

Multiple Phase Behaviors of Polymer Gels

M. Annaka, M. Sugiyama¹, K. Hara², M. Tokita³,
M. Shibayama⁴ and T. Nakahira

Department of Materials Technology, Chiba University, Chiba 263-8522, Japan

Fax: +81-43-290-3401, e-mail: annaka@galaxy.tc.chiba-u.ac.jp

¹Faculty of Science, Kyushu University, Fukuoka, 812-8581 Japan

Fax: +81-92-642-2553, e-mail: sugi8scp@mbox.nc.kyushu-u.ac.jp

²Faculty of Engineering, Kyushu University, Fukuoka, 812-8581 Japan

Fax: +81-92-633-6958, e-mail: haratap@mbox.nc.kyushu-u.ac.jp

³Department of Chemistry for Materials, Mie University, Tsu, 514-8507, Japan

Fax: +81-92-865-6030, e-mail: tokita@chem.mie-u.ac.jp

⁴Neutron Scattering Laboratory, The Institute of Solid State Physics,
The university of Tokyo, Tokai, 319-1106, japan

Fax: +81-29-287-8904, e-mail: shibayama@issp.u-tokyo.ac.jp

The conditions for multiple phase behavior are extracted as common factors from various examples of polymer gels that undergo multiple phase transitions: the polymer should be ionized, have sufficiently high degree of hydrogen bonding plus the other attractive interaction. The multiple phase behavior of the 4-acrylamidosalicylic acid gel has remarkable memory, which depends on whether the gel has experienced the most swollen phase or the most collapsed phase in the immediate past. The information is stored and reversibly erased in the form of macroscopic phase transition behavior.

Key words : polymer gel, volume phase transition, multiple phase behavior, memory effect, mean field theory

1 INTRODUCTION

Various polymer gels are known to exist in two phases, swollen and collapsed. Volume phase transition occurs between the phases either continuously or discontinuously.^{1,2} Recently more than two phases are found in some gels. They are characterized by distinct degrees of swelling: the gel can take one of a set of values, but none of intermediate values. The number of phases depends on the polymer composition of gel.³⁻⁵ In this paper first we summarize the multiple phase of gels, then describe the memory effect of phase behavior.

2 MULTIPLE PHASES OF POLYMER GELS

The first example of gels that undergo the multiple phase transition was observed in the copolymer gels of acrylic acid (AAc) and methacrylamido-propyl-trimethylammonium-chloride (MAPTAC).³ They were copolymerized in various molar ratios while the total molar amount was fixed at 700mM. In these gels, polymer segments interact with

each other through attractive or repulsive electrostatic interactions and through hydrogen bonding (Fig.1). Thus two attractive interactions, hydrogen bonding and electrostatic interaction, are incorporated in these gels with different portions. Fig.2 shows the swelling curve of copolymer gel which consists of 450mM AAc and 250mM MAPTAC. In the neutral pH's the gel was at phase 1.0 ($=d/d_0$). As pH was increased the gel swelled discontinuously to phase 2.7 at pH 8.5. If pH was lowered from pH 8.5 the gel collapsed back to phase 1.0 at pH 7.0. If instead pH was further increased from pH 8.5 the gel swelled discontinuously into phase 3.0 at pH 9.8. As pH was lowered from pH 9.8 the gel collapsed into phase 1.0 at pH 6.4. If instead pH was increased up to pH 12 the gel diameter changed continuously. When pH was lowered from pH12 the gel went to phase 3.3 continuously. As pH was lowered the gel collapsed to phase 1.0 at pH 4.9. Three phases 1.0, 1.7, and 2.6 were found in the lower pH region.

Copoly(styrene/acrylic acid) gel also exhibits the multiple phase behavior, in which polymers interact with each other through hydro-

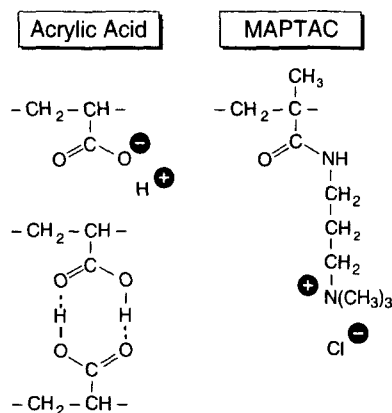


Fig. 1. Chemical structures of AAc and MAPTAC.

gen bonding and hydrophobic interactions.⁴ A systematic change in the macroscopic phase behavior was observed when the polymer composition was gradually varied. From the results of experiments described above, in order that a gel shows multiple phase behavior, it seems necessary that first, a gel should have a sufficient degree of ionization leading to polymer-polymer repulsion. Second the polymer should have attractive interaction: hydrogen bonding plus another kind of attractive interactions, i.e. electrostatic or hydrophobic interaction. In the case of copoly(acrylic acid/MAPTAC), the attraction is the electrostatic one between the charges of opposite kinds. For copoly(styrene/acrylic acid) gels, hydrophobic interaction plays the major role. It is important to note that out of the multiple phases only one corresponds to the stable phase with the lowest free energy minimum at a particular pH, whereas the rest should be the metastable phases. Which one is the stable phase depends on pH and it switches from one phase to another as pH is varied.⁵

3 MEMORY EFFECT OF PHASE BEHAVIOR

4-acrylamidosalicylic acid gel (PASA gel, Fig.3) exhibits multiple phases. Four phases were found in the gel, each of which was denoted by its diameter normalized by the original diameter: $d/d_0 = 0.81, 1.3, 3.4,$ and 4.9 (Fig.4). When pH or temperature was varied, the gel changed its volume discontinuously. The phase behavior appears to be a

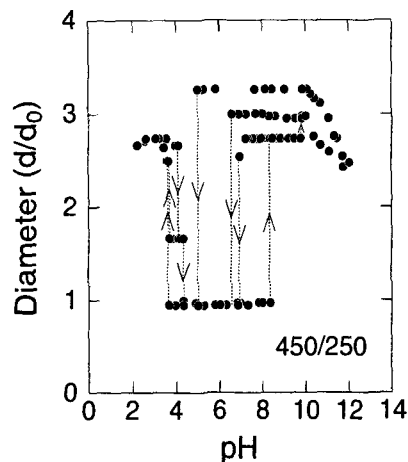


Fig. 2. Equilibrium swelling degree d/d_0 of copolymer gel consisting of 450 mM of AAc and 250 mM of MAPTAC in water as a function of pH at 25°C.

result of the combination of hydrogen bonding and hydrophobic interaction between polymer segments.⁶

PASA gel has remarkable memory: the phase behavior of the gel depends on whether the gel has experienced the most swollen phase (phase 4.9) or the most collapsed phase (phase 0.81) in the immediate past. The gel remained in the hysteresis loop shown in Figs. 4a and 4d when the pH was changed from phase 1.3. On the other hand, once the gel experienced phase 0.81, the phase transition loop remained in that which was shown in Fig. 4c. Therefore, the information is stored and reversibly erased in the form of macroscopic phase transition behavior.

The finding indicates that the equation of state for polymer systems, in which only a single variable, χ -parameter, is used to describe the polymer-polymer interaction, needs a fundamental modification. According to the mean field theory, the swelling behavior of a gel is described by the following equation:^{8,9}

$$\begin{aligned} \tau &\equiv 1 - \frac{\Delta F}{kT} \\ &= \frac{2\nu\nu_0}{N_A\phi_0^2} \left[\left(\frac{\phi}{\phi_0} \right)^{-5/3} - \left(f - \frac{1}{2} \right) \left(\frac{\phi}{\phi_0} \right)^{-1} \right] \\ &\quad + 1 + \frac{2}{\phi} + \frac{2 \ln(1-\phi)}{\phi^2}, \end{aligned} \quad (1)$$

where N_A is Avogadro's number, k the Boltzmann constant, T the temperature, ν the molar volume of the solvent, ϕ the volume frac-

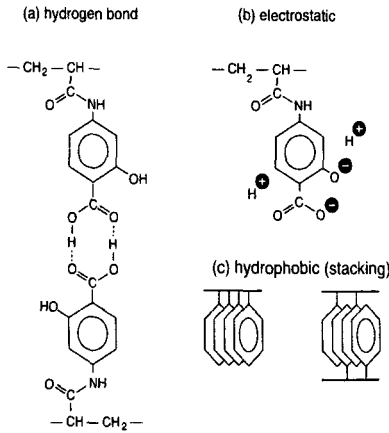


Fig. 3. Chemical structures of 4-acrylamido-salicylic acid polymers. They interact with each other through hydrogen bonding, hydrophobic interaction or ionic repulsive interaction.

tion of the polymer network, ϕ_0 the volume fraction of polymer network at the reference state, ΔF the excess free energy for the association between polymer segment and solvent, ν_0 the number of elastically active chains per unit volume at ϕ_0 , and f the number of dissociated counter ions per effective chain. The equation of the state of a gel uniquely determines the equilibrium swelling degree of the gel, $V/V_0 = \phi_0/\phi$ at a given value of the reduced temperature. Three values of ϕ , which correspond to two minima and one maximum value of the free energy, satisfy eq. 1 for a certain value of τ . Eq. 1, however, do not predict well the experimental results shown in Fig. 4 because this equation apply to only the non-hydrogen-bonding network. The phase behavior suggests that a new, attractive and short-range interaction arises in the polymer network of the gel after the gel experiences the most collapsed phase (phase 0.81). In the case of PASA gel, carboxylic acid groups can lead to the formation of both ionic and hydrogen bonds. When a hydrogen bond is formed, it influences the equation of state: it adds a new cross-linking between polymers and effectively shortens the polymer chain length, and the energy is lowered due to hydrogen bonding, ΔF_{HB} . Therefore we obtain the equation of the state of a gel by considering hydrogen bonds to form a new crosslinking under the following three assumptions. (1) Hydrogen bonding gives rise to physical crosslinking

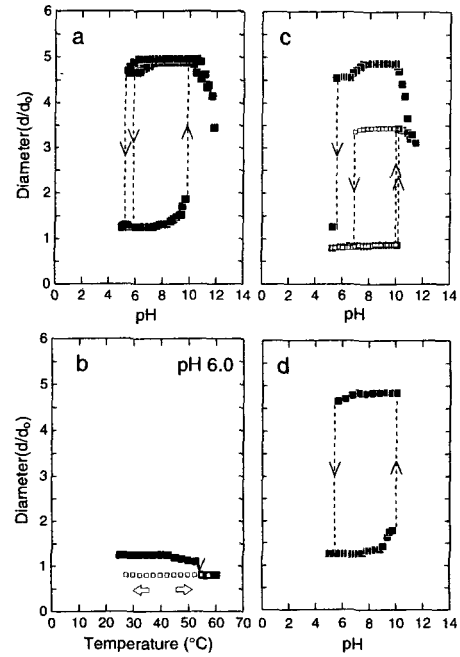


Fig. 4. Equilibrium swelling degree d/d_0 of PASA gel in water as a function of pH and temperature.

points in the chains, which comprise the gel. The formation of these crosslinking points divides a chain into short connected chains of equal length. (2) Physical cross-linking points are randomly distributed in the network, and no cooperative interactions are considered. (3) Solvent molecules and monomers composing the gel system have the same molar volume.

$$\begin{aligned} \tau &\equiv 1 - \frac{\Delta F}{kT} \\ &= \frac{2\nu\nu_0}{N_A\phi^2} \left[(h+1)^{1/2} \left(\frac{\phi}{\phi_0} \right)^{1/3} - (h+1)^{-3/2} \right. \\ &\quad \times \left. \left\{ \frac{(1-h/f)}{h+1} f + \frac{1}{2} \right\} \left(\frac{\phi}{\phi_0} \right)^{-1} \right] \\ &\quad + \frac{2\nu\nu_0}{N_A} \frac{h}{2} \frac{\Delta F_{HB}}{kT} + 1 + \frac{2}{\phi} \\ &\quad + \frac{2 \ln(1-\phi)}{\phi^2}. \end{aligned} \quad (2)$$

It is worthy to note that eq. 2 coincides with the equation of state for a non-hydrogen-bonding network (1) when the number of hydrogen bonds, $h = 0$. In the case of hydrogen-bonded networks, eq. 2 determines the equilibrium volume fraction of the polymer network ϕ as a function of the reduced tempera-

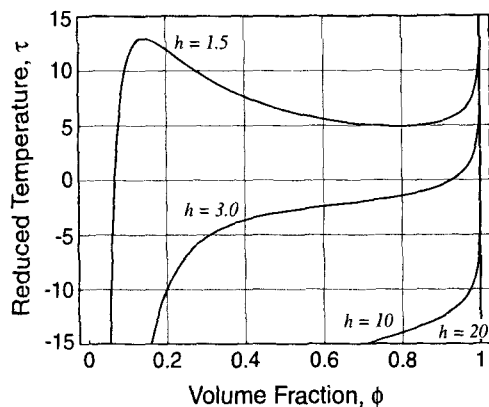


Fig. 5. Swelling curves of the gel for various values of h , the number of hydrogen bonds on an active chain, calculated using eq.2.

ture and h . Thus, a set of swelling curves corresponding to different h 's is obtained. The calculated results are shown in Fig.5. Phase behaviors of the PASA gel shown in Fig. 4b is considered to correspond to the hydrogen-bonded network. The discrete volume phase transition temperature of the gel becomes lower as increasing the number of the hydrogen bond in the gel, then it disappears at a critical value of h , i.e., $h = h_c$. The volume change at the phase transition temperature becomes smaller as increasing the value of h . The swelling curves of the gel are monotonous above h_c . The swelling ratio of the gel in the swollen state becomes smaller as increasing the number of hydrogen bond in the gel while that of collapsed state is insensitive to the number of hydrogen bond. The numerical calculation yields that the critical value of the number of the hydrogen bond h_c is 2.8 under the present conditions. It indicates that formation of only three hydrogen bonds out of ten acrylic acid units in an intact active chain causes a drastic change in the swelling behaviors of the gel. These results imply that the hydrogen bond in the polymer network effectively changes the phase behavior of the gel.

4 SUMMARY

From the results of experiments described above, in order that a gel shows multiple phase behavior, it seems necessary that first, a gel should have a sufficient degree of ionization leading to polymer-polymer repulsion. Sec-

ond the polymer should have attractive interaction: hydrogen bonding plus one of the other three attractive interactions.

These phenomena are explained by the mean field theory where the effects of the formation of hydrogen bonds are considered. The experiments shown above did not look into the structure of the phases. Recent studies using neutron scattering seems to indicate some structures in the gels at the phases but no structure when they are not in the phase.⁹ Further experiments are clearly needed to investigate the uniqueness of these structures to construct a theory which takes into account the cooperativity which is essential feature of hydrogen bonding.

ACKNOWLEDGEMENT

This work was partly supported by the Grant-in-Aid from the Ministry of Education, Science, Culture and Sports, Japan.

References

- [1] T. Tanaka, *Phys. Rev. Lett*, **40**, 820 (1978).
- [2] T. Tanaka, D. J. Fillmore, S. -T. Sun, I. Nishio, G. Swislow and A. Shah, *Phys. Rev. Lett*, **45**, 1636 (1980).
- [3] M. Annaka and T. Tanaka, *Nature*, **355**, 430 (1992).
- [4] M. Annaka, D. Berling, J. Robert and T. Tanaka, *Macromolecules*, **26**, 3234 (1993).
- [5] M. Annaka and T. Tanaka, *Phase Transit.*, **B47**, 143 (1994).
- [6] M. Annaka, M. Tokita, T. Tanaka, S. Tanaka and T. Nakahira *J. Chem. Phys.*, **112**, 471 (2000).
- [7] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York (1953).
- [8] P. G. de Gennes, "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, New York (1979).
- [9] M. Annaka, M. Shibayama, F. Ikkai, M. Sugiyama, K. Hara, T. Tanaka and T. Nakahira, *submitted*.