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# Multiple Phase Behavior of Interpenetrating Polymer Networks of Copolymer Gels

[†]Yoshiaki Hara, Masahiko Annaka[*], [††]Toyoichi Tanaka, Takayuki Nakahira,
[†]Toyoaki Matsuura and [†]Mototsugu Saishin
[†]Department of Ophthalmology, Nara Medical University, Kashihara, Nara 634-8522, Japan
Fax: +81-744-23-8032, e-mail: tmastuur@nmu-gw.naramed-u.ac.jp
[††]Department of Physics, Massachusetts Institute of Technology, Cambridge. MA 02139, USA
Fax: +1-617-225-2585, e-mail: toyo@mit.edu
Department of Materials Technology, Chiba University, Chiba, Chiba 263-8522, Japan
Fax: +81-43-290-3401, e-mail: annaka@planet.tc.chiba-u.ac.jp

Equilibrium swelling degrees of interpenetrating polymer networks of copolymer gels consisting of acrylic acid and methacryl-amido-propyl-trimethyl-ammonium-chloride are determined in aqueous solutions as a function of pH. As pH is varied, the gel changes its volume discontinuously among many phases distinguished by different volumes. The composition of the gel determines the number of phases and threshold pH for each transition. The largest number of phases was four and the smallest number was one. The topological restrictions of an IPN prevents the separation of the subnetworks, the cooperative contributions of the mutual entanglements and the attractive interactions remains effective over the whole pH and temperature ranges studied here.

Key Words: Polymer Gel, Volume Phase Transition, Multiple Phases, IPN

## 1. INTRODUCTION

Various polymer gels are known to exist in two phases, swollen and collapsed[1,2]. Volume phase transition occurs between the phases either continuously and discontinuously. Recently more than two phases are found in gels consisting of copolymers randomly distributed positively and negatively charged groups[3]. They are characterized by distinct degrees of swelling: the gel can take one of the sets of values, but none of intermediate values. The number of phases depends on the polymer composition of gel.

In these gels, polymer segments interact with each other through attractive or repulsive electrostatic interactions, hydrophobic interaction, and through hydrogen bonding. The combination of these forces appears to result in multiple phases.

In this paper we present a study of interpenetrating polymer networks (IPN) of copolymer gels of acrylic acid (AAc) and methacryl-amido-propyl-trimethyl-ammonium-chloride (MAPTAC) (Figure 1). IPNs are a type of polymer blend consisting of two or more network polymers. They are more or less intimate mixtures of two or more distinct polymer networks that held together by permanent entanglements with only accidental covalent bonds between the polymers, i.e. they are catenated polymers. The entanglements in IPNs must be of a permanent nature and are made by homo-network formation of two or more polymers.

IPN can be expected to have vectorial properties and sensitivity to stereochemistry. For example, if the hydrogen-bond donors and acceptors are arranged in particular geometry, the hydrogen bonding interactions become cooperative and effective. The AAc interact with themselves through hydrogen bonding and ionic repulsion. Therefore the interaction in the IPN copolymer gel is expected to be stronger than between polymers in ordinary gels.

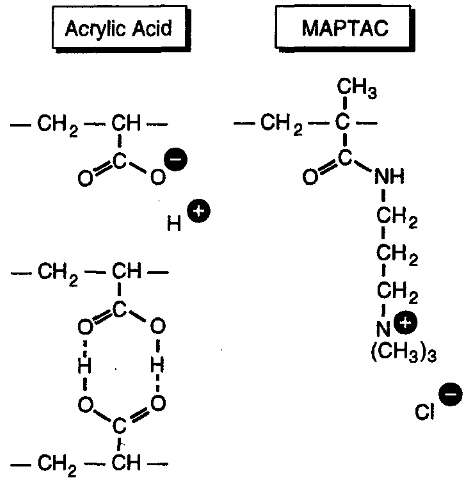

**Figure 1.** Chemical structures of AAc and MAPTAC. AAc is a weak acid ionized at pH > 4.5 and can form hydrogen bonding with another acrylic acid. MAPTAC is a strong base and considered to be ionized in most of the pH range of our measurement.

## 2. EXPERIMENTAL

2.1 *Materials*: AAc (Aldrich) was purified by distilled under reduced pressure before use. MAPTAC (50 % aqueous solution, Polyscience), N, N-methylenebis-acrylamide (cross-linker, BioRad), and ammonium persulfate (initiator, Kanto Chemical Co.) were used without further purification.

2.2 *Sample Preparation*: IPN of copolymer gels of acrylic acid and MAPTAC were studied for various compositions of the first and second polymer networks. The IPNs are prepared by free radical polymerization: polymer network I was made. The reactants to form network II, for example monomer II, crosslinker and initiator, are swollen into network I and reacted *in situ* (Figure 2). To prepare IPNs consisting of acrylic acid and MAPTAC, we first prepare a copolymer gel consisting of acrylic acid and MAPTAC at a certain ratio in capillaries. Gels were taken out from capillaries, washed, and dried. The dried gels were re-inserted into capillaries of same diameter and were allowed to swell in pregel solutions having the composition for the second network. The molar ratio of each network was varied while the total amount was fixed 700 mM at each network. For example, the following is the preparation recipe for the gel labeled 400/700: First a gel was made of 400 mM of acrylic acid and 300 mM of MAPTAC and second network consists of 700 mM of acrylic acid and 0 mM of MAPTAC. More specifically, the first network is made of 400 mM of acrylic acid, 300 mM of MAPTAC, 0.133 mg of N, N'-methylenebisacrylamide (cross-linker) and 40 mg of ammoniumpersulfate (initiator) were dissolved in 100 ml of water.

The solution was degassed under vacuum and polymerized in capillaries of inner diameter $d_0 = 340$ mm at 60 °C for 8 hours. The gels were extracted from capillaries, and were washed with large amount of water to remove unreacted monomers. Then the gels were dried and were inserted into capillaries of same diameter. The dried gels were allowed to swell in the solution of 700 mM of acrylic acid, 0.133 mg of N, N'-methylenebisacrylamide and 40 mg of ammoniumpersulfate in 100 ml of water. Gelation took place at 60 °C for 8 hours. After gelation was completed, gels were removed from capillaries, and were cut into small cylinders of length 1 mm. Then gels were immersed in a large amount of water to wash away residual chemicals. The water was repeatedly changed until the diameter of the gels reached an equilibrium value.

2.3 *Determination of Phase Diagram*: The gel was placed in a glass cell whose temperature was controlled to within 0.1 °C and was continuously flushed with water from a reservoir, the pH of which was controlled by addition of HCl solution (to lower pH) or water (to increase pH) below pH 7. NaOH solution was used above pH 7. The gel diameter at equilibrium, $d$, was measured under a microscope. To avoid the effect of carbon dioxide in air, all the experiment was carried out under nitrogen gas atmosphere. The temperature was controlled to within ± 0.1 °C by circulating water from LAUDA RC-3 during the measurement.

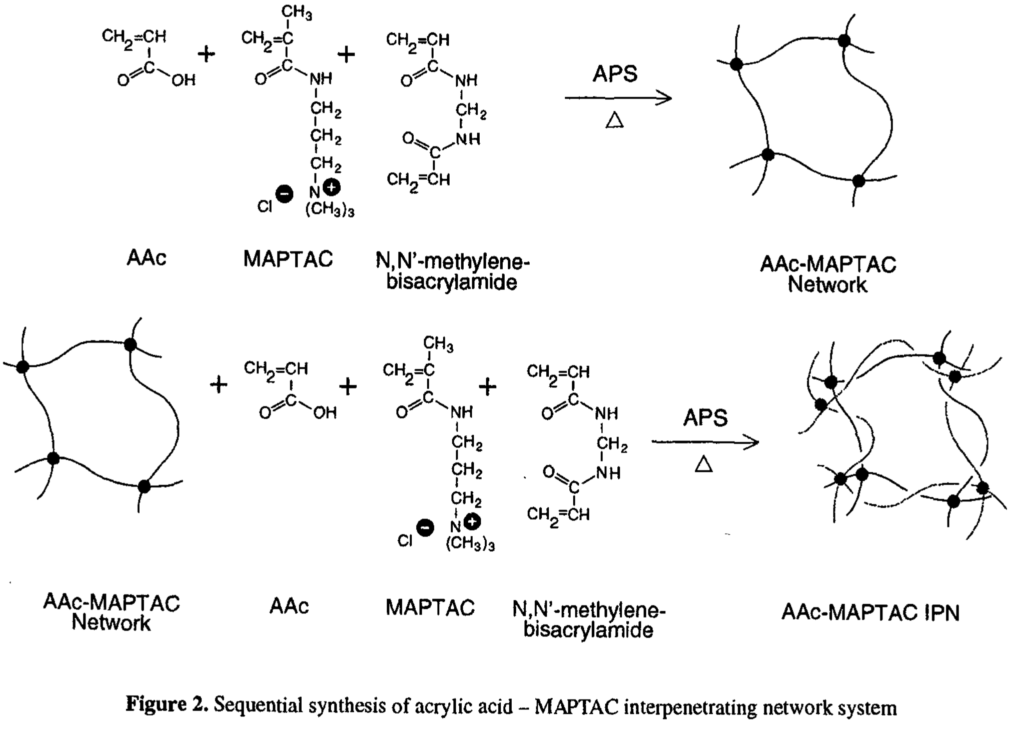

**Figure 2.** Sequential synthesis of acrylic acid – MAPTAC interpenetrating network system

## 3. RESULT AND DISCUSSION

Figure 3 shows the equilibrium swelling degrees, $d/d_0$ , of IPN copolymer gel made at various ratios of acrylic acid and MAPTAC as a function of pH at 25 °C. More than two phases are found in these gels. They are characterized by distinct degrees of swelling; the gel can take one of a set of swelling values, but none of the intermediate values. Swelling curves are very complicated for some of the gels and the following rule was adopted so that no branches of swelling curves are missed. First, the gel was let swollen at high pH. Then pH was gradually lowered until the gel shrinks into a phase of smaller volume. Every time a volume phase transition occurs the pH change was reversed to complete all the hysteresis cycles. Each cycle was repeated at least twice for confirmation of reproducibility. Then the pH was changed in the opposite direction after the last swelling transition occurred.

There were three distinct volume phases in the 400/700 IPN copolymer gels at higher pH. Each phase is denoted by its diameter normalized by the original diameter: $d/d_0$ = 0.4, 2.2, and 2.6. In the neutral pH's the gel was at phase 0.4 (= $d/d_0$). As pH was raised it swelled discontinuously to phase 2.2 at pH 8.5. As pH was lowered from pH 8.5, the gel collapsed to phase 0.4 at pH 5. If, instead, pH was increased from pH 8.5, the gel diameter changed continuously up to pH 12. As pH was lowered from pH 12, the gel swelled continuously into phase 2.6. Upon further reduction of pH, the gel collapsed into phase 0.4 discontinuously at pH 3.8. These cycles were repeated with excellent reproducibility.

A systematic change in the macroscopic phase behavior was observed when the polymer composition was gradually varied. The largest number of phases was four and the smallest number was one.

Figure 4b shows the pH dependence of equilibrium swelling degrees, $d/d_0$ , of copolymer gel consisting of 700 mM of acrylic acid and 700mM of MAPTAC prepared by one-step radical polymerization. The monomer composition of this gel is same as 700 / 0 IPN gel, it is however important to note that the shrunken phase shown in the figure 4b is not a most compact phase, which was found in the IPN gel with same monomer composition.

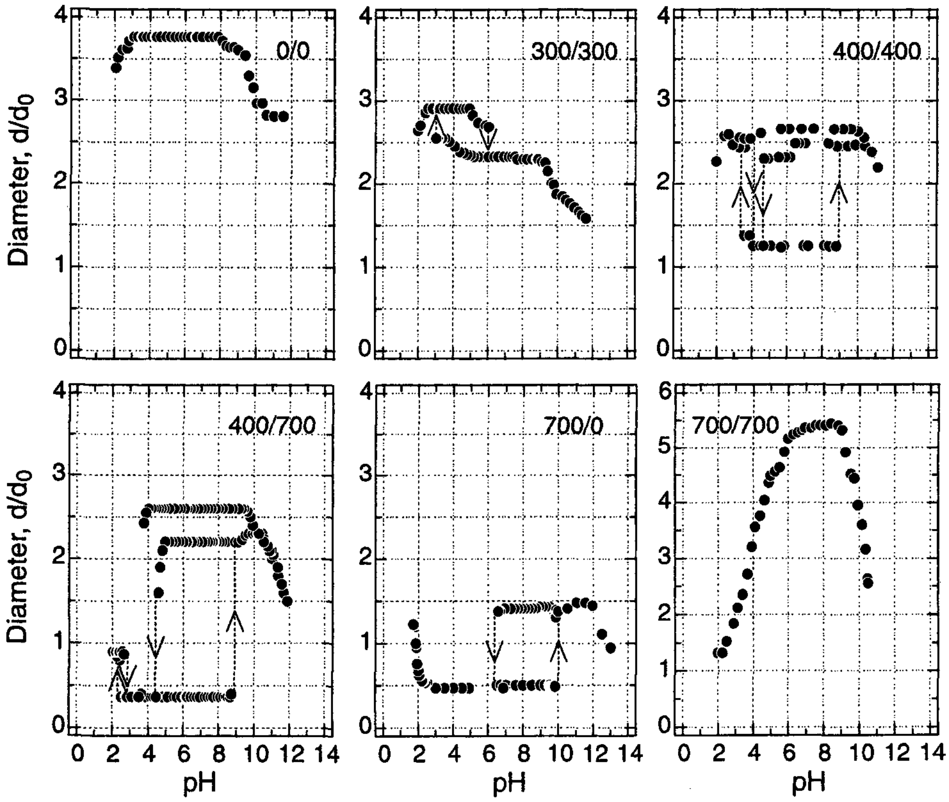

**Figure 3.** Equilibrium swelling degree $d/d_0$ of IPN gels consisting of acrylic acid and MAPTAC as a function of pH at 25 °C. The amounts of acrylic acid of first and second networks are indicated respectively. For example, 400/700 means that the first network of the gel consists of 400 mM of acrylic acid and 300 mM of MAPTAC, the second network 700mM acrylic acid and 0 mM of MAPTAC.

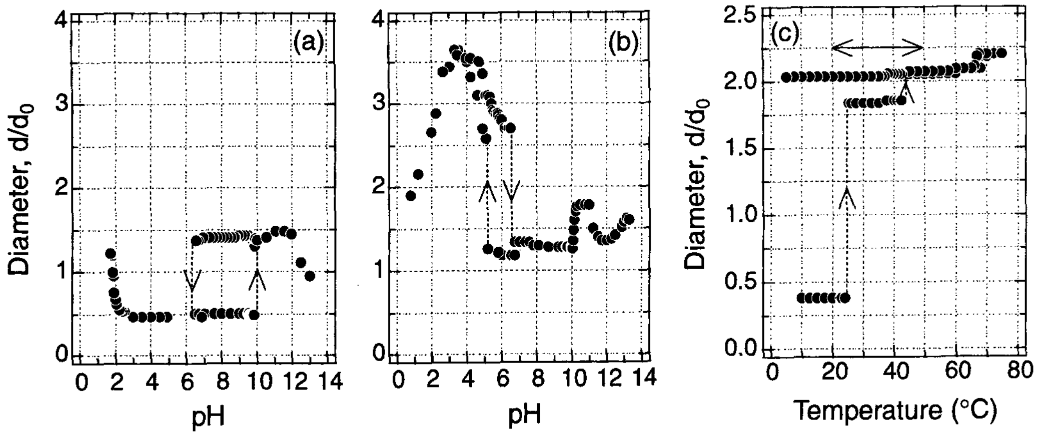

**Figure 4.** Equilibrium swelling degrees d/d₀ of (a) 700/0 IPN gel as a function of pH at 25 °C, (b) copolymer gel consisting of 700 mM of acrylic acid and 700 mM of MAPTAC as a function of pH at 25 °C and (c) 400/ 700 IPN gel as a function of temperature at pH 8.5.

Although the chemical cross-linking points and entanglements of the network chains are irreversibly fixed, the compositional structure depends strongly on the temperature or, equivalently, on the Flory-Huggins interaction parameter $\chi(T)$. Note that a blend of polymer chains undergoes phase separation if this $\chi$ parameter becomes large enough. In comparison, the topological restrictions of an IPN (permanent mutual entanglements as a result of the irreversibly formed chemical cross-linking points) make the gel collapse to the most compact phase. Furthermore, since this topological restrictions prevents the separation of the subnetworks, the cooperative contributions of the mutual entanglements and the attractive interactions remains effective over the whole pH range studied here: electrostatic attractive interaction between AAc and MAPTAC (pH 7 <) and hydrogen bonding (< pH 7).

Figure 4c shows the temperature dependence of the swelling curve of 400/700 gel at pH 8.5. Three distinct phases were observed in the gel. The gel underwent discontinuous transition between some of the phases confirmed in the pH experiment.

Coexistence of multiple phases is possible if they each correspond to a minimum in free energy. However, the lowest minimum is the stable equilibrium state and the others represent metastable phases. As the environment varies the minima can cross, leading to a discontinuous phase transition. The fact that observed transitions always involve a discrete set of swelling degrees and none of the intermediate values, suggests that these swelling degrees correspond to separate free energy minima. The different stimuli create the different minima crossings, which leads to the discontinuous phase transitions between different phases.

Theoretically, multiple phases may be understood as a result of competition among various factors. The mean field free energy consists of terms for rubber elasticity, osmotic pressure by counter ions, net charge repulsion, and virial interactions[4,5]. The effect of having equal amount of cationic and anionic charges on polymers, the polyampholyte effect, results in long range attractive interactions due to the Debye-Hückel energy[6-9], and in short range repulsive interactions due to local charge imbalance[10]. These six or seven terms with different powers of polymer density can create free energy minima at three distinct densities. Clearly it is not enough to describe the four multiple phases. It is therefore necessary to introduce new order parameters in addition to the polymer density to predict more than three phases.

Hydrogen bonding density $\rho_{HB}$ may be a natural choice for a new order parameter. Formation of hydrogen bonding is energetically favorable, but entropically undesirable since it restricts freedom of chain configurations. This competition can create two free energy minima for a fixed polymer density $\rho$. Since $\rho_{HB}$ and $\rho$ are coupled, the free energy $F(\rho, \rho_{HB})$ can have six minima in the $\rho$ - $\rho_{HB}$ plane.

All functions of proteins, molecular recognition, catalysis, and motions, can be achieved only when the polypeptide chain folds to a specific structure. The principle with which the one-dimensional sequence is transformed into the three dimensional structure, and the principle with which the function emerges from the structure are still unsolved problems. However, it seems necessary that a unique structure should be thermodynamically stable in order that it is reversibly quickly reproduced by the polypeptide as demonstrated in various in vitro experiments[11]. We believe that the IPN gels showing the multiple phase behaviors may have such thermodynamic stable states.

## 4. CONCLUSION

Equilibrium swelling degrees of IPN copolymer gels consisting of AAc and MAPTAC are determined in aqueous solutions as a function of pH and temperature. As pH is varied, the gel diameter changes discontinuously among many phases distinguished by different volumes. The composition of the gel determines the number of phases and threshold pH for each transition. The largest number of phases was four and the smallest number was one.

The most compact phase was observed in the IPN gel, which was not observed in the random copolymer gel with same monomer composition. Since the topological restrictions of an IPN prevents the separation of the subnetworks, the cooperative contributions of the mutual entanglements and the attractive interactions remains effective over the whole pH and temperature ranges studied here.

The finding indicates that the equation of state for polymer systems, in which only a single variable, $\chi$-parameter, is used to describe the polymer-polymer interaction, needs a fundamental modification. It will also provide a physical basis with which to understand the structure and specific functions of polymers only known to biopolymers.

## 5. FUTURE WORKS

The experiments shown above did not look into the structure of the phases. Recent studies using dynamic light scattering seems to indicate some structures in the gels at the phases but no structure when they are not in the phase[12]. Further experiments are clearly needed to investigate the uniqueness of these structures. For example, NMR, neutron scattering, and various spectroscopic methods should be employed to study the microscopic random structures of the gels at and off the phases. Theories are also needed to understand the multiple phases. Recent theories of heteropolymers such as the one by Shakhnovich and Gutin[13], where Spin glass theory is modified to understand the protein folding problem may be useful to develop a theory for multiple phases.

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