Volume-phase transitions of cationic polyelectrolyte gels

Shinichi Kudo, Norio Kosaka, Mikio Konno* and Shozaburo Saito
Department of Molecular Chemistry and Engineering, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai, Japan 980

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The swelling equilibrium behaviour of *N*-n-butyl-*N*,*N*-dimethyl-4-vinyl benzylammonium bromide (BBABr) gel was measured in aqueous solutions of various inorganic electrolytes: HBr, LiBr, NaBr, KBr, NH_4Br, NaCl, NaI and $NaClO_4$. The equilibrium swelling volume of BBABr gel does not depend strongly on the cationic species but on the anionic species. In aqueous solutions containing I^- and ClO_4^- ions, the volume-phase transitions of the BBABr gel were induced by a change in the concentration of the electrolytes. It was verified experimentally with ^{79}Br n.m.r. and an ion electrode that the volume-phase transition is controlled by the change in the association state of the charged groups in the gel.

(Keywords: volume-phase transition; polyelectrolyte gel; *N*-n-butyl-*N*,*N*-dimethyl-4-vinylbenzylammonium bromide gel; ionic association; electrolyte aqueous solution)

INTRODUCTION

Experimental study[1–11] on the volume-phase transitions of polyelectrolyte gels has usually employed gels which introduce charged groups at low concentration levels on their polymer network. Typical examples are acrylamide derivative gels prepared by a copolymerization of acrylamide monomers and a small amount of ionic monomers. However, for a better understanding of the transition, it seems useful to obtain experimental data of the swelling of a gel which introduces charged groups at high concentration levels. Recently[12] it has been pointed out that such a gel may show a peculiar behaviour during swelling, which is considered to result from polyelectrolyte effects. However, only a few experimental data[13] have been obtained with gels which introduced charged groups at high concentration levels. In the present work, we prepared a *N*-n-butyl-*N*,*N*-dimethyl-4-vinylbenzylammonium bromide (BBABr) gel which contained a charged group in each monomer. The BBABr gel was subjected to swelling experiments in aqueous solutions of various inorganic electrolytes.

EXPERIMENTAL

To prepare the BBABr gel, a free radical polymerization was conducted according to the following procedure. A solution containing *N*,*N*-dimethyl-4-vinylbenzylamine (monomer, 1 ml), azobisisobutyronitrile (AIBN) (initiator, 0.01 g), divinylbenzene (crosslinking agent, 0.05 ml) and toluene (reaction solvent, 1 ml) was transferred to a glass tube (i.d. 1 mm). After the removal of residual oxygen from the reactant mixture, the glass tube was sealed off under nitrogen atmosphere. The temperature of the reactant mixture was raised to 60°C to start the polymerization, and kept constant for 12 h. After the polymerization, the *N*,*N*-dimethyl-4-vinylbenzylamine gel synthesized was taken out of the glass tube and immersed in an excess amount of toluene to remove the residual monomer and the crosslinking agent. Subsequently, the gel (about 30 mg polymer content in dry base) was quaternized at 60°C for 40 h in a reaction solvent of *N*,*N*-dimethylformamide/methanol (75/25 vol%, 20 ml) containing a quaternization agent, n-butyl bromide (5 ml). The BBABr gel prepared was characterized with ^1H n.m.r. in methanol-d_4. As shown in *Figure 1*, the signals were assigned to the corresponding protons. The degree of quaternization was determined from the ratio of the signal intensity of the aromatic ring to that of the butyl group, and was found to be 100%, which was consistent with the value determined from elemental analysis.

To measure the swelling equilibria, the cylindrical gel was immersed in aqueous solutions (50 ml) of various inorganic electrolytes for 3 days at 30°C. The diameter of the gel was measured to determine the swelling ratio, defined as V/V_0 $(=d^3/d_0^3)$, where, respectively, V and d are equilibrium volume and diameter of the gel, and V_0 and d_0 are the volume and diameter of the gel at synthesis.

To obtain information about the ionic association of the polymer constituting the BBABr gel, a linear poly(BBABr) was synthesized. Synthesis of poly(BBABr) followed the same procedure as for the BBABr gel, but without the crosslinking agent. The quaternization degree of the poly(BBABr) was examined by ^1H n.m.r. and elemental analysis, and was confirmed to be 100%. The number average molecular weight of the poly(BBABr) was 5.6×10^4, and its molecular weight heterogeneity was 2.0. The ionic association of the poly(BBABr) was analysed with ^{79}Br n.m.r. (Bruker MSL-400 spectrometer) at 30°C.

Additional experiments were carried out using *N*-n-butyl-*N*,*N*-dimethyl-4-vinylbenzylammonium iodide

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* To whom correspondence should be addressed

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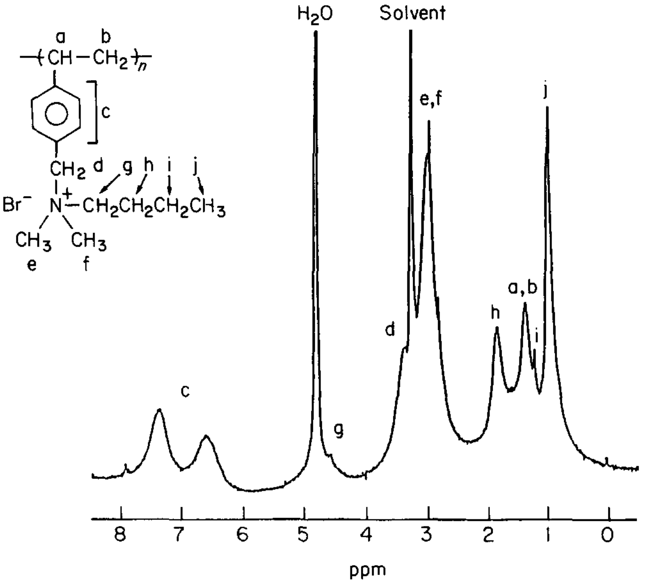

Figure 1 ^{1}H n.m.r. spectrum of BBABr gel dissolved in methanol-d$_4$ at 30°C

(BBAI) gel, which was prepared by the quaternization of the *N*,*N*-dimethyl-4-vinylbenzylamine gel with n-butyl iodide as quaternization agent. The BBAI gel (a cylinder 1 mm in length and 1 mm in diameter at synthesis) was immersed in an aqueous solution of NaBr (50 ml) at different concentrations, and the swelling volumes of the gel were measured. In addition, the concentration of the I^- ion in the outer solution of the gel was measured with an ion electrode (Horiba N-8F ion meter). The amount of I^- ion released from the gel to the outer solution was determined from the I^- concentration in the outer solution and its volume.

RESULTS AND DISCUSSION

Figure 2 shows the swelling ratio of the BBABr gel in aqueous solutions of inorganic electrolytes, which commonly contained Br^- ion as an ionic species. The swelling ratio continuously decreased with an increase in the electrolyte concentration, indicating no strong dependence on the cationic species. *Figure 3* shows the swelling ratio of the BBABr gel in aqueous solutions of electrolytes containing different anionic species. A continuous change in the gel volume was only observed in the NaCl and NaBr solutions, while a discontinuous change was observed in the NaI and $NaClO_4$ solutions. The order of association constants of anionic species for the ammonium ion in protonic solvents[14] is generally given as follows: $ClO_4^- > I^- > Br^- > Cl^-$. This coincides with the order of effectiveness of the electrolytes which brought about shrinkage of the gel in *Figure 3*. Thus, the association of the gel seems important for the swelling behaviour of the gel.

The ionic association of charged groups of the poly(BBABr) was examined with ^{79}Br n.m.r. *Figure 4* shows the ^{79}Br n.m.r. spectrum of the aqueous solution of poly(BBABr). For comparison, the n.m.r. spectra of the aqueous solutions of NaBr and *N*-n-butyl-*N*,*N*-dimethylbenzylammonium bromide (QABr) are also presented. A narrow peak of Br^- ion was observed in the NaBr and QABr aqueous solutions, whereas a quite broad peak was detected in the poly(BBABr) aqueous solution. Since half-height line width in ^{79}Br n.m.r. is inversely proportional to the molecular mobility of Br^- ion[15], the line broadening suggests that the ionic association occurs in the poly(BBABr) aqueous solution. *Figure 5* shows half-height line widths measured with the poly(BBABr) aqueous solutions to which various amounts of NaI were added. The line widths are plotted against the molar ratio of I^- ions to the charged groups of the poly(BBABr), $[I^-]/[\text{charged group}]$. Beyond the cloud point, indicated by an arrow in *Figure 5*, the half-height line width began to decrease with an increase in concentration, accompanied by a sharp change at

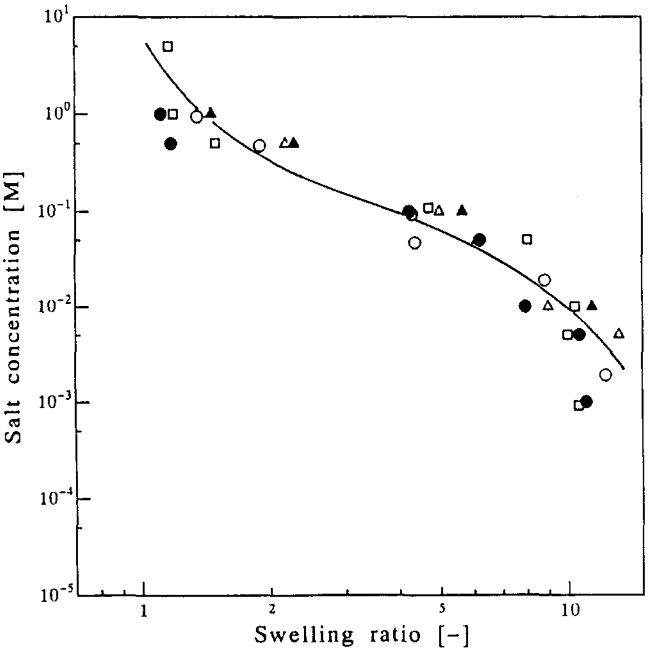

Figure 2 Swelling ratio of BBABr gel in aqueous solutions of various inorganic electrolytes containing different cations: ○, HBr; △, LiBr; □, NaBr; ●, KBr; ▲, NH_4Br

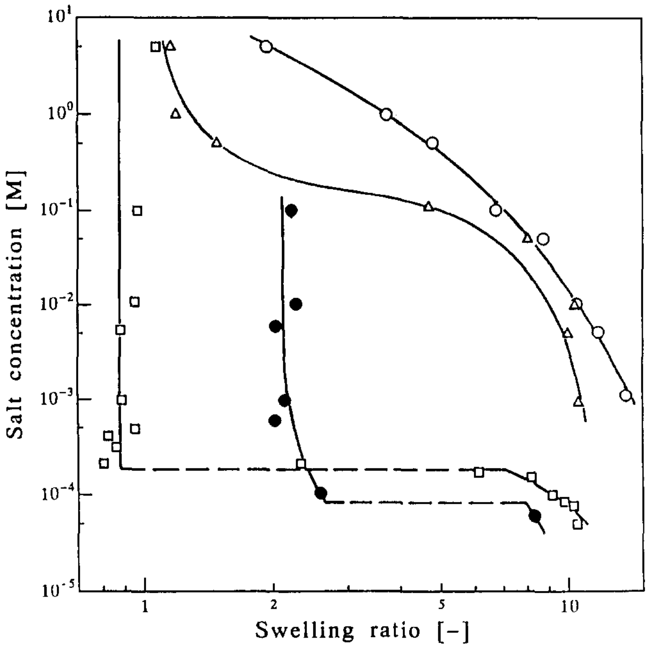

Figure 3 Swelling ratio of BBABr gel in aqueous solutions of various inorganic electrolytes containing different anions: ○, NaCl; △, NaBr; □, NaI; ●, $NaClO_4$

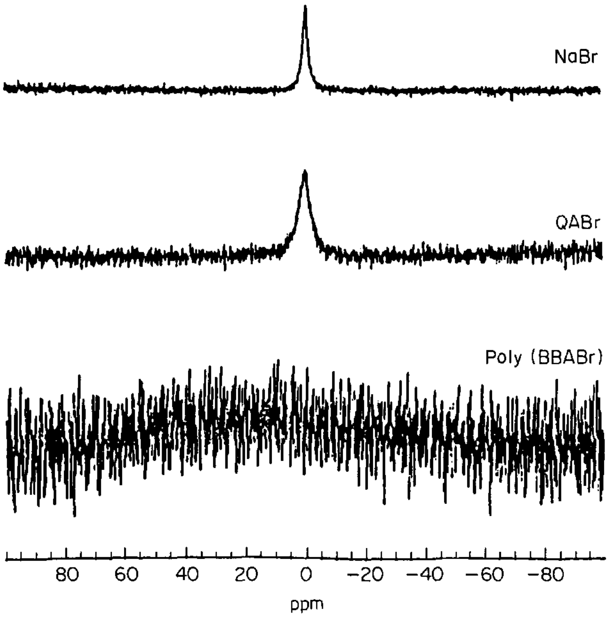

Figure 4 ^{79}Br n.m.r. spectra of aqueous solutions of NaBr, *N*-n-butyl-*N*,*N*-dimethylbenzylammonium bromide (QABr) and poly(BBABr) at 30°C

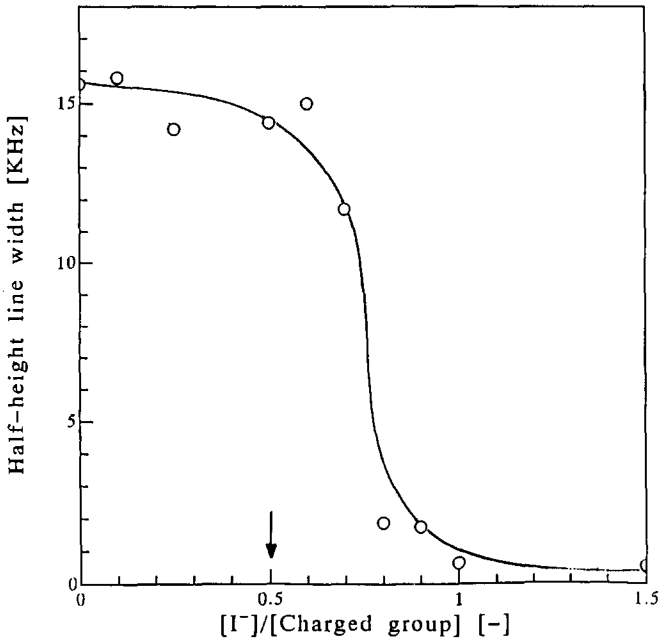

Figure 5 Half-height line width in ^{79}Br n.m.r. against the molar ratio of I^- ion to the charged group of poly(BBABr), [I^-]/[charged group], in various concentrations of NaI solutions at 30°C. The arrow indicates the cloud point of the solution

around the point [I^-]/[charged group] = 0.8. The line width finally attained was almost the same as that in the NaBr aqueous solution. These results suggest that the association state of the ions was greatly changed by the addition of the electrolyte. This change in the association state may appear as ion exchange between the outside and inside of the gel.

Figure 6 shows the quantity of I^- ion released from the BBAI gel to the outer solution to which different amounts of NaBr were added. The quantity of I^- ion released and the quantity of Br^- ion added are presented as a value normalized by the moles of the charged groups in the gel. The quantity of released I^- increased roughly in proportion to the amount of added Br^-. It should be noted that the amount of released I^- is much less than the amount of added Br^-. This indicates that the association of charged groups in the gel has a higher selectivity for I^- than Br^-. In *Figure 7*, the values of [I^- released]/[charged group] of the BBABr gel are plotted against the swelling ratio of the gel. The volume-phase transition occurred at the point [I^- released]/[charged group] = 20%. This value means that the I^- ions in the gel constituted 80% of the charged groups in the gel; this

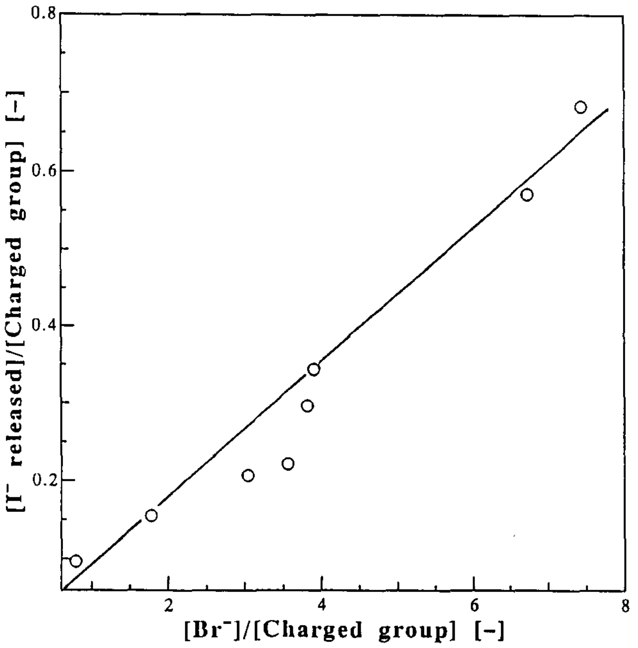

Figure 6 Relation between the molar ratio of I^- ion released from the BBAI gel to charged group, [I^- released]/[charged group], and the molar ratio of Br^- ion in the outer solution to the charged group at 30°C

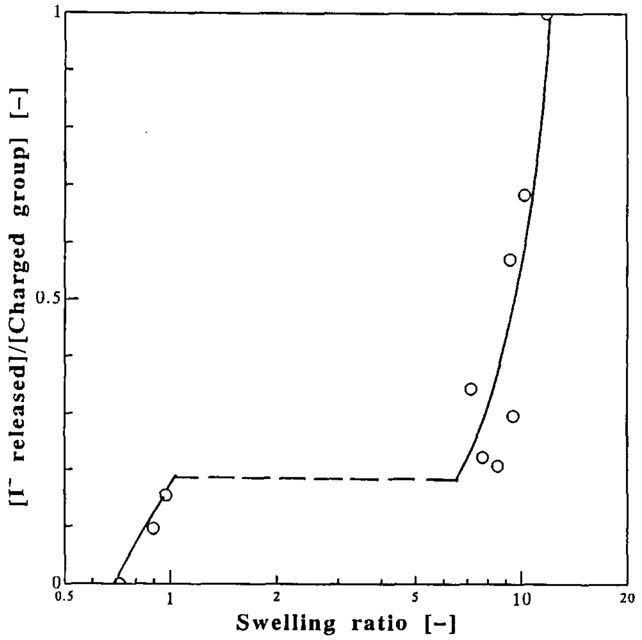

Figure 7 Relation between the molar ratio of I^- ion released from the BBABr gel to the charged group, [I^- released]/[charged group], and the swelling ratio of the BBAI gel at 30°C

shows substantial agreement with the value of the molar ratio at which the half-height line width in ^{79}Br n.m.r. of the poly(BBABr) sharply decreased in *Figure 5*. Therefore the change in the association state in the gel seems to be a major factor in the phase transition of the gel.

CONCLUSIONS

In aqueous solutions of inorganic electrolytes containing Br^- or Cl^- ions, the swelling volume of the BBABr gel continuously decreased with an increase in the electrolyte concentration in the concentration ranges examined. On the other hand, a discontinuous change in the gel volume was observed in the electrolyte solutions containing I^- or ClO_4^- ions. It was shown that the order of effectiveness of the electrolytes which brought about the shrinkage of the gel was consistent with that of the association constants of anionic species for ammonium ion in protonic solvents.

The ^{79}Br n.m.r. and ion electrode experiments indicated a mechanism by which transition results from ion exchange of the anions between the gels and the outer solutions.

REFERENCES

1 Tanaka, T. *Phys. Rev. Lett.* 1978, **40**, 820
2 Tanaka, T., Fillmore, D. J., Sun, S. T., Swislow, G. and Shah, A. *Phys. Rev. Lett.* 1980, **45**, 1636
3 Ilavasky, M. *Macromolecules* 1982, **15**, 782
4 Ohmine, I. and Tanaka, T. *J. Chem. Phys.* 1982, **77**, 5725
5 Katayama, S., Hirokawa, Y. and Tanaka, T. *Macromolecules* 1984, **17**, 2641
6 Ricka, J. and Tanaka, T. *Macromolecules* 1984, **17**, 2916
7 Ilavsky, M., Hroutz, J. and Havlicek, I. *Polymer* 1985, **26**, 1514
8 Ricks, J. and Tanaka, T. *Macromolecules* 1985, **18**, 83
9 Katayama, S. and Ohta, A. *Macromolecules* 1985, **18**, 2781
10 Hirokawa, Y., Tanaka, T. and Sato, E. *Macromolecules* 1985, **18**, 2782
11 Hirotsu, S., Hirokawa, Y. and Tanaka, T. *J. Chem. Phys.* 1987, **87**, 1392
12 Konak, C. and Bansil, R. *Polymer* 1989, **30**, 677
13 Siegel, R. A. and Firestone, B. A. *Macromolecules* 1988, **21**, 3254
14 Matesich, S. M. A., Nadas, J. A. and Evans, D. F. *J. Phys. Chem.* 1970, **74**, 4568
15 Farrer, T. C. and Becker, E. D. 'Pulse and Fourier Transform NMR', Academic Press, New York, 1970