity value of LPEI. On the other hand, the viscosity of BPEI changed little over the wide range of pH 2—10. LPEI and BPEI gels were prepared by cross-linking with a bis-epoxide. The swelling-contraction behaviors of these gels were examined at various pH, ionic strength, and metal ions (Cu^{2+} and Ni^{2+}) concentration. The LPEI gel showed a large response with respect of these factors. The response of the BPEI gel, however, was much smaller than that of LPEI gel.

KEY WORDS Linear Polyethylenimine / Branched Polyethylenimine / Micro-Structure / Viscosity Behavior / Polyethylenimine Gel / Swelling-Contraction Behavior /

Polyamines are known to form chelating complexes with various metal ions. We have already reported quantitative investigations on the chelating abilities of polyamines, linear polyethylenimines and branched polyethylenimines (LPEI and BPEI, respectively),¹ poly(vinylamine) (PVAm),² and poly(allylamine) (PAAm),³ which provide a full set of primarily different micro-structures for amine functional groups. During the the course of these studies,



the chelating abilities and viscosity behaviors of these polyamines are found to be closely related with the micro-structures. Moreover, we have recently found a dramatic viscosity change of PVAm with respect to pH change, ionic strength, and cupric ion concentrations.⁴ A PVAm gel prepared by using an epoxide as a cross-linking agent has been found to show a good response to these factors.⁴

LPEI has only secondary amino groups in the main chain. A commercial BPEI, on the contrary, contains primary, secondary, and tertiary amino groups in a ratio of approximately 25%, 50%, and 25%, respectively.⁵ In this study we report viscosity behaviors of LPEI and BPEI and the swelling-contraction behaviors of LPEI and BPEI gels with varying pH, ionic strength, and metal ion concentrations.

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials

LPEI was prepared by the acid hydrolysis of poly(*N*-benzoylethylenimine), which was obtained by the cationic ring-opening polymerization of 2-phenyl-2-oxazoline with 2-phenyl-2-oxazolinium tosylate initiator, followed by reprecipitation (chloroform-ethanol). The average molecular weight of LPEI was 30,000 calculated from that of poly(*N*-benzoylethylenimine) determined by gel permeation chromatographic (GPC) analysis.⁶ BPEI (the average molecular weight of 30,000)⁷ was obtained from Nihon Shokubai Chemical Co. and used after reprecipitation from ethanol (solvent)/*n*-hexane (non-solvent). A bis-epoxide, nonaethylene glycol diglycidyl ether (EX830) used as a cross-linking agent was a gift from Nagase Kasei Co.

Preparation of Gel

All gel specimens were prepared in the following procedures. A mixture of 4.3 ml of 2.33 mol l^{-1} LPEI aqueous solution and the 1.4 ml aqueous solution of the bis-epoxide (0.18 mol l^{-1}) was placed in a cylindrical teflon mold, which was allowed to stand for 3 h at 80°C to give a transparent gel. The diameter and the thickness of the gel is 10.0 mm and 2.0 mm, respectively. The gel was immersed in the distilled water at room temperature for several days before use. BPEI gel was synthesized in a similar way.

Measurements

The reduced viscosity of polymer solutions was measured with an Ubbelohde viscometer at 25°C . All measurements were performed under CO_2 -free conditions. Gel permeation chromatographic (GPC) analysis was performed by using a Hitachi 655A apparatus with UV detector under the following conditions: Gelpack GL-A150 column and chloroform eluent at a flow rate of 1.0 ml min^{-1} .

RESULTS AND DISCUSSION

Viscosity Behavior of LPEI and BPEI

Figure 1 indicates the relationships between pH and the reduced viscosity of LPEI and BPEI (molecular weight of both samples, 30,000) at the various ionic strength. The viscosity behavior of LPEI is similar to that of PVAm observed by us.⁴ At lower ionic strength ($\mu = 0$ and 0.01 mol l^{-1} with NaCl), a relatively steep peak appears for LPEI at $\text{pH} \sim 3$, where polymer chains take the most stretched structure in this pH region. The value of the viscosity decreased dramatically in the region of $\text{pH} > 3$ since the repulsion was relaxed and the flexibility of polymer chain was enhanced due to the neutralization of ammonium group. At higher ionic strength ($\mu = 1.0$ and 0.1 mol l^{-1} with NaCl), the viscosity of LPEI steeply increased with decreasing pH ($\text{pH} < 4$).

On the other hand, the reduced viscosity value of BPEI is almost independent of ionic strength as well as pH showing a lower value of $\eta_{\text{sp}}/c \sim 0.1$. These observations indicate that BPEI does not cause the conformation change of polymer chain in aqueous solution due to a highly branched globular structure.¹ Previously similar viscosity behaviors of BPEI were observed by Liu.⁸

Swelling-Contraction Behavior of LPEI and BPEI Gels

The viscosity behaviors above described explored us to develop new gels from LPEI and BPEI. LPEI and BPEI gels were synthesized by using a bis-epoxide, nonaethylene glycol diglycidyl ether as a cross-linking agent.^{3,9} The degree of volume swelling Q of the gel was defined by the following equation

$$Q = [(V/V_0) - 1] \times 100$$

where V_0 and V are the volume of the gel before and after swelling.⁴

Figure 2 shows the swelling-contraction behaviors of the gels in 0.01 N NaOH and 0.01 N HCl solutions with $\mu = 1.0 \text{ mol l}^{-1}$

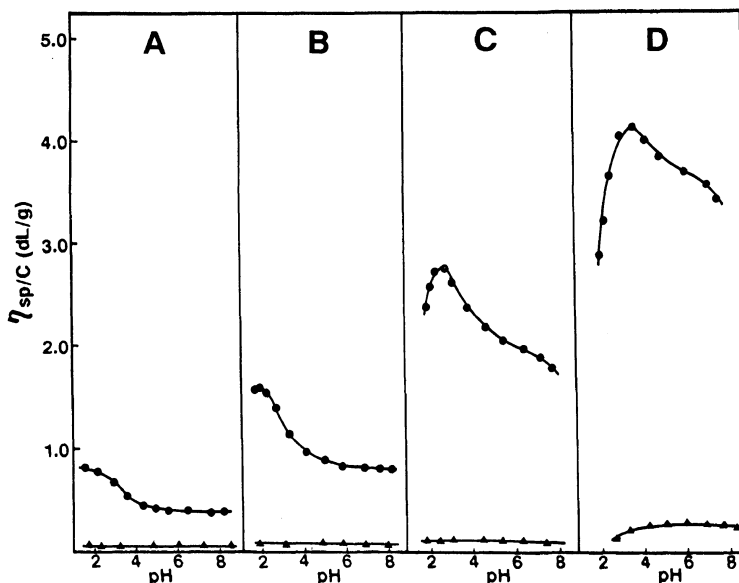


Figure 1. Effect of the salt (NaCl) concentration on the viscosity of LPEI (—●—) and BPEI (—▲—) (mol. wt. 30,000, $c=0.2 \text{ g dl}^{-1}$) at 25°C ; $\mu=1.0 \text{ mol l}^{-1}$ (A), $\mu=0.1 \text{ mol l}^{-1}$ (B), $\mu=0.01 \text{ mol l}^{-1}$ (C), and $\mu=0$ (D).

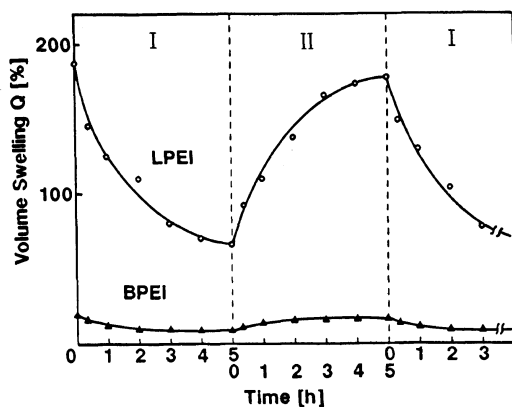


Figure 2. Swelling-contraction behaviors of LPEI and BPEI gels in 0.01 N NaOH and $1.0 \text{ mol l}^{-1} \text{ NaCl}$ (region I), and in 0.01 N HCl and $1.0 \text{ mol l}^{-1} \text{ NaCl}$ (region II).

(NaCl). First the gel was immersed in 0.01 N HCl solution with $\mu=1.0 \text{ mol l}^{-1}$ (NaCl). LPEI gel swelled until 180% in Q value. BPEI gel, however, swelled only until 30% in Q value. The difference in swelling behavior of the two gels is highly related to the conformational difference in an acidic solution; LPEI has highly stretched structure and BPEI has still globular

structure due to highly branched structure. The swollen gels were transferred into 0.01 N NaOH solution with $\mu=1.0 \text{ mol l}^{-1}$ (region I). The LPEI gel shrank, but the BPEI gel shrank to only a small extent, which is closely related to the viscosity change on the change of pH as seen in Figure 1. The contracted gels were immersed again in 0.01 N HCl solution with $\mu=1.0 \text{ mol l}^{-1}$ (NaCl) (region II), and then the LPEI gel highly swelled much again. The swelling-contraction behaviors of the two gels in pH change could be repeated.

Figure 3 shows the dependency of the volume swelling Q of the gels on the concentration of NaCl in 0.01 N HCl solution. The gels were immersed in 0.01 N HCl solution prior to the experiment. LPEI gel began to contract at the NaCl concentration of $10^{-3} \text{ mol l}^{-1}$, but BPEI gel little contracted. These phenomena reflect the viscosity behaviors due to the ionic strength variation.

The effect of ionic strength of swelling-contraction behaviors of the gels is shown in Figure 4. At a lower concentration of NaCl

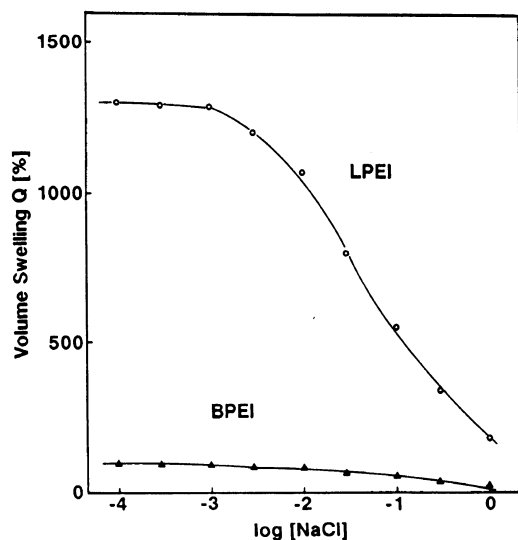


Figure 3. Dependency of the volume swelling Q on salt (NaCl) concentration for LPEI and BPEI gels.

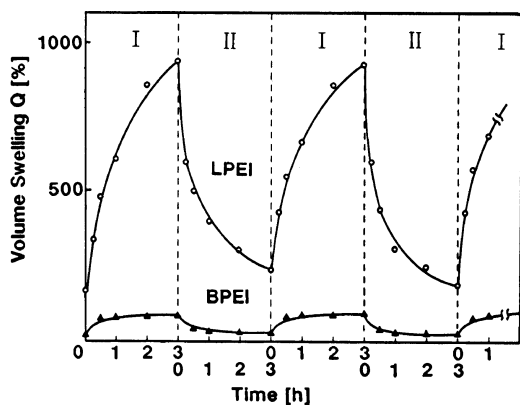


Figure 4. Effect of salt concentration on swelling-contraction behaviors of LPEI and BPEI gels in 0.01 mol l^{-1} NaCl and 0.01 N HCl (region I), and in 1.0 mol l^{-1} NaCl and 0.01 N HCl (region II).

(0.01 mol l^{-1}) in 0.01 N HCl solution (region I), the shrunk LPEI gel highly swelled. The BPEI gel, however, little swelled. The gels were immersed at a higher concentration of NaCl (1.0 mol l^{-1}) in 0.01 N HCl solution (region II). LPEI gel contracted highly and BPEI gel little contracted. These swelling-contraction behaviors could be repeated without the destruction of the gel.

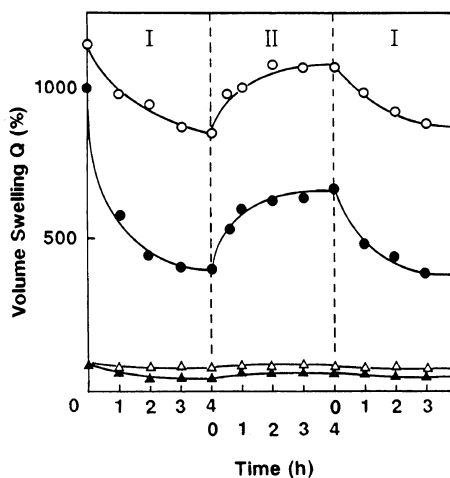


Figure 5. Effect of chelation on swelling-contraction behaviors of LPEI and BPEI gels in M^{2+} solutions of 0.01 mol l^{-1} (region I), and in 0.01 N HCl and 0.01 mol l^{-1} NaCl (region II); (—●—) LPEI gel in Cu^{2+} solution, (—○—) LPEI gel in Ni^{2+} solution, (—▲—) BPEI gel in Cu^{2+} solution, (—△—) in Ni^{2+} solution.

Figure 5 shows the effect of chelation on swelling-contraction behaviors of the gels. The heavy metal ions used are cupric ion and nickel ion. We have already reported the quantitative chelating abilities of LPEI and BPEI on these metal ions.^{1,2} The gels were immersed in 0.01 mol l^{-1} of M^{2+} solutions (region I). LPEI gel shrank highly in Cu^{2+} solution and shrank moderately in Ni^{2+} solution. The shrinkage was due to the chelate-formation with the metal ions and this difference of the shrinking degree may be due to the chelating abilities of LPEI toward these metal ions; the chelation of LPEI is stronger for Cu^{2+} than for Ni^{2+} .^{1,2} BPEI gel, however, shrank only little. In acidic solution (region II), the metal ions are liberated and the LPEI gel swelled again. This swelling-contraction cycle could be repeated several times.

Acknowledgment. S. K. is indebted to Grant-in-Aid for Scientific Research on Priority of Area of "Macromolecular Complex" (No. 63612502 and 01612001) from the Ministry of Education, Science, and Culture of

Japan for partial support of this study.

REFERENCES

1. S. Kobayashi, K. Hiroishi, M. Tokunoh, and T. Saegusa, *Macromolecules*, **20**, 1469 (1987).
2. S. Kobayashi, K.-D. Suh, and Y. Shirokura *Macromolecules*, **22**, 2363 (1989).
3. S. Kobayashi, M. Tokunoh, T. Saegusa, and F. Mashio, *Macromolecules*, **18**, 2357 (1985).
4. S. Kobayashi, K.-D. Suh, Y. Shirokura, and T. Fujioka, *Polym. J.*, **21**, 971 (1989).
5. C. R. Dick and G. E. Ham, *J. Macromol. Sci.-Chem.*, **A4**, 1301 (1970).
6. R. Tanaka, I. Ueoka, Y. Takaki, K. Kataoka, and S. Saito, *Macromolecules*, **16**, 849 (1983).
7. "EPOMIN® (polyethylenimine)," Nihon Shokubai Chemical Co. (Osaka), Catalogue No. 1000(F) (1984).
8. K.-J. Liu, *Macromolecules*, **1**, 390 (1968).
9. S. Kobayashi, T. Tanabe, T. Saegusa, and F. Mashio, *Polym. Bull.*, **15**, 7 (1986).