SYNTHESIS AND PHYSICAL PROPERTIES OF ENVIRONMENTALLY RESPONSIVE POLYMER GELS

DISSERTATION

Presented to the Graduate Council of the University of North Texas in Partial Fulfillment of the Requirements For the Degree of

DOCTOR OF PHILOSOPHY

By

Xiaomin Zhang, B.E., M.S.

Denton, Texas

May, 1996
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Polymer gels undergo the volume phase transition in response to an infinitesimal environmental change. This remarkable phenomenon results in many potential applications of polymer gels. This dissertation systematically investigates the chemical and physical properties of polymer gels.

It is found that infrared radiation laser not only induces a volume phase transition in N-isopropylacrylamide (NIPA) gel, but also causes the gel to bend toward the laser beam. The transmission of visible laser light through a NIPA gel can also be controlled by adjusting the infrared laser power.

A new class of environmentally responsive materials based on spatial modulation of the chemical nature of gels has been proposed and demonstrated. Three simple applications based on the modulated gels are presented: a bi-gel strip, a shape memory gel, and a gel hand. The bending of bi-gels has been studied as a function of temperature, acetone aqueous solution, and salt solution.

As the polymer network concentration increases, the behavior of shear modulus of acrylamide (PAAM) gels deviates significantly from the classical theory. The ionic NIPA gels undergo two sequential volume phase transitions: one occurs in dilute NaCl solution, the other occurs in concentrated NaCl solution. An interpenetrating polymer network (IPN) of PAAM--NIPA has also been synthesized using free radical polymerization. It is found that the IPN gels preserve the essential properties of individual components. The volume phase transition of the IPN gels can be triggered by multiple external stimuli including temperature, acetone concentration, and salt concentration.
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A gel is a form of matter intermediate between a liquid and a solid. A polymer gel consists of a cross-linked polymer network, and a solvent which fills the pores of the network. Mechanically, it is similar to natural rubber. The hydrogels consist of a polymer network obtained by chemical cross-links and water as solvent. The gels swell until equilibrium is established between osmotic forces and the elasticity of the chains, which is determined by the degree of cross-linking [1]. A common feature of hydrogels is that their properties are usually very sensitive to changes of ionic strength, pH, etc. of the solvent [2]. Because of its large swelling ability, a gel has a very high deformability and recoverability.

Gels are found everywhere. In our bodies, the cornea, vitreous humor, and connective tissues are gels. The surface of internal tracts such as the stomach and lung are covered with gels. Basement membranes for the kidney and blood vessels are also gels. These membranes are believed to play a fundamental role in the transport of water and solute molecules. Softness, elasticity, and the capacity to store a fluid make gels unique materials.

The capacity of the gels to absorb water or solvent is enormous and can be as much as 1000 times the weight of the dry gel [3]. This makes the gel an ideal absorption material, useful as a baby diaper or plant soil. The large swelling ability also makes gels useful in industrial cosolute separation technology [4, 5], and biological slurry dewatering technology [6], etc.
The applications of polymer gel systems for drug delivery devices have been of increasing interest. Changes in swelling states of gels can influence the diffusion of solutes from within the gels to the outside aqueous media [7, 8] and make polymer gel a good material for drug release. Using hydrogel membranes, it has been shown that it is possible to design human implantable, self-regulating insulin delivery systems sensitive to glucose concentration [9].

There are many other applications of gels. Disposable diapers and sanitary napkins use gels as super water absorbers. Sheets of gels are developed that tightly wrap fish and meats, keeping them moist but absorbing unnecessary excess water, for efficient transportation and storage. Gels are used for agricultural purposes as retainers of water and solutes. Gels are indispensable materials as molecular sieves to separate molecules according to size in gel permeation chromatography and electrophoresis. Soft contact lenses, artificial lenses, artificial vitreous humor, and materials used in plastic surgeries are made of gels. Gels are also used as control delivery systems for drugs and perfumes. The gels also play a vital role in the fields of medicine, foods, chemical, agricultural, and other industries.

Since Tanaka [10, 11] and co-workers observed the critical behavior of polyacrylamide gel using light scattering spectroscopy in 1977 and later observed the density (volume) phase transition of acrylamide gel in acetone-water mixtures, the intensive study of gel phase transition and related phenomena has begun. The volume change at a volume phase transition is reversible and can be as large as several thousands times. The original using such gels many researchers are now developing artificial muscles, actuators, controlled release systems, sensors, chemical memories, optical shutters, matrices for molecular separation, and toys. For example, polyelectrolyte gels that expand and contract under electrical control can be used as switches, artificial muscles [12], or can serve as general-purpose chemical valves [13]. For these reasons, they are called "intelligent gels"
The triggering stimuli to induce the volume phase transition include temperature, solvent composition, pH, ionic composition, electric field, light, and specific molecules. The phenomenon is universal to all gels: They are observed in synthetic gels and gels made of natural polymers. The reversible phase transition of polymer gels makes it possible to use gels as sensors.

For applications of polymer gels, the understanding of their physical properties and developing new gel materials are very important. This dissertation systematically studies a novel polymer gel synthesis and the physical properties of polymer gels.

In this work, polyacrylamide (PAAM) and N-isopropylacrylamide (NIPA) were used as the basic monomers to make our gel samples. Some experiments also incorporate sodium acrylate (SA) with any one of the above two monomers as an ionic component in the gels. These copolymerized gels are called polyelectrolyte gels or ionic gels because of the extra ionic charges in the polymer chains. The NIPA gel is temperature sensitive and salt sensitive because of its hydrophobic property. The NIPA gel shows low critical solution temperature (LCST). On the other hand, PAAM gel is a hydrophilic, solvent sensitive but temperature and salt insensitive.

The dissertation is organized as follows: In chapter 2, the phase transition and bending induced by infrared light in NIPA gels is described. Light-induced phase transitions in polymer gels have attracted considerable interest [3, 14-16] because light as an external stimulus can be controlled remotely, changed rapidly, and it is clean compared with traditional stimuli such as temperature, pH, electric field, and solvent concentration [17,18]. One challenging area in gel research is to develop optical gel devices based on the volume phase transitions. There have been several successful experiments reported, including volume phase transitions in gels induced by ultraviolet light [3] and visible light [14, 15]. By initiating the ionization reaction in a gel, the ultraviolet radiation causes an
increase of the internal osmotic pressure and makes the gel swell [3]. On the other hand, visible light is used to directly heat the polymer network in a thermally sensitive NIPA gel that has been copolymerized with chlorophyll molecules [14,15]. Such heating compels the gel to undergo a discontinuous volume phase transition. Since the volume change of gels is caused by the direct laser heating of the polymer network, the rate of the transition is faster than that under ultraviolet light, which depends on a slow photochemical ionization process [3].

Infrared light is not visible and is easily absorbed by hydrogel. There are particular benefits in the use of infrared irradiation to stimulate the phase transition of polymer gels. Unlike the visible light method, which requires the incorporation of photosensitive molecules into the gel network to provide photon absorbency [14,15], the infrared light method can be readily applied to hydrogels due to the high infrared light absorbency of water. Our infrared spectroscopy measurements show that the NIPA gel has a strong infrared absorbency band around the wavelength 10.6 μm. This absorbency is primarily due to the electric dipole moments of the water molecules. Here, a CO₂ infrared laser has been used to induce the volume phase transition and bending effect in a straight cylindrical NIPA gel. The bending effect has been measured as a function of CO₂ laser power, time, and the sample cell temperature.

In chapter 3, a systematic study of visible light transmission in the ionic NIPA gel under the influence of a CO₂ infrared laser is presented. It is known that in addition to the volume phase transition near the transition point, a transparent NIPA gel also becomes opaque. This opacity may be due to the spinodal decomposition [19], which occurs when the network concentration decomposes into domains with two different values, one dilute and the other dense, as the laser causes the temperature to increase from below \( T_c \) to above \( T_c \). If the domain sizes are comparable with the wavelength of visible light, the light will be effectively scattered, resulting in the reduction of the transmitted light through the
gel. Recently, Suzuki reported visible light-induced opacity in NIPA gel which had been co-polymerized with photosensitive chlorophyll molecules [18]. Since the NIPA gel has a strong infrared absorbency band around the wavelength 10.6 \( \mu \text{m} \) [20], there is no need to incorporate photosensitive molecules into the gel network to provide photon absorption.

It is found that the infrared light can effectively control the transmission of a He-Ne laser beam in the NIPA gel when the He-Ne visible laser beam is aligned along the same optical axis as the infrared beam. The change of transmission of the visible light as the infrared laser is turned on is completely reversible. The response time required for the change of the transmission is much faster than that required for the change of gel volume. Since the response time is short, the sample cell temperature remains almost constant during the infrared laser on-and-off cycles. The advantage of using infrared light to induce the transparent-to-opaque transition is threefold: first, the gel devices can be remotely controlled; second, the external stimulus of the infrared laser power can be changed rapidly; and third, a focused infrared laser can make the gel surface opaque locally, while the sample cell temperature remains almost unchanged. Results of this experiment show clearly that excellent possibilities exist for developing fast-response gel devices based on the gel's transparent-opaque transition.

In chapter 4, a new class of materials based on spatial modulation of the chemical nature of gels is proposed and demonstrated. The modulation is achieved by inter-penetrating only part of one gel network with another gel network. The potential application of gel materials as artificial muscles was first demonstrated by Katchalsky's group in his famous collagen engine [21]. Subsequently, gels have been explored to perform various functions including drug-delivery devices [22-24], chemical valves and actuators [14, 25, 26], and magnetic resonance monitoring agents [27]. The gels used in all of these reports had macroscopically uniform structures. In homogeneous polymer gels, it is necessary to use an external gradient field to induce bending effect.
Here, the modulated gels have an internally heterogeneous, or modulated, structure without the need of having a gradient environment to induce the bending or shape change. Three simple applications based on the modulated gels are presented: a bi-gel strip, a shape memory gel, and a gel hand. These three applications are based on the volume phase transitions of gels in response to external environmental changes, and that different gels are responsive to different aspects of the environment [14]. In particular, the temperature sensitivity of the NIPA gel and acetone concentration sensitivity of the PAAM gel [16] are the controlling mechanisms for the three applications presented here. The bi-gel strip bends almost to a circle when its temperature or solvent is changed. The shape memory gel changes its shape among straight, pentagonal, and quadrangle forms at different temperatures. The gel hand can grasp or release an object by simply adjusting its temperature. The results reported here have far-reaching significance for making active gel devices and sensors.

In chapter 5, the bending process of the bi-gels is reported in detail. Previously, there have been some reports about bipolymer strips. For example, the bipolymer strip was made by attaching a polymer layer to an inert (non-swelling) elastic backing [28]. The behavior of this composite sample is similar to that of a bimetallic strip except that the bending is caused by humidity rather than temperature. Another kind of bipolymer strip is made of a polypyrrole (PPy) layer and a polyethylene layer bound together. The bending is caused by the volume change of the PPy layer [29]. The bending of a bi-gel (IPN and PAAM) strip induced by temperature, aqueous acetone solution, and salt solution is discussed here. The bending kinetic process and the collective diffusion coefficient of the IPN gel are also quantitatively described. The results reported here will be helpful for making intelligent gel devices, actuators, and sensors.

In chapter 6, the network concentration dependence of the shear modulus of PAAM gel over a broad concentration ranging from 0.02 to 1.0 g/cm³ is presented. The
elasticity of polymer gels is an important characteristics for applications. Gels are three-dimensional networks of crosslinked polymers immersed in solvent. The mechanical properties of polymer gels are determined by the bulk modulus and shear modulus. The application of scaling methods to these elastic moduli has led to some dramatic successes in both theoretical understanding and experimental applications [12]. A variety of polymer gel systems have been tested and it was found that the concentration-dependent shear modulus of gels follows the classic theoretical scaling law with the scaling exponent equal to 1/3 [30-32]. To our knowledge, all of these tests were performed on gels that have the network concentration below 0.25 g/cm$^3$. A higher concentration is hard to obtain using the conventional deswelling methods which rely on osmotic pressure to squeeze water out [30-32]. It is of interest to explore the scaling behavior at high concentrations. Here, the experiment clearly shows that the classic theory cannot explain the behavior of shear modulus in a high network-concentration regime. A non-classical scaling model based on the heterogeneity of the gel network has been proposed and seems to describe the data well.

In chapter 7, swelling equilibria of the neutral and ionic NIPA (NIPA copolymerized by sodium acrylate) gels are determined as a function of NaCl concentration in aqueous solutions. It is found that the same ionic NIPA gels exhibit two phase transitions in aqueous NaCl solutions at room temperature: One in diluted NaCl solutions (NaCl ~ 0.1 M), and the other in aqueous salt solutions with a higher NaCl concentration (NaCl greater than 0.8 M). From an application point of view, polyelectrolyte gels offer some unique opportunities. They have much higher swelling capability for given stiffness. Typically, these gels are sensitive to pH [33], solvent ionic strength (salt concentration) [34], and external electric field [35]. Most of these works, however, are verified by swelling data and do not deal with the network mechanical properties directly. More detailed study of the mechanical properties of polyelectrolyte
gels is thus needed to meet the challenges of both theoretical understanding and practical applications. Therefore, the shear modulus of ionic NIP A gels is investigated in NaCl solutions here.

In chapter 8, the synthesis and study of PAAM and NIPA interpenetrating polymer network gels, or PAAM-NIPA IPN gels are reported. Most of the polymers studied previously are responsive to only one kind of stimulus. But, for some applications, independent responsiveness to several factors, such as temperature, solvent, and salt concentration, may be required [33]. The gels which are sensitive to more than one variable—in particularly—temperature and pH, have been investigated in drug delivery systems [33, 37, 38]. The interpenetrating (IPN) technique is one useful method to get multifunctional gels. Previous experiments [39] on IPNs of poly (acrylamide) PAAM and poly(acrylic acid) PAAc gels showed that the IPN exhibited rapid swelling changes, in contrast to random gels composed of the same monomer composition, which only exhibited gradual swelling changes near the transition temperature. The PAAM and NIPA polymers show good compatibility in aqueous solution [40]. Their hydrogels possess contractive swelling behavior [14,15], i.e., PAAM gel undergoes the volume phase transition in acetone/water mixture, while NIPA gel shrinks and eventually collapses with the increase of temperature. In the case of the interpenetrating PAAM gel with NIPA network, it is expected that the IPN gel will form. The volume change of IPN gels can be triggered by both acetone concentration and temperature. The swelling properties of the IPN system are compared with that of its network components. The elastic property of gels can be modified by interpenetrating two kinds of networks [41].

Finally, this work is summarized in Chapter 9.
CHAPTER 1 REFERENCES


CHAPTER 2

INFRARED-LIGHT INDUCED VOLUME PHASE TRANSITION AND BENDING IN N-ISOPROPYLACRYLAMIDE GEL

2.1 Introduction

One challenging area in gel research is to develop optical gel devices based on volume phase transitions. Light-induced phase transitions in polymer gels have attracted considerable interest [1-4] because light as an external stimuli can be controlled remotely, changed rapidly, and it is clean compared with traditional stimuli such as temperature, pH, electric field, and solvent concentration [5,6]. There have been several successful experiments reported, including volume phase transitions in gels induced by ultraviolet light [2], visible light [1, 3], and infrared light [4]. By initiating the ionization reaction in a gel, the ultraviolet radiation causes an increase of the internal osmotic pressure and makes the gel swell [7]. On the other hand, visible light is used to directly heat the polymer network in a thermally sensitive N-isopropylacrylamide (NIPA) gel which has been co-polymerized with chlorophyll molecules [8,9]. Such heating compels the gel to undergo a discontinuous volume phase transition. Since the volume change of gels is caused by the direct laser heating of the polymer network, the rate of the transition is faster than that under ultraviolet light, which depends on a slow photochemical ionization process [2].

In this chapter, we report the study of the infrared light induced volume phase transition and bending in the NIPA gel. The NIPA gel is temperature sensitive and exhibits the phase transition near 33.4 °C with a reversible, near continuous volume change [7]. Unlike the visible light method, which requires the incorporation of photo-
sensitive molecules into the gel network to provide photon absorbency [1,3], since both the gel network and water have strong light absorption bands located in the infrared frequency range between 9 \( \mu m \) to 11 \( \mu m \), there is no need to copolymerize photo-sensitive molecules into the gel network. The infrared light method can be readily applied to hydrogels due to the high infrared light absorbency of water. Our infrared spectroscopy measurement indicate that the NIPA gel has a strong infrared absorbency band around the wavelength of 10.6 \( \mu m \). This absorbency is primarily due to the electric dipole moments of water molecules. Here, we present detailed experimental results and analysis of CO\(_2\) infrared laser-induced physical property changes in NIPA gels. Since the neutral NIPA gel is temperature sensitive and exhibits a phase transition near 33.6 °C with a reversible, nearly continuous volume change [5], and the transition temperature increases with an increase of the ionic groups attached to the polymer network [6,8], the NIPA gel is an ideal system for the study of gel properties under thermal stimuli.

2.2 Experiment

The NIPA gel samples were made by free radical polymerization. A mixture of 7.8 g of N-isopropylacrylamide (Kodak, Co.), 133 mg of methylene-bis-acrylamide as a crosslinker, and tetra-methyl-ethylene-diamine (240 \( \mu l \)) as an accelerator, were dissolved in 100 ml of deionized and distilled water. The ionic NIPA gel was made by incorporating 100 mg sodium acrylate into the pregel solution. Nitrogen gas was bubbled through the solution to remove dissolved oxygen. Ammonium persulfate (40 mg) was added to the solution as an initiator. The pre-gel solution was then poured into cylindrical glass tubes with a diameter of around 2 mm, and the gel formed in about 15 min. To enhance the visibility of the gels, a small amount of blue dextran was added to samples. The swollen samples used were about 18 mm long with diameters from 2.1 mm to 2.8 mm.

The Figure 2.1 shows a block diagram of the experimental setup. A grating
tunable continuous wave CO₂ laser was operated at wavelength of 10.6 μm. The light intensity was adjusted by varying a commercial attenuator. An incident laser beam was divided using a 50/50 beam splitter, one part going to a laser power gauge and the other going to the sample. The error in laser power measurement was about 10%. The laser spot was 0.75 mm with a condenser/collimator, and 1.9 mm without it. Two BaF₂ (3 mm thickness) infrared windows were installed in a transparent plastic sample cell, which had inner cell dimension of 18.7 mmx9.3 mmx18.7 mm, along the path of the laser beam. The cell was constructed such that the sample could be suspended in water with its upper end fixed to a clamp. A telescope was used to measure the sample size to an accuracy of 0.1 mm, and a camera was used to record gel bending. The sample temperature was measured using a platinum resistance thermometer inserted into the sample cell. The distance between the thermometer and the sample was about 5 mm. The accuracy of the temperature measurements is estimated to be ±0.1 °C.

2.3 Results and Discussion

2.3.1 Volume phase transition induced by infrared light

Figure 2.2 shows the ratio of final to initial diameters as a function of infrared laser power for a neutral NIPA gel (cross), and an ionic NIPA gel (SA=100 mg) (circle), respectively. The data were taken with the laser power increasing at a rate of about 50 mW/h. From this figure one can see that, as the power increases, the gel shrinks and eventually collapses. This transition is reversible, i.e., after removing the laser, the gel regains its original size and shape.

The infrared laser induced transition may be attributed to laser heating. Over the range of the laser power used, the temperature is changed linearly as a function of laser power as shown in Figure 2.3. From this relation we found that the critical points for neutral and ionic gels are about 33.5 °C and 34.7 °C, respectively. The transition
Figure 2.1. A block diagram of the experimental setup.

Figure 2.2. The swelling curves for the neutral gel (plus) and the ionic gel (circle) under infrared laser irradiation.
temperature for the ionic gel is higher than that for the neutral gel. This is because ionic interaction in the ionic gel has produced a positive osmotic pressure which pushes the transition point to a higher value. Combining Figures 2.1 and 2.2, one can clearly see that the infrared laser light acts like a heating source, triggering the volume phase transition.

The advantage of using infrared light to induce the gel volume change is three-fold: first, the gel devices can be remotely controlled, second, the external stimuli can be changed rapidly, and third, there is no need to add photosensitive molecules in the gel systems, as required when visible light is used.

![Graph](image.png)

Figure 2.3. The relation between the laser power and the temperature in the vicinity of the gel.
Figure 2.4 shows the swelling ratio of the final diameter to the reference diameter for an ionic NIPA gel (SA=100 mg) as a function of temperature. The temperature change was provided in two ways: (1) with a thermal bath (+), and (2) with a CO₂ infrared laser (O). The data taken with the thermal bath are quasi-equilibrium values with a temperature scanning rate of 0.1 °C/15 min. The data taken with laser power are also quasi-equilibrium values at a laser power increase rate of about 50 mW/h. For equilibrium values, the gel should undergo a discontinuous phase transition. As the temperature increases, the gel shrinks and eventually collapses.

Since our gel sample contains more than 90% of water, the thermal conductivity and specific heat of it are approximately the same as the corresponding values of water. The infrared laser power is attenuated significantly within 0.1 mm due to the high infrared absorption coefficient of water. As a result, the infrared laser power can be considered as

![Swelling ratio vs Temperature](image)

Figure 2.4. The swelling ratio of an ionic gel as a function of temperature with (O) and without (+) laser irradiation. The swelling ratio is defined as the ratio of the final diameter of the gel to its diameter at 24 °C.
a point heating source located at the beginning of the laser path inside the sample cell. The thermal diffusion constant $D_0$ of water is related to its thermal conductivity $K$, specific heat $c$, and density $\rho$ by the equation $D_0 = K/(c\rho)$. Near room temperature, $K = 6.09$ mW/(Kcm), $c = 4.18$ J/(gK), and $\rho = 1$ g/cm$^3$. The value of $D_0$ can be calculated from these values, $D_0 = 1.5 \times 10^{-3}$ cm$^2$/s. After the infrared power is turned on, the characteristic time needed for the temperature profile to reach a steady state is of the order of $L^2/D_0$ (with the sample cell dimension $L \sim 1$ cm), approximately 10 minutes.

After reaching a steady-state, i.e., the late-time limit, the temperature ($T$) of the sample can be approximated as

$$T = T_0 + B I_0 e^{-\alpha x}$$  \hspace{1cm} (2.1)$$

where $T_0$ is the ambient temperature, $I_0$ is the light intensity, $B$ and $\alpha$ are constants, and $x$ is the distance away from the laser spot. The transition temperature difference in the two curves comes from the fact that the thermometer was located 5 mm away from the laser spot and therefore the temperature in the gel sample is underestimated.

### 2.3.2 CO$_2$ laser-induced bending in gels

The infrared laser not only makes the gel shrink, but also causes the gel to bend. Figure 2.5 shows six typical photographs for an ionic gel at room temperature under different laser powers. As the laser power increases, the gel bends toward the laser beam. The exact threshold of the laser power for which the bending takes place depends on the distance between the sample and the optical window, the laser spot size, the sample's dimensions, and the sample cell temperature. It is 200 mW when the distance between the sample and the window is about 1 mm, the laser spot is around 0.7 mm, and the sample has a diameter of 2.8 mm and a length of 18.3 mm.

The gel strain caused by bending can be quantitatively determined using a
Figure 2.5. The ionic gel under different laser powers after a fixed time of 30 min. (a) 0, (b) 250, (c) 300, (d) 375, (e) 400, (f) 450 mW. The direction of the laser beam is from left to right.
deflecting parameter, \(Y\), which is defined as the distance traveled by the free end of the gel during its bending process. Following the argument of Shiga et al [10], we assume that the bending of a gel under infrared light is similar to a bending in a three-point mechanical bending test, and that the osmotic pressure difference is equal to a maximum tensile stress, \(\sigma\). Considering the fact that our definition of \(Y\) is bigger than that of Shiga et al by a factor of 2, the relation between elastic strain, \(s\), and the deflection parameter, \(Y\), is given by

\[
 s = \frac{3DY}{L^2} \tag{2.2}
\]

where \(D\) and \(L\) are the gel diameter and length, respectively. Figure 2.6 shows the elastic strain, obtained after about 30 min at each designated laser power, as a function of laser power for the ionic gel. The error in the measurement of strain is estimated to be less than 8%. The strain increases initially upon increase of the laser power, and reaches a maximum value. As the laser power increases further, the strain decreases. It is noted from Figure 2.6 that the elastic strain is as large as 16%, which is comparable to the strain in the poly(vinyl alcohol)-poly(sodium acrylate) (PVA-PAA) copolymer gels under an electric field [10-11].

2.3.3 Kinetic process of the bending

The bending of gels is a kinetic process. A typical time series of the bending in a cylindrical gel with the initial diameter of 2.1 mm and the length of 18 mm is shown in Figure 2.7, where (a), (b), and (c) show the gel bending under an infrared irradiation of 300 mW, and (d), (e), and (f) show the gel restoring its shape after blocking the laser.

Based on the pictures such as in Figure 2.7, we have obtained measurements of the time dependent strain as shown in Figure 2.8(a) (open circles). The corresponding laser
Figure 2.6. The elastic bending strain, obtained after about 30 min at each designated laser power, as a function of laser power for the ionic gel.

The power profile is shown in the same figure. From Figure 2.7, one can see that the bending strain increases with time when the gel is subjected to 300 mW of laser irradiation. After blocking the laser, the gel gradually restores its original shape and size. This process is completely reversible as indicated by the second cycle in Figure 2.8(a).

The data in Figure 2.8(a) have also been plotted in Figure 2.8(b) using a semi-log plot. The solid straight lines are least-square fits to the data using the following equation:

\[ s = s_0 \exp\left(-\frac{t}{\tau}\right) \]  \hspace{1cm} (2.3)

where \( s \) is the strain, \( t \) is the time measured from the point at which the laser power is removed, and \( \tau \) is relaxation time constant. \( s_0 \) is the maximum strain at \( t=0 \). It is clear that the gel's restoring process after blocking the laser can be described by the single
Figure 2.7. The ionic gel under 300 mW laser power at different times. The CO₂ laser has been on for: (a) 0, (b) 0.5, (c) 3; the CO₂ laser has been off for: (d) 4 min, (e) 6, (f) 19 min. The direction of the laser beam is from right to left.
exponential form. This is expected from gel swelling kinetic theory [12]. On the other hand, the bending behavior as indicated by dashed lines involves a shrinking process which is much more complicated and cannot generally be described using a single exponential form [3]. The data obtained here are not sufficient for detailed analysis in terms of a multi-exponential equation.

From the least square fit lines shown in Figure 2.8(b), we have obtained the relaxation time of 8.5±0.5 min for the gel bending under the current experimental conditions. For comparison, the relaxation time of the volume change for a similar size gel has also been measured and it is found that the time required for the volume change is 10 times longer than that required for the gel bending. This is expected since the bending involves the volume change of only a small part of the gel.

It is noted that the bending in the polyelectrolyte gel under the electric field is associated with ion drift [10]. The drifting velocity depends on the mobility of an ion and the intensity of the electric field. In our case, the bending is associated with the temperature field in the gel. It is the localized heating that causes the gel to bend. Therefore, the bending cannot occur if the gel is uniformly heated.

2.3.4 Sample cell temperature dependence of the bending

The laser-induced bending of gels depends on the initial sample cell temperature, \( T_i \) which is defined as the equilibrium temperature of the sample cell before the laser is turned on. Figure 2.9 shows time dependent strain with and without the laser irradiation at \( T_i = 24, 28, \) and 32 °C. The laser (300 mW) is turned on at \( t=0 \). The initial half of the cycle corresponds to the laser on, while the final half of the cycle corresponds to laser off. During the laser irradiation, the sample cell temperature 5 mm away from the heating point can change by as much as 4 °C. The amplitude of the strain, obtained after 300 mW of laser irradiation for 3 min, is shown in Figure 2.10. As the value of \( T_i \) increases, the strain
Figure 2.8. (a) Two cycles of the time dependence of the bending strain of the ionic gel with and without infrared light irradiation. The corresponding laser power profile is also plotted using a solid line. The initial sample cell temperature is 32 °C. (b) log (strain) versus time. The dashed lines represent the CO₂ laser being on, and solid lines represent the laser being off. The solid lines are also the best least-square fits to the data.
Figure 2.9. One cycle of the bending at different initial sample cell temperature, $T_i=32$ (O), 28 (+), and 24 °C (Δ), where $T_i$ is defined as the equilibrium temperature of the sample cell before the laser is turned on. The laser power used is 300 mW.

Figure 2.10. The amplitude of bending change at 3 min after laser irradiation of 300 mW laser power, as a function of the initial sample cell temperature.
amplitude increases. This indicates that increasing the sample cell temperature closer to the gel transition temperature can enhance the bending effect during constant CO$_2$ laser irradiation.

For the same $T_i$ the degree of gel bending is dependent on the ionic group. The time dependence of bending with and without ionic groups at $T_i = 25$ °C is plotted in Figure 2.11 for comparison. The ionic gel exhibits a larger degree of bending than that of the neutral gel. This may be related to the shrinking ratio of the gels. It is known that the shrinking ratio of ionic gels is larger than that of the neutral gel. For the same laser power and period of time, the surface layer of the ionic gel can produce a larger shrinking ratio and thus can cause itself to bend more than the neutral gel does. Figure 2.11 also indicates that the local temperature of the irradiated spot is higher than the transition temperature $T_c$. In other words, the laser heating causes the temperature to increase by at least $T_c - T_i$.

2.3.5 Discussion

After extensive investigation of the volume phase transition of gels, there are increasing interests in gel bending stimulated by environmental change [10, 11, 13, 14]. It was found that PVA-PAA copolymer gel in Na$_2$CO$_3$ aqueous solutions bends toward the negative electrode under an electric field and comes back to its original shape and size after removing the field. The effect of bending has been explained in terms of the gradient of the ionic distribution due to the influence of the electric field [10-11]. Recently, a new type of gels (poly(2-acrylamide-2-methylpropanesulfonic acid) or PAMPS) has been synthesized [13-14]. When an electric field is applied to a sheet of PAMPS gel suspended in the surfactant solution, the gel bends toward the anode. The mechanism of the bending is associated with the electrophoretic molecular assembly reaction of solvated cationic surfactant to the PAMPS gel [14].
The mechanism for the gel bending under the infrared light is different from the mechanism for electric field-induced gel bending. Figure 2.12 shows a proposed mechanism for CO₂ laser-induced gel bending. According to Eq. (2.1), the temperature of the sample decreases exponentially as \( x \) increases (Fig. 2.12(a)). Combining Figure 2.12(a) and the relation between the swelling ratio \( (D/D_0) \) and temperature as shown in Figure 2.12(b), we obtain the gel local swelling ratio as a function of \( x \), the distance away from the heating point (Fig. 2.12(c)). The shrinking ratio is the highest at the front of the sample, and the lowest at the back of the sample. In other words, the front part of the gel is warmer, resulting in a higher negative osmotic pressure, \( \pi_1 \). The rest of the gel is not as warm, and thus has a lower negative pressure, \( \pi_2 \). It is the osmotic pressure difference \( (\Delta \pi = \pi_2 - \pi_1 > 0) \) that makes the gel bend toward the laser beam as shown in Fig. 2.12(d). Since only part of the gel is involved in the deformation, the bending is much faster than the volume change. This is in agreement with the experimental observation.

![Figure 2.11](image.png)

Figure 2.11. Comparison of bending strain between the neutral gel (+) and an ionic gel (O).
Figure 2.12. A sketch of bending mechanism. (a) Infrared laser intensity and temperature decrease exponentially with the light penetration length. (b) Temperature versus swelling ratio. (c) Swelling ratio versus the penetrating length. (d) The gel bends due to the osmotic pressure difference.
2.4 Conclusion

The volume phase transition of NIPA gels can be induced by a CO\textsubscript{2} laser. Under a CO\textsubscript{2} laser, the gel not only shrinks, but also bends toward the laser beam. The degree of the bending depends on CO\textsubscript{2} laser power and on the sample cell temperature. After blocking the CO\textsubscript{2} laser, the gel restores its original shape with a relaxation time about 8.5 min. The bending phenomenon can be explained in terms of thermally-induced volume phase transition in gels. The bending of a gel in this fashion may have application in photon-response devices, which can convert laser energy into mechanical energy. It is noted that the gel bending effect, similar to bi-metal strips, may have applications for remote control, optical switches, and mechanical arms.
CHAPTER 2 REFERENCES


3.1 Introduction

The N-isopropylacrylamide (NIPA) gel in water is transparent and swollen at room temperature. Upon the increase of temperature, the gel shrinks and eventually collapses to a condensed phase at a transition temperature ($T_c$) about 34 °C [1-2]. Since the volume change is through a collective polymer network diffusion process, the time required for completion of the volume change is rather long [1]. Therefore, the gel devices based on the volume phase transition generally have a very slow response time (on the order of hours). Such slow response time is one of the major hurdles for applications of gels as sensors and devices. Thus, research on fast response gel devices has both scientific and technological importance.

It is known that in addition to the volume phase transition near the transition point, a transparent NIPA gel also becomes opaque. This opacity may be due to the spinodal decomposition [3], which occurs when the network concentration decomposes into domains with two different values—one dilute and the other dense, as the temperature is increased from below $T_c$ to above $T_c$. If the domain sizes are comparable with the wavelength of visible light, the light will be effectively scattered, resulting in the reduction
of the transmitted light through the gel. Recently, Suzuki reported visible light-induced opacity in NIPA gel that had been co-polymerized with photo-sensitive chlorophyll molecules [4]. Our recent infrared spectroscopy measurement indicates that the NIPA gel has a strong infrared absorbency band around the wavelength of 10.6 μm [5]. Therefore, there is no need to incorporate photo-sensitive molecules into the gel network to provide photon absorbency.

Here we present a systematic study of visible light transmission in the ionic NIPA gel under the influence of a CO₂ infrared laser. It is found that the infrared light can effectively control the transmission of a He-Ne laser beam in the NIPA gel when the He-Ne visible laser beam is aligned along the same optical axis as the infrared beam. When the infrared laser is turned on, a part of the gel is heated locally above the transition temperature and becomes opaque. The visible light is thus blocked. When the infrared laser is turned off, the gel is restored to its original transparent state. This process is completely reversible. The time required for the transparent-opaque transition is much faster than that for the volume phase transition.

The advantage of using infrared light to induce the transparent-to-opaque transition is three-fold: first, the gel devices can be remotely controlled, second, the external stimulus of the infrared laser power can be changed rapidly, and third, a focused infrared laser can make the gel surface opaque locally, while the sample cell temperature remains almost unchanged. Thus, the results of this experiment show clearly that excellent possibilities exist for developing fast-response gel devices based on the gel's transparent-opaque transition.
3.2 Experimental

The NIPA gel samples were made by the same method as description in chapter 2. The basic experimental setup has been previously described [5]. A modified version of this experiment is shown in Figure 3.1. A grating tunable continuous wave CO₂ laser was operated at a wavelength of 10.6 µm. The light intensity was adjusted by varying a commercial attenuator. The duty-cycle of the infrared light was adjusted by changing the blade of a light chopper. The incident infrared laser beam was divided using a 50/50 beam splitter, one part going to a laser power monitor and the other going to the sample. The fluctuation of infrared laser power measurement was about 10%. A laser spot of about 0.7 mm in diameter was produced at the sample position by using a lens of 8 cm focal length. A transparent plastic sample cell, which had inner cell dimensions of 18.7 mm x 9.3 mm x 18.7 mm, was constructed using two BaF₂ (3 mm thickness) infrared windows installed along the path of the laser beam. The cell was constructed such that the sample could be suspended in water with its upper end fixed to a clamp. The gel was placed with one side in contact with the optical window so that the water attenuation was minimal. The visible light source was a He-Ne laser with a wavelength of 633 nm. The beam diameter and the power of the He-Ne laser were about 0.5 mm and 0.5 mW, respectively. The common beam splitter was used to direct the He-Ne beam so that it shared the same optical axis with the CO₂ laser. The He-Ne laser beam was modulated by another chopper for signal analysis. Once passing through the sample cell, the visible beam was focused on a detector. The signal was then amplified and displayed on an oscilloscope. The sample cell temperature was measured using a platinum resistance thermometer inserted into the
sample cell. The accuracy of the temperature measurements is estimated to be ±0.1 °C. A temperature controller was used to regulate the sample cell temperature.

![Block diagram of the experimental setup.](image)

Figure 3.1. Block diagram of the experimental setup. The duty-cycle of the infrared light was adjusted by changing the blade of a light chopper. The incident infrared laser beam was divided using a 50/50 beam splitter, one part going to a laser power monitor and the other going to the sample. The common beam splitter was used to direct the He-Ne beam so that it shared the same optical axis with the CO₂ laser.
3.3 Results and Discussion

3.3.1 Infrared-induced opacity in ionic NIPA gel

The visible light transmission through a NIPA gel in the sample cell is defined as $I_0$. When the external control is needed, the CO$_2$ laser is turned on, and the transmission is defined as $I(t)$, which is a function of time $t$. The values of $I_0$ and $I(t)$ are directly proportional to the signal voltages exhibited on the oscilloscope. Thus, the relative transmission can be written as $I(t)/I_0$. Figure 3.2 shows the relative transmission ($I(t)/I_0$) of the He-Ne laser beam through the ionic NIPA gel under influence of a CO$_2$ laser. From this figure, one can see that the transmission of the He-Ne laser through the gel is high if the infrared laser is off. When the CO$_2$ laser is on, the transmission decreases drastically, indicating that the sample becomes opaque. The depth to which the opaque region penetrates is estimated less than 0.1 mm due to the high infrared absorption coefficient of water. Once the infrared light is blocked, the transmission returns to its original value again. The relative transmission is completely reversible, as indicated by the two cycles shown in Figure 3.2. Following the conventional definition of switching time used in electronic industry (i.e., the 10%--90% points in the dynamic range), the switching-off time required for the relative transmission change is about 15 s, and the switching-on time is about 0.5 s. Such a time scale is considerably shorter compared with the time scale, usually in units of hours, associated with the transition between the swollen and collapsed volume in the gels [1-2]. Thus, this experiment provides a prototype optical gel switch controlled by an infrared laser. Since the transparent-opaque transition takes place very quickly, the change of the sample cell temperature under the infrared light during one
complete cycle is small—about +1°C near room temperature. This means that the transmission is only controlled by the local area of the gel where it is hit by the infrared laser. In contrast with the conventional temperature-induced volume phase transition (which requires raising the temperature of the whole water/gel system to the transition temperature), the infrared laser-controlled transmission creates only small perturbation to the whole system.

Figure 3.2. Time-dependent relative transmission (I(t)/I₀) of visible light when the infrared light is on and off. The transparent-opaque transition is completely reversible, as indicated by the two cycles shown in the figure. The sample cell temperature (26.5°C) remains almost unchanged during the transition. This means that the transition is conducted locally by the infrared laser. In the figure, the straight line indicates when the CO₂ is on and when it is off. The laser power is 375 mW.
3.3.2 Laser power dependence of opacity

The relative transmission of He-Ne light through the gel is shown in Figure 3.3 as a function of time for various CO$_2$ laser powers. The CO$_2$ laser is turned on at time $t=0$ s and is blocked at $t=30$ s. During the experiment, the sample cell temperature was about $26 \pm 1^\circ$C. For CO$_2$ power at 110 mW, there is no significant change of transmission as indicated by the open circles. Once CO$_2$ power is higher than a value of about 200 mW, transmission starts to change significantly with time.

![Graph showing time-dependent relative transmission](image)

Figure 3.3. Time-dependent relative transmission ($I(t)/I_0$) at various laser powers: 110 (o), 260 (+), 340 (Δ), 380 (◇), 450 (*) and 530 mW (□). The sample cell temperature is about $26^\circ$C. At $t=30$ s, the CO$_2$ laser is blocked and the original transmission values are restored quickly in all cases.
Figure 3.4 shows that the relative transmission $I(t=30\text{ s})/I_0$ decreases with CO$_2$ laser power, where $I(t=30\text{ s})$ is the transmission intensity at $t=30\text{ s}$. Since the opaque area of the gel forms more quickly and penetrates more deeply at higher CO$_2$ laser power, the visible light is blocked more effectively. It was found that to reach the same value of relative transmission difference ($\Delta I/I_0=[I_0-I(t=30\text{ s})]/I_0$), the higher the CO$_2$ power, the shorter the response time required.

Figure 3.4. Relative transmission ($I(t=30\text{ s})/I_0$) as a function of CO$_2$ laser power. During the experiment, the sample cell temperature is kept constant at around 26° C. As CO$_2$ power increases, transmission decreases rapidly.
Figure 3.5 shows the response time required for $\Delta I/I_0 = 0.25$ (○) and 0.50 ($\Delta$) as a function of CO$_2$ laser power. Therefore, one can use a higher laser power to achieve the fast response.

In the infrared spectroscopy measurement, the infrared continuous wave (CW) is often chopped to obtain a better signal-to-noise ratio for data analysis. It is noted in this experiment that the time-dependent transmission in the gel under the infrared laser is independent of the chopping infrared signal frequency, as long as the average

![Graph showing response time as a function of laser power](image)

Figure 3.5. Response time as a function of laser power for the relative transmission difference, $[I_0 - I(t=30\text{ s})]/I_0$, reaching a fixed value: 0.25 (○), and 0.5 ($\Delta$), respectively. The sample cell temperature is around 26 °C.
power of the CO$_2$ laser remains the same. Figure 3.6 shows He-Ne light relative transmission ($I(t)/I_0$) plotted as a function of time for an average CO$_2$ power of 350 mW at different infrared chopping frequencies of 0, 150, 1600, and 3200 Hz. The transmission profiles from such a broad range of infrared signal frequencies are almost identical. This means that the opacity is a pure thermal effect instead of an optical effect. Therefore, we can use a single infrared laser for both controlling visible light transmission and spectroscopy measurement, which requires changing the chopping frequency.

![Figure 3.6](image)

Figure 3.6. Time-dependent visible light relative transmission ($I(t)/I_0$) at various infrared chopper frequencies of 0 (o), 150 (+), 1600 (Δ) and 3200 Hz (□). As long as the average power of the infrared laser is fixed, shown here at 350 mW, the transmission behavior remains the same. The sample cell temperature is about 28 °C. The CO$_2$ laser is blocked at t=40 s.
3.3.3 Sample cell temperature dependence of visible light transmission

The infrared laser-controlled transmission also depends on the sample cell temperature. Figure 3.7 shows the relative transmission \( I(t)/I_0 \) as a function of time at a fixed \( \text{CO}_2 \) laser power of 300 mW for various sample cell temperatures. The \( \text{CO}_2 \) laser is turned on at \( t=0 \), and blocked at \( t=30 \text{ s} \). For a lower sample cell temperature \( (T=24.5^\circ \text{C}) \), the transmission change is not significant. However, if the sample cell temperature is raised close to the volume phase transition temperature, the transmission changes more drastically between on and off period of the \( \text{CO}_2 \) laser.

![Figure 3.7](image_url)

Figure 3.7. Time-dependent relative transmission \( (I(t)/I_0) \) at various sample cell temperatures for a fixed \( \text{CO}_2 \) laser power at 300 mW: 24.5(○), 26.5 (+), 27.5 (△), 28.5 (*), 30 °C (□).
The relative transmission difference, $\Delta I/I_0 = [I_0 - I(t=30s)]/I_0$, increases linearly with the sample cell temperature, as shown in Figure 3.8. Furthermore, the response time for a fixed transmission difference decreases as the sample cell temperature increases, as shown in Figure 3.9. This suggests that at a fixed laser power, increasing the sample cell temperature to $T_c$ makes the gel form a larger opaque volume element and thus have a faster response time.

Figure 3.8. The relative transmission difference, $([I_0 - I(t=30\text{ s})]/I_0)$, plotted against sample cell temperature for a fixed CO$_2$ laser power at 300 mW. The higher the sample cell temperature, the larger the transmission difference.
3.3.4 Discussion

The incident light beam attenuated by the gel can be generally described according to Lambert-Beer's law:

$$I_0 = A \exp(-\alpha_0 x)$$  \hspace{1cm} (3.1)

where $I_0$ and $A$ are the transmitted and incident intensities, respectively, $x$ is the depth of the opaque region in the gel sample, and $\alpha_0$ is the average turbidity coefficient over $x$. Under normal conditions, the gel is transparent to the visible light, and the value of $\alpha_0$ is thus small. However, once the infrared laser hits the gel, the turbidity is a function of time and is represented by $\alpha(t)$. Therefore, the attenuation of the visible light can be written as
\[ I(t) = A \exp(-\alpha(t)x) \]  
(3.2)

The relative transmission is thus expressed by

\[ \frac{I}{I_0} = \exp[-\Delta \alpha(t)x] \]  
(3.3)

where \( \Delta \alpha(t) = \alpha(t) - \alpha_0 \) is mainly due to scattering. As a transparent gel is heated above its phase transition point by the infrared laser radiation, it forms many micro-domains with two different network concentrations—dilute regions and dense regions \([6]\). This is called spinodal decomposition. When sizes of the micro-domains are comparable with the wavelength of the visible light, the light is scattered quite effectively. Within a short period of time after the infrared laser is turned on, the sample turbidity is low and the multiple scattering does not occur. Therefore, the reduction in the transmitted intensity due to the scattering of the radiation can be described by \([7]\)

\[ I(t) = I_0 - 2\pi I \int I_s(K,t) \sin \theta d\theta \]  
(3.4)

with

\[ K = \frac{4\pi n_0}{\lambda_0} \sin \left( \frac{\theta}{2} \right) \]  
(3.5)

where \( l \) is the light path in the sample, \( I_s(K,t) \) is the scattered light intensity ratio for unpolarized light, \( K \) the scattering wave vector, \( \theta \) the scattering angle, \( n \) the refractive index of the gel sample, and \( \lambda_0 \) is the wavelength of the visible light in a vacuum.

Following the linear theory proposed for the early stage of spinodal decomposition \([8]\), the time variation of scattered light intensity is expressed as
\[
\frac{l(I,K,t)}{I_0} = \exp[2R(K)t]
\]  

(3.6)

where \(R(K)\) is the relaxation rate representing the growth rate of the composition fluctuation at wave vector \(K\).

For small \(K\), we have \(I(t)/I_0 = 1-I(t)/I_0\). Figure 3.10 shows a semi-logarithmic plot of the relative scattering intensity \((\log(1-I(t)/I_0))\) versus time. The dashed lines represent the period that the CO\(_2\) laser is off and solid lines represent the period that the CO\(_2\) laser (power=375 mW) is on. In the region where the infrared laser irradiation is incident, the kinetic behavior can be characterized by two straight lines (I) and (II). From the slopes of these lines, we obtain two average relaxation times: \(\tau_1=2\) s, and \(\tau_2=120\) s. The value of \(\tau_1\) may be related to the fluctuation growth rate: \(\tau_1=1/R(K)\), and \(\tau_2\) may indicate that the spinodal decomposition enters an intermediate state [9].

From an application point of view, it is interesting to compare the response time for the initial stage of the volume phase transition, infrared-induced bending, and infrared-controlled transmission for gels with the same sizes. The time scale for a gel of one cubic centimeter volume is measured in a matter of hours. However, since the gel bending involves only the distortion of part of the bulk gel, the response time is faster than that for the volume change and is on the order of minutes [10]. To influence the transmission of the visible light by local infrared laser heating, the time scale involved is only seconds. Therefore, the laser-controlled transmission provides us with possibilities for the design of gel devices with fast response time.
Figure 3.10. $\log(1-I(t)/I_0)$ versus time. Solid lines represent data obtained with the CO$_2$ laser on and dashed lines with the CO$_2$ laser off. The relaxation times in regions (I) and (II) are $\tau_1 = 2\text{ s}$, and $\tau_2 = 120\text{ s}$, respectively.

3.4. Conclusion

The transmission of He-Ne light through a gel sample can be controlled by a CO$_2$ laser. The switching time from 90% to 10% relative transmission is about 15 s and from 10% to 90% is about 0.5 s. The sample cell temperature during the transmission cycles remains almost unchanged. The CO$_2$ laser acts like a strong local heating source which raises the temperature of the gel surface past its spinodal phase transition temperature. Therefore, the gel surface is decomposed into two different concentration domains: one is
swollen (dilute) and the other is a condensed state. The visible light is strongly scattered
by such domains when their sizes are comparable with the size of the optical wavelength.
Since the switch time from the transparent to opaque is very fast, such effects may lead to
the development of fast-response gel devices.
CHAPTER 3 REFERENCES


4.1 Introduction

Polymer gels have attracted much interest because their volume can be changed by three orders of magnitude in response to the change of an external environment such as solvent, temperature, electric fields, and light [1-6]. The potential application of gel materials as artificial muscles was first demonstrated by Katchalsky's group in his famous collagen engine [7]. Subsequently, gels have been explored to perform various functions including drug-delivery devices [8-10], chemical valves and actuators [11-13], and magnetic resonance monitoring agents [14]. The gels used in all these reports had macroscopically uniform structures. In this chapter, we propose and demonstrate a new class of materials based on spatial modulation of the chemical nature of gels. The modulation is achieved by interpenetrating only part of one gel network with another gel network. Therefore, these gels have an internally heterogeneous, or modulated, structure. In this report, three simple applications based on the modulated gels are presented: a bi-gel strip, a shape memory gel, and a gel hand. These three applications are based on the volume phase transitions of gels in response to external environmental changes, and that different gels are responsive to different aspects of the environment [15]. In particular, the
temperature sensitivity of the N-isopropylacrylamide (NIPA) gel and acetone concentration sensitivity of the acrylamide (PAAM) gel [16] are the controlling mechanisms for the three applications presented here. The bi-gel strip bends almost to a circle when its temperature or solvent is changed. The shape memory gel changes its shape among straight, pentagonal, and quadrangle forms at different temperatures. The gel hand can grasp or release an object by simply adjusting its temperature. The results reported here have far-reaching significance for making active gel devices and sensors.

4.2 Experimental

The bi-gel strip was synthesized by first making a NIPA gel slab. Two glass slides with \( \sim 1.0 \text{mm} \) gap between them were immersed in 100 ml of an aqueous solution with 690 mM N-isopropylacrylamide, 8.6 mM methylene-bis-acrylamide (BIS), and 8 mM sodium acrylate. The polymerization of the solution was initiated by adding 240 \( \mu \text{l} \) of tetra-methyl-ethylene-diamine (TEMED) and 40 mg ammonium persulfate [for experimental details, see (6)]. In the second step, a PAAM gel slab was made between two glass slides (approximately 2.0 to 3.0 mm apart) with the presence of the NIPA network \( \sim 1.2 \text{mm} \) between them and in contact with one of the glass slides. Notice that the distance between the two glass slides is larger than that of the swollen NIPA network. A sufficiently long time \( \sim 1 \text{hour} \) was allowed for the acrylamide gel "ingredient" to diffuse into the NIPA network before the polymerization was initiated. This ensures the formation of the NIPA/PAAM interpenetrating networks. The acrylamide gel consisted of 700 mM acrylamide and 8.6 mM BIS. The end product is a gel slab 2.0 to 3.0 mm thick with layered network structure: A 0.8 to 1.8 mm thick PAAM network, and a 1.2 mm PAAM
network interpenetrated by a NIPA network as shown in Fig. 4.1A.

4.3 Results and Discussion

It is well known [16] that the volume of the ionic NIPA gel (with 8 mM sodium acrylate) shrinks drastically at temperatures higher than 37°C, whereas the volume of the PAAM gel does not. Similarly, the volume of the PAAM gel shrinks much more in acetone-water mixtures (>34 wt%) than does the NIPA gel. The fully swollen bi-gel strip at room temperature (~22 °C) bends slightly toward the PAAM gel side. Upon increasing the temperature above 37°C, the NIPA gel would respond by shrinking drastically, whereas the PAAM gel is insensitive to the temperature change. As a result, when the bi-gel strip is heated uniformly, it gradually bends into an arc (Fig. 4.1B and C). However, because the PAAM gel shrinks drastically in acetone-water mixtures and the NIPA gel does not, the bending in the opposite direction occurs as the bi-gel strip is immersed in an acetone-water solvent (Fig. 4.1D and E). The transition between the straight and the arc forms is reversible. The variation of the degree of bending in nine sequential straight-bending-straight cycles is less than 3%.

The amount of bending can be quantified by the bending angle, \( \theta \), defined by the angle between the two tangents of the gel arc at the two ends. The strain \( (s) \) induced in the gel is then equal to \( s = (\theta d)/L \), where \( d \) and \( L \) are the thickness and length of the gel, respectively. This equation is valid for large bending (large \( \theta \), as for twisting into a spiral), whereas the result of Shiga et al. [17] is based on a three-point bending model and is valid for small bending only. For small \( \theta \) (small bending), the above equation differs from that of Shiga et al. by a factor of \( 3/4 \), which comes from the difference in assumptions of the
Fig. 4.1. (A) Sketch of the bi-gel strip with one PAAM gel (empty area) modulated by interpenetrating one side of PAAM gel with NIPA gel, i.e., PAAM-NIPA interpenetrating polymer network (IPN) (shaded area). (B) and (C) The bending of the bi-gel in water at a temperature of (B) 30.0°, and (C) 37.8 °C. The PAAM gel of the bi-gel strip is coated with blue color for better visualization. The gel in the right of each picture is the pure NIPA gel as a reference. (D and E) The bending of the bi-gel in water-acetone mixture at an acetone concentration of (D) 20, and (E) 45 wt%. The gel in the right of each picture is a pure PAAM gel as a reference. The black bars in the pictures indicate 5 mm.
sample cross section shape (circle versus rectangle). Using this equation, we found that the maximum strain for the bi-gel is ~49% and occurs after the volume phase transition point of the ionic NIPA gel (~37°C). This strain is much higher than the strain of 20% in the poly(vinyl alcohol)-poly(sodium acrylate) (PVA-PAA) copolymer gels under an electric field [17]. The kinetics of bending is shown in Fig. 4.2. Starting from 22 °C, the sample temperature is raised quickly to 38°C by transferring the sample from one water bath to another. The strain was obtained from photos taken from the sample at various times. The strain increases with time when the gel is immersed in the high-temperature bath. Upon cooling, the bi-gel gradually restores its original shape and size. This process has been repeated up to nine cycles with the change of the maximum strain less than 5%.

The mechanism of the bi-gel bending reported here is different from that introduced by the electric field [11, 12, 17] or infrared laser heating [6]. In those previous cases, the gradient of the electric potential field or the gradient of the temperature field has to be applied to trigger the bending of the gels, which are macroscopically homogeneous. Limited by the ability of providing the complex external field gradient, a high degree of bending (θ>180°) cannot be easily obtained by those methods. In our experiment, the external environment is uniform, while the samples are internally modulated. Therefore, the sample bends directly in response to the environmental changes such as temperature and solvent composition without the need of having a gradient environment. Large bending such as a spiral can be achieved by either increasing the sample length, or temperature. We note that the difference of the thermal expansion coefficients between two gels can be much larger than that between two metals. For example, the difference
Fig. 4.2. The two cycles of the time dependence of the bending strain of the bi-gel. The increase of strain is obtained at 38 °C and the decrease of strain at 22 °C.

of expansion coefficients for a typical bimetallic strip of brass and steel is about $7 \times 10^{-6}$ °C$^{-1}$. However, for the PAAM-NIPA bi-gel, such difference can be as high as 0.5 °C$^{-1}$ (the ionic NIPA gel with 8 mM sodium acrylate shrinks to a half of its linear size per degree near the transition point at about 37 °C [16], while the PAAM gel has no volume change in this temperature range), which is five orders of magnitude greater. Therefore, bi-gels can be far more sensitive to their environment than bi-metals.

A gel with a more complex modulated structure is sketched in Fig. 4.3A. The sample preparation is similar to that of the bi-gel sample. Here, the PAAM gel is modulated with the NIPA gel at four locations so that the gel can only bend at these
Fig. 4.3. (A) The sketch of the shape memory gel with the PAAM gel modulated with NIPA gels at four locations (shaded area). The sample was made by polymerizing the PAAM gel in the presence of four NIPA gel pieces which were placed on a glass plate. The separation between adjacent NIPA gel pieces is about 12 mm. (B-D) The gel shape at various temperatures: (B) 22°, (C) 39°, and (D) 41 °C. The black bar indicates 15 mm in (B) and 6 mm in (D); the length scales in (C) and (D) are the same.
modulated sites upon increasing the temperature. At room temperature, the modulated gel is straight in shape (Fig. 4.3B). Upon an increase of temperature, the gel parts at modulated sites start bending, forming a pentagon (39 °C, Fig. 4.3C) and a quadrangle (41 °C, Fig. 4.3D). The change from pentagon to quadrangle is related to the higher shrinking ratio of NIPAA at 41 ° than that at 39 °C. As a result, the bi-gel at 41°C bends more (about 90 degree, i.e., a quadrangle) than one at 39°C (about 70 degree, i.e., a pentagon). The transition between different shapes is reversible. Note that a variety of shapes, including from a straight line to a sinusoidal form, from a flat sheet to a hollow tube, and from a long strip to a spiral [18], of the gels at various temperatures can be obtained by designing the modulation pattern of the system, while the previous gel memory effect induced by chemical cross-linking under elongation is much more limited [19].

To further demonstrate the potential of the modulated polymer gels, a gel hand consisting of two bi-gel strips was made and is shown immersed in water in Fig. 4.4. These bi-gel strips are identical to the bi-gels discussed earlier. At room temperature (Fig. 4.4A), the fingers of the hand are open and an object is released. At 35°C (Fig. 4.4B), the fingers are closed and the object is grasped.

4.4 Conclusion

The novel gel functions obtained from the modulation method is based on the fact that the volumes of different gels are sensitive to different aspects of the environment. The applications of the modulation method could be extensive: for example, a modulated bi-gel of the pH sensitive gel (polyacrylic acid) with the acetone concentration sensitive gel (PAAM) should bend in pH environment as well. Because a large amount of strain can
be produced, the modulated gels may be used to make gel display devices, switches, or valves.

Fig. 4.4. The gel hand made by two bi-gel strips. The two bi-gel strips have the same structure as shown in Fig. 4.1A and are tied together at one end with a spacer. The NIPA modulated sides are facing each other. The thicknesses of the PAAM gel and the NIPA modulated side are 2.1 mm and 1.5 mm, respectively. (A) At 22 °C, the fingers are open and a red object is released. (B) At 35 °C, the fingers are closed and the object is caught.
CHAPTER 4 REFERENCES


CHAPTER 5

BENDING OF BI-GELS

5.1 Introduction

The volume phase transition of polymer gels can be triggered by many external stimuli such as solvent, temperature, pH value, electric fields, and visible or infrared light[1-5]. Gels with such a phase transition have been explored for their ability to perform many functions including drug delivery devices, chemical valves and actuators, biological switches, or magnetic monitoring agents in biological system [6-12]. To enhance the physical and mechanical properties in gel applications, a variety of synthesis methods has been used, such as co-polymerization [4], grafting [7], and interpenetration [15].

Recently, we reported the synthesis of a new class of gels by modulating the chemical nature of the gels in space. Using this novel technique, we have made bi-gel strips, shape memory gels, and gel fingers [16]. The bi-gel strip is made by interpenetrating N-isopropylacrylamide (NIPA) gel into poly-acrylamide (PAAM) gel networks. Since the NIPA gel is sensitive to temperature and the PAAM gel is sensitive to acetone concentration, the bi-gel can bend to an arc in response to temperature or solvent changes. Because the difference of the size change between the two sides of the bi-gels is enormous, the bending effect reported here is much larger than the bending either induced by electric field [10] or induced by infrared light [5].

Previously, there have been some reports about bipolymer strips. For example, a bipolymer strip was made by attaching polymer layer to an inert (non-swelling) elastic
except that the bending is caused by humidity rather than temperature. Another kind of bipolymer strip is made of a polypyrrole (PPy) layer and a polyethylene layer bound together. The bending is caused by the volume change of the PPy layer [18].

In this chapter, we present the bending of a bi-gel (IPN and PAAM) strip induced by temperature, water-acetone mixture, and NaCl solution. The bending kinetic process and the measurement of the collective diffusion coefficient of the bi-gel will be discussed. The results reported here will be helpful for making environmentally responsive gel devices, actuators, and sensors.

5.2 Theory

From the bi-polymer strip model [18], the bending can be described by the curve radius of the strip. As shown in Fig. 5.1 (a), the curve radius is expressed by

$$R_t = \frac{L^2 + h^2}{2h}$$

(5.1)

where $L$ is the projection of the bent strip on the undeflected strip, and $h$ is the deflection of the gel end. The curvatures of the strip are denoted as $1/R_t$ corresponding to time $t$. $d_1$ is the thickness of the PAAM side and $d_2$ is the thickness of the IPN side of the bi-gel at time $t$. In Figure 5.1 (b), $b$ is the width of a bi-gel. We chose the interface of a bi-gel as the reference zero point for $y$. The total strain $S$ in the bi-gel caused by bending along the $z$-axis at a distance $y$ from the interface is therefore

$$s = \gamma \left( \frac{1}{R_t} - \frac{1}{R_0} \right) + \varepsilon_0$$

(5.2a)

where $1/R_0$ is the curvature of the strip before bending (usually close to 0), and $\varepsilon_0$ is the strain at the interface.
Fig. 5.1. Schematic diagram of polymer bi-gel (IPN-PAAM) strip. (a) construction and deflection of the bi-gel strip while bending. (b) a cross-sectional view and coordinate description.
In equilibrium, by the force balance and moment balance conditions, and the requirement of dimensional matching at the interface of the bi-gel [17], one can obtain $\varepsilon_0$ as follows:

$$
\varepsilon_0 = \frac{1}{R_t} \frac{2}{bd} \left( E_i^* \frac{d_1^3}{12} + E_2^* \frac{d_2^3}{12} \right) \left( \frac{1}{d_1 E_i^*} - \frac{1}{d_2 E_2^*} \right) \cdot \frac{d_1}{2}
$$

(5.2b)

where $b$ is the width of the bi-gel, $d=d_1+d_2$ is the total thickness of the bi-gel, and $E^*$ is the diaxial modulus with $E^*=E/(1-v)$, where $E$ is Young's modulus, and $v$ is Poisson's ratio. In the following discussion, we will only concern the relative bending strain $S_r$ referring to the interface of the bi-gel, as a function of $y$. Therefore, Eq. (5.2a) can be written as

$$
S_r = -\varepsilon_0 = \gamma \left( \frac{1}{R_t} - \frac{1}{R_0} \right)
$$

(5.2c)

By measuring the curvature and the strain of a bi-gel, the stress in both sides of the bi-gel can be calculated. Specifically, the stress at the distance $y$ from the interface is

$$
\sigma_2 = E_2^* \left[ \gamma \left( \frac{1}{R_t} - \frac{1}{R_0} \right) \cdot \varepsilon_0 - \alpha \right], \quad 0 \leq y \leq d_2
$$

(5.3a)

$$
\sigma_1 = E_1^* \left[ \gamma \left( \frac{1}{R_t} - \frac{1}{R_0} \right) \cdot \varepsilon_0 \right], \quad -d_1 \leq y \leq 0
$$

(5.3b)

where $0 \leq y \leq d_2$ is in the IPN side, and $-d_1 \leq y \leq 0$ is in the PAAM side. $\alpha$ is the lateral linear strain at distance $y$ from the junction due to swelling or shrinking in the IPN side. In general, $\alpha$ is a function of $y$.

Due to the fact that there are no external forces acting on the bi-gel strip, all forces
acting over any cross-section of the strip must be in equilibrium. Therefore, the total normal force at any cross section of the strip is zero. Thus we get

\[ F_2 - F_1 = \int_0^{\alpha_2} \sigma_2 b dy \cdot \int_{\alpha_1}^{\alpha_2} \sigma_1 b dy = 0 \]  

(5.4a)

where \( F_2 \) and \( F_1 \) are the total force on the IPN side and on the PAAM side of the bi-gel, respectively, \( b \) is the width of the sample. In equilibrium, the total moments from the internal forces must be counter-balanced as following

\[ \int_0^{\alpha_2} \sigma_2 b dy \cdot \int_{\alpha_1}^{\alpha_2} \sigma_1 b dy = M_2 + M_1 \]  

(5.4b)

with

\[ M_i = \frac{b E_i d_i^3}{12 R_i} \]  

(5.4c)

where \( M_i \) is the bending moment of the \( i \)th gel layer and \( d_i \) is the thickness of the \( i \)th gel layer.

In order to derive the relationship between the curvature \( R \) and the network collective diffusion coefficient \( D \) in polymer materials, it is useful to introduce a dimensionless bending curvature variation ratio \( \Omega \), which is defined as

\[ \Omega = \frac{\frac{1}{R_i} - \frac{1}{R_{0i}}}{\frac{1}{R_{0i}} - \frac{1}{R_{00}}} = \frac{S_{r,} y_{\cdot}}{S_{r,} y} \]  

(5.5)

where \( 1/R_0 \) and \( 1/R_i \) are the curvatures in equilibrium and at time \( t \) in a fixed temperature, respectively. \( S_{r,} \) and \( y_{\cdot} \) are the relative strain and the value of \( y \) corresponding to \( 1/R_0 \).

For convenience, we define another parameter \( K \) as
\[ K = \frac{2}{(1 + \frac{d_1}{d_2})\left(1 - \frac{d_2}{d_1}\right)} \]  

\[ \text{from the force balance and moment balance conditions as above, using the mathematics model for the bending-beam measurement method of solvent diffusion in multi-polymer layer films [19], one can obtain} \]

\[ \Omega = 2(1 + \frac{K}{2})(\frac{D_{c}^t}{d_2^2})^{1/2} [n^{1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \text{erfc}(\frac{nd_2}{(D_{c}^t)^{1/2}}) + 4K(\frac{D_{c}^t}{d_2^2})^{1/4} + 2 \sum_{n=1}^{\infty} (-1)^n \text{erfc}(\frac{nd_2}{(D_{c}^t)^{1/2}}) \]  

\[ \text{where } i \text{ is the } i^{th} \text{ layer material, and } D_c \text{ is the diffusion constant of solvent in the } i^{th} \text{ layer material.} \]

\[ \text{Within a relatively short period of diffusion time, i.e., } t < 0.54d_2^2/D_c \text{ or } \Omega < 0.82(1+K/2), \text{ all the summation terms in equation (5.7) can be ignored, and equation (5.7) is reduced to the following simplified form with an error less than 5\%[19]:} \]

\[ \Omega = 2(1 + \frac{K}{2})(\frac{D_{c}^t}{d_2^2})^{1/2} \]  

\[ \text{From Eq. (5.8), in accordance with the bending kinetic process, and by knowing the curvature variation ratios at various times in the initial diffusion stage, one can readily calculate the diffusion coefficient, } D_c. \text{ Alternatively, by linearly fitting the data of } \Omega \text{ vs. } (t^{1/2}/d_2) \text{ in the initial diffusion stage } (t < 0.54d_2^2/D_c), \text{ one can also obtain the diffusion coefficient } D_c \text{ from the slope of this fit. This is the theoretical base from the experimental data of bending kinetic process to obtain the diffusion coefficient } D_c. \]

\[ \text{5.3 Experiment} \]

\[ \text{The bi-gel strips were synthesized as described in chapter 4. The final product is a} \]
2.0–3.0 mm thick gel strip with a layered network structure composed of a homogeneous PAAM network (0.8–1.8 mm thick) and an IPN network (1.2 mm thick). After the gelation, the bi-gel (IPN and PAAM) strips were put into deionized and distilled water a few days, until the bi-gel samples reached the equilibrium swelling state. The lengths of the bi-gel samples are 2.0–2.5 cm and the widths are about 3 mm in our experiments. For convenience, we refer to these as 2 mm and 3 mm thick bi-gel strips, in reference to the spacings of the glass slides and subsequent gel thicknesses.

There are two sides of a bi-gel strip; one side is the NIPA/PAAM interpenetrating layer (IPN side), the other side is the pure PAAM layer (PAAM side). Since the deflection of our bi-gels are usually in the range of millimeters and centimeters, we used a camera to take pictures, and then used the pictures to measure the deflection and to determine the curvatures. The accuracy of the measurements of temperature and solvent concentration are ±0.1 °C and ±2%, respectively. The total error in the measurement of strain is estimated to be less than 8%.

5.4 Results and Discussion

5.4.1 Bending induced by different stimuli in bi-gels

From the bending pictures, L and h (see Fig. 5.1) are measured. Substituting L and h into equation (5.1), R, is obtained. Using R, and Eq. (5.2C), the bending strain S, is calculated and shown in Fig. 5.2 (a) as a function of temperature for the 3 mm thick bi-gel in water. Here we define that the compressive strain and stress are positive and the extensive strain and stress are negative. The data are obtained after about 2 hours at each designated temperature. The bending shows almost no change when the sample is kept at the same temperature for a longer time. The strain increases initially upon the increase of temperature. After reaching the phase transition point of the IPN side (about 37 °C), the strain becomes flat as the temperature increases further.

From Fig. 5.2 (a) one can see that the bending strain magnitude in the PAAM side
is larger than that of the IPA side of the bi-gel. This can be explained by Eq. (5.2c). To the same curvature, the larger the thickness (y) is, the larger the strain is. Although the PAAM side and the IPN side of the bi-gel have almost the same thickness initially, the thickness of the IPN side decreases dramatically with the increase of temperature because of the volume phase transition. On the other hand, the PAAM thickness remains the same.

The absolute maximum strain value for this bi-gel is about 25% in the IPN side and 60% in the PAAM side, which is higher than the strain in the poly(vinyl alcohol)-poly (sodium acrylate)(PVA-PAA) copolymer gels under an electric field[20-22] and the bending strain induced by infrared light in NIPA gels[5]. Using Eqs. (5.3a) and (5.3b), one can calculate the stresses caused by bending strain in both sides of the bi-gel. In our experiments, because the thickness of the IPN side of the bi-gel is small, the average value \( \alpha_m \) is used to substitute the function \( \alpha(y) \) for estimation of the maximum stress value in IPN side. Generally, the maximum stress value corresponds to the maximum bending curvature. Between temperature from 37 °C to 40 °C, Young's modulus of the PAAM side and the IPN side is \( E_1=7.50\times10^4 \) dyne/cm\(^2\), and \( E_2=2.40\times10^5 \) dyne/cm\(^2\) (measured in our laboratory), respectively, and Poisson's ratio \( \nu_1 \) is about 0.30 and \( \nu_2 \) is about 0.25[23]. From 30-34 °C, \( E_1 \) and \( \nu_1 \) remain unchanged, while \( E_2 \) and \( \nu_2 \) are about \( 1.20\times10^5 \) dyne/cm\(^2\) and 0.22, respectively. The corresponding maximum stresses at various temperatures in both sides of the bi-gel are shown in Fig. 5.2 (b). The maximum stress values of the IPN side increase sharply (almost by one order magnitude) with the temperature. This is due to the phase transition results in the increase of both the elastic modulus and the bending curvature. Since the elastic modulus is almost the same in the PAAM side at various temperatures, and the increase of stress depends only on the bending increases, the stress values in the PAAM side are always smaller than that in the IPN side. It is noted that the absolute maximum stress value in the PAAM side at 39 °C is still much smaller than the stress value \( 3\times10^5 \) dyne/cm\(^2\) at the yield point[24], as expected.
Fig. 5.2. (a) The elastic bending strains $S_r$ in both sides of the bi-gel, obtained after about 120 min at each designated temperature, as a function of temperature. IPN side (o) and PAAM side (□); (b) The maximum bending stresses $\sigma_{\text{max}}$ in both sides of 3 mm bi-gel at various temperatures.
Due to the unique structure of the bi-gel, it can bend not only in a homogeneous temperature field but also in some uniform solvents. Figure 5.3(a) shows the bending strain of a 3 mm bi-gel in acetone/water mixture at room temperature (about 22 °C) as a function of acetone concentration. The strain decreases slowly at first upon increasing the acetone concentration. After 30 wt% the strain increases dramatically with the increase of acetone concentration. The strains become flat as the acetone concentration increases above 50 wt%. In pure water, the bi-gel sample bends toward the PAAM side, because the swelling ratio for the ionic IPN gel is larger than that of PAAM gel. To better understand the strain curve, the shrinking ratios of the ionic IPN and PAAM gels are shown Fig. 5.3 (b) as a function of acetone concentration (note: these are not bi-gel). The shrinking ratios of both IPN and PAAM gels are almost the same below 30 wt% acetone concentration, resulting in no obvious change of the strains. As the acetone concentration increases further (over 30 wt%), because the PAAM side has a volume phase transition in this concentration region, it shrinks much more than the IPN side, and the bi-gel strip bends to the PAAM side sharply. The bending strain values of the both sides increase drastically. Finally, since both the PAAM side and the IPN side collapse and are no longer shrinking (after the volume phase transition), the bending strain curves become flat.

The bi-gel can also bend in salt solutions. As shown in Fig. 5.4 (a), the bending strain of a 2 mm bi-gel strip is plotted against the NaCl concentration at about 22 °C. From Fig. 5.4 (a) one can see that the bending strain has a large increase in dilute NaCl solution. As the NaCl concentration increases over 1 M, the bending strains in both sides of the bi-gel increase greatly. The change of the bending strain of the bi-gels in NaCl solvent is caused by the volume phase transition of the NIPA component in the IPN side. As shown in Fig. 5.4 (b), the ionic IPN gel exhibits a volume change at a dilute NaCl concentration due to the Donnan-equilibria effect [25]. There is a second volume phase transition that is due to the suppression of the transition temperature by salt concentration.
This effect makes the bi-gel bend more, and produces the second sharp increase of the bending strains.

Fig. 5.3. At about 22 °C, (a) the elastic bending strain \( S \), as a function of acetone concentration in both sides of a bi-gel. In both graphs, IPN side (○) and PAAM side (□); (b) the swelling ratio of IPN and PAAM gels in acetone/water mixture, dependent of acetone concentration.
Fig. 5.4. At room temperature (about 22 °C), (a) The bending strain $S_r$ in both sides of a bi-gel strip, as a function of NaCl concentration, IPN side (o) and PAAM side (□); (b) The swelling ratio of the IPN gel in NaCl solution.
5.4.2. The bending kinetic process of a bi-gel

The total thickness of the bi-gel is \( d = d_1 + d_2 \), where \( d_1 \) is the thickness of the PAAM side and \( d_2 \) is the thickness of the IPN side. Since the PAAM gel is sensitive to neither temperature nor NaCl concentration, \( d_1 \) shows almost no change in our kinetic process experiments. \( d_2 \) varies with temperature and NaCl concentration, and this makes the whole bi-gel bend.

At a fixed temperature, the bending of a gel is a kinetic process. The time-dependent strains in both sides of a 2 mm bi-gel is obtained as shown in Figure 5.5 (a). Starting at room temperature (about 22 °C), the sample was suddenly immersed into a 37 °C thermal bath. The bending of the sample is monitored with the time zero point corresponding to the time when the sample was put in the thermal bath. After the sample reaches a quasi-stable state, its temperature is quickly reduced to room temperature. From the Figure 5.5 (a) one can see that the bending strain increases with time when the sample is immersed in the high temperature bath. Upon cooling the bi-gel gradually restores its original shape and size. This process is reversible as indicated by the two cycles in Figure 5.5 (a). It is clear that the change of the strain in the PAAM side is larger than that in the IPN side corresponding to the same curvature.

The data of the IPN side in Fig. 5.5 (a) are also plotted in Fig. 5.5 (b) by use of a semilog plot. To estimate the relaxation time of the restoring process, we use the exponential form to fit the data. The solid straight lines are least-square fits to the data using the following equation [5,26]:

\[
S_r = S_{r0} \exp \left[-\left(\frac{t - t_0}{\tau}\right)\right], \quad (t \geq t_0)
\]

(5.9)

where \( S_r \) is the bending strain, \( t \) is the time measured from the point at which the sample was moved from high temperature bath to room temperature bath, and \( \tau \) is the relaxation
time constant of restoring process. \( S_{r0} \) is the maximum strain and \( t_0 \) is the time when the strain values reach the maximum. It is clear that the gel's restoring process after removing the sample from higher temperature bath to room temperature bath can be described by the single exponential form. This is expected from gel swelling kinetic theory. From the least-square fit line shown in Fig. 5.5 (b), the relaxation time is 34.3±2.5 min for the bi-gel from bending state returning to straight line state under the current experimental conditions.

On the other hand, we also estimated the bending time constant by following equation:

\[
S_r = S_{r0}[1 - \exp\left(-\frac{t}{\tau_s}\right)]
\]  
(5.10)

where \( \tau_s \) is the bending time constant induced by shrinking process of the IPN side. The dashed lines in Fig. 5.5 (b) are fitted to the data by equation (5.10). \( \tau_s \) is about 54.8±7.4 min here.

The bending process of the bi-gel induced by NaCl solvent depends on the sample temperature, since the IPN side of the bi-gel is sensitive not only to NaCl concentration but also to the temperature. Because both sides of the bi-gel in a kinetic process show the similar behavior except the sign and magnitude of the strain, we will discuss the kinetic process of the IPN side of a bi-gel as follows. Figure 5.6 shows the time-dependent strain in the IPN side of the 2 mm bi-gel with and without NaCl solvent at T=20, 26, and 33 °C. The initial half of the cycle corresponds to the sample in 1 M NaCl solution, while the final half of the cycle corresponds to the sample in pure water at the same temperature. The shape of the curve is similar to the kinetic process curve of temperature-induced bending in the bi-gel. From Figure 5.6, one can see that as the temperature increases, the amplitude of the strain increases. This indicates that raising the sample temperature can enhance the
Fig. 5.5. (a) Two cycles of the time dependence of the bending strain $S_r$ in both sides of a bi-gel. The increase of strain is obtained in a water bath at about $37 \, ^\circ C$ and the decrease of strain is obtained in a room temperature (about $22 \, ^\circ C$) water bath, IPN side (o) and PAAM side (□). The corresponding temperature profile is also plotted using a solid line. (b) log (strain $S_r$ in IPN side) vs time. The solid lines represent the best least-square fit to the data.
bending effect at constant NaCl concentration. Using Eq. (5.9) to fit the data, the relaxation time at various temperatures has been obtained as shown in Fig. 5.7. From Figure 5.7, it is clear that the relaxation time $\tau$ increases with temperature. The relationship between $\tau$ and temperature is linear. On the other hand, the bending behavior involves a shrinking process, which is induced by both temperature and NaCl here, is quite complicated and cannot generally be described using a single exponential form [27]. Therefore, Eq. (5.10) is not suitable to be used here to fit the data.

At a fixed room temperature (about 22 °C), the kinetic processes in the IPN side of the 2 mm bi-gel in various NaCl concentrations are shown in Figure 5.8. At $t=0$, the bi-gel sample was put into NaCl solution and the sample began bending. After about 30 minutes, the sample was changed to pure water. From Figure 5.8, one can see that the amplitude of the strain increases with the NaCl concentration within the same period of time. By Eq. (5.9), from the restoring process data, one can also get the relaxation time of a bi-gel in pure water. It is found that the relaxation time ($\tau = 35.7 \pm 2.3$ min) is about the same for different initial...

![Fig. 5.6. One cycle of kinetic process of the bending strain $S_r$ in the IPN side of the bi-gel from 1 M NaCl solution to pure water at different temperature $T_f$: 21 °C (o), 26 °C (□) and 33 °C (△). The solid lines are a guide to the eye.](image-url)
NaCl concentrations within our experimental accuracy. It is suggested that the relaxation process in pure water is independent of initial NaCl concentration at the fixed temperature.

Fig. 5.7. The relaxation time constant from 1 M NaCl solution to pure water at different temperatures. The solid line is the best least-square fits to the data.

5.4.3. Diffusion coefficient estimation by bending kinetic process

According to the theoretical model, from the data in bending kinetic processes of a bi-gel and using equation (5.8), we have estimated the collective diffusion coefficients of ionic IPN in water and in salt solution. At about 37 °C the curvature variation ratio $\Omega$ with respect to $t^{1/2}/d_z$ is shown in Figure 5.9. By use of linear fitting in the initial diffusion stage, one obtains the collective diffusion coefficient $D_c$ of IPN in water to be about $1.1 \times 10^{-7}$ cm²/s. When the diffusion time is longer, since $t$ increases and $d_z$ decreases and the condition $t<0.54d_z^2/D_c$ can not be satisfied, the equation (5.8) is not suitable. This is why the last few points in Fig. 5.9 deviate from the fitted line. Since in the IPN gel, only the ionic NIPA component is sensitive to temperature, the diffusion coefficient of IPN gel in water should be the same order as the relevant NIPA gels. Our results indeed are in
Fig. 5.8. One cycle of the time dependence of the bending strain $S_r$ in the IPN side of a bi-gel from different NaCl concentrations to pure water at about 22 °C, NaCl concentration 1.0 (○), 1.5 (□) and 2.0 M (△). The solid lines are a guide to the eye.

good agreement with that previously measured by another group with light-scattering experiments for NIPA gels[28]. By the same method described as above, we obtained some collective diffusion coefficients in the IPN side of the bi-gels under various conditions as summarized in Table 5.1.

From Table 5.1, one can see that the collective diffusion coefficient becomes smaller after the phase transition point of the IPN gel in pure water. A similar effect can be seen for the IPN gel in NaCl solution when the temperature is fixed at room temperature (about 22 °C). Finally, when NaCl concentration is fixed at 1 M, the collective diffusion coefficients $D_c$ at various temperatures show no obvious change.

Because the shear modulus of the PAAM side is much smaller than that of the IPN side when the temperature is higher than phase transition temperature (about 37 °C), and the thickness of the PAAM side is small (less than 2 mm), the influence of PAAM side to the measurement can be neglected in our experiment.
TABLE 5.1. Collective diffusion coefficients ($D_c$) of ionic IPN gels under different temperatures and salt concentrations.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>NaCl(M)</th>
<th>$D_c(10^{-7} \text{cm}^2/\text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>0.0</td>
<td>0.50</td>
</tr>
<tr>
<td>37</td>
<td>0.0</td>
<td>1.1</td>
</tr>
<tr>
<td>33</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>26</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>21</td>
<td>1.0</td>
<td>1.8</td>
</tr>
<tr>
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<td>0.58</td>
</tr>
<tr>
<td>21</td>
<td>2.0</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Fig. 5.9. The measured bending curvature variation ratio $\Omega$ at various times for the diffusion of pure water in IPN side of a bi-gel at 37 °C, where $d_z$ is the thickness of IPN side of the bi-gel. Solid line is also the best least-square fits to the data.
5.4.4. Discussion

Any bending effect in materials is due to non-uniformity of the internal stress distribution in the material. If the material is homogeneous, the bending can only be induced by the external gradient fields. The mechanism of the bi-gel bending here is different from the bending introduced by electric field [10,29,30] or infrared laser heating[5]. In those cases the sample is uniform, and the gradient of electric field or the gradient of temperature field has to be applied to trigger the bending. For example, it is localized heating that causes the gel to bend in infrared induced bending[5]. Therefore, the bending cannot occur if the gel is uniformly heated.

In this experiment, it is not required to apply external gradient fields. The structure of gels is heterogeneous. Therefore, the gel responds directly to an environmental change that can induce the phase transition in either side of the bi-gel. This quality of a bi-gel can be easily used as adaptive sensors and devices. The bi-gel strip has several advantages over the traditional bi-metallic strip. First, the difference of the thermal coefficients between the two sides of the bi-gel is much larger than that between two metals. For example, the difference of expansion coefficients for a typical bimetallic strip of brass and steel is about $7 \times 10^{-6} \degree C^{-1}$. However, for an IPN-PAAM bi-gel strip such difference can be as high as $0.5 \degree C^{-1}$. This is true because only one side of the bi-gel is sensitive to the external stimulus, and the other side shows almost no change at all. Therefore, the bi-gel strip may have a larger degree of flexibility in a narrow temperature range. Secondly, the bi-gel strip can be used in biological system as adjustable automatic switches, where the conventional bimetallic strip might be not suitable.

Because the bi-gel is composed of two types of gels with different characteristics, any external variable can induce the bi-gel bending if it affects one side of the bi-gel. Thus, one can use many variables to induce bi-gel bending, such as temperature, salt solution, solvent etc. There is a great flexibility in bi-gel bending compared with the bending of a
uniform gel. In this way, it opens a door for many applications of polymer gels in various fields.

5.5. Conclusion

The bending of a bi-gel strip (IPN-PAAM) can be induced by temperature, acetone/water mixture, and salt solution. The maximum strain values in the IPN side and in the PAAM side are about 0.25 and 0.60 respectively. At 37 °C the restoring relaxation time of a 3 mm bi-gel is 34.3±2.5 minutes in pure water. In 1 M NaCl solution the restoring relaxation time of a 2 mm bi-gel linearly increases with the increase of temperature within 20–34 °C range. At about 22 °C, the restoring relaxation time of a bi-gel shows no obvious change when it is transferred from salt solution to pure water. The collective diffusion coefficients of ionic IPN gels in pure water at 37 °C and 39 °C are about 1.1×10⁻⁷ cm²/s and 0.50×10⁻⁷ cm²/s, respectively. They are in the same order as the ionic NIPA in water at the same temperature. At about 22 °C, the collective diffusion coefficient of IPN salt solution decreases about two-thirds with the increase of NaCl concentration within the 1~2 M region. The bending effect of a bi-gel, similar to bi-metal strips, may have applications in biological engineering or the biomedical field.
6.1 Introduction

Gels are three dimensional networks of crosslinked polymers immersed in solvent. The mechanical properties of polymer gels are characterized by the bulk modulus and shear modulus. The application of scaling methods to these elastic moduli has led to some dramatic successes in both theoretical understanding and experimental applications [1]. A variety of polymer gel systems has been tested and it was found that the concentration dependent shear modulus of gels follows the classic theoretical scaling law with the scaling exponent equal to 1/3 [2-4]. To our knowledge, all of these tests were performed on gels which have the network concentration below 0.25 g/cm$^3$. The higher concentration is hard to obtain using the conventional deswelling methods which rely on osmotic pressure to squeeze water out [2-4]. It is of interest to explore the scaling behavior at high concentrations.

In this chapter, we present the network-concentration-dependence of the shear modulus of polyacrylamide (PAAM) gel over a broad concentration ranging from 0.02 to 1.0 g/cm$^3$. The experiment clearly shows that the classic theory cannot explain the behavior of shear modulus in a high network-concentration regime. A non-classical scaling model based on the heterogeneity of the gel network has been proposed and seems
to describe our data well.

The free energy of a gel can be written as a summation of two terms:

\[ F = F_1(\phi) + F_2(\alpha_x, \alpha_y, \alpha_z) \]  

(6.1)

where \( \phi \) is the polymer concentration, the \( \alpha_i \)'s are the principal elongation ratios relative to the gel dimensions when it was made. The first term is network-concentration dependent, corresponding to the free energy of an uncrosslinked polymer solution. The second term, \( F_2 \), is sensitive to the network-swelling anisotropy, and is usually called the elasticity term. In the classical rubber elasticity theory [5], this term is expressed as:

\[ F_2 = B[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3] \]  

(6.2)

where \( B \) is temperature and gel-crosslinking-concentration dependent. For a gel with concentration equal to \( \phi \), \( F_2 \) can be written as

\[ F_2 = B \left( \frac{\phi}{\phi_0} \right)^{2/3} [\Lambda_x^2 + \Lambda_y^2 + \Lambda_z^2 - 3] \]  

(6.3)

with \( \Lambda \) the elongation ratio relative to the isotropic state at concentration equal to \( \phi \),

\[ \Lambda_i = \alpha_i \left( \frac{\phi}{\phi_0} \right)^{1/3} \]  

(6.4)

If a cylindrical gel is uniaxially elongated along its z-direction with \( \Lambda_z = \Lambda \), then the deformations perpendicular to the elongation axis are \( \Lambda_x = \Lambda_y = \Lambda^{-1/2} \). The elongation pressure, defined as the force divided by the cross section area of the undeformed gel, can be obtained from Eq. (6.3) as
\[ p = \frac{2B}{V_0} \left( \frac{\phi}{\phi_0} \right)^{1/3} [\Lambda - \Lambda^2] = G [\Lambda - \Lambda^2] \quad (6.5) \]

This result is the Mooney-Rivlin equation and \( G \), by definition, is the shear modulus of the gel,

\[ G = G_0 \left( \frac{\phi}{\phi_0} \right)^m \quad (6.6) \]

where \( G_0 = \frac{2B}{V_0} (\phi_c/\phi_0)^m \). The exponent \( m \) is equal to 1/3 in the classical elasticity theory.

The exponent \( m \) has been measured for several systems [2–4]. For all these systems studied, the gel network concentrations were less than 0.25 g/cm³, and were controlled by osmotic deswelling, i.e., by placing the gel samples in semipermeable bags immersed in a polymer solution. Due to the practical limit of the polymer concentration, the osmotic pressure is limited to a certain range. Therefore the highest network concentration due to the osmotic deswelling is limited. Here, we varied the network concentration by evaporating a controlled amount of solvent. This method allowed us to explore gel properties in the whole concentration range.

**6.2 Experimental**

The samples (all cylindrical) measured were six series of polyacrylamide gels crosslinked with methylene-bis-acrylamide (BIS) [6]. The monomer (acrylamide) concentration of all samples at polymerization was 5 wt%. The crosslinker concentrations were varied as 0.61, 0.92, 1.23, 1.84, 2.46, and 4.91 mole percent (mol\%) relative to acrylamide number concentration. In the following, we shall use BIS concentration of
1.23 mole percent as a standard unit for convenience. Thus the six BIS concentrations will be represented by BIS equal to 0.5, 0.75, 1.0, 1.5, 2.0, and 4.0, respectively. Fully swollen segments of samples were placed in a 45 °C oven for a varying amount of time to evaporate a desired amount of the gel water. Then the samples were sealed in vials for several days to ensure uniformity of the network concentration.

The shear modulus, defined by Eq. (6.5), was measured using a simple compressional method, similar to the one described in Ref. 2. The maximum deformation ranged from 10% to 30%, depending on samples. For each sample, the compressional force and sample height were recorded during both force increasing and force decreasing processes. The two processes yielded almost identical stress-strain relation and the average value of \( G \) obtained from them was used. Based on the resolution of the force gauge and the sample height measurement, the uncertainty in shear modulus value was estimated to be about 3%. The sample weight loss (water evaporation) during the measurements was found to be insignificant (less than 2%), which satisfied the constant volume requirement of the technique. The sample network concentrations were calculated by knowing the weights of the samples and their dry weights, obtained after the shear modulus measurements. To further reduce the evaporation, and to overcome the gravitational effect on weakly crosslinked gels, we immersed some of our samples in oil during the shear modulus measurement. No difference was observed between the results obtained from samples in air and in oil. This indicates that the loss of solvent is negligible in our experiment.

6.3 Results and discussion
Figure 6.1 is the network concentration dependence of shear modulus $G$ of samples of different crosslinking concentrations. The data have been shifted to the indicated amount in the figure for clarity. The first data point of each sample (the ones with lowest network concentration) is the shear modulus of the fully swollen sample. For the network concentration below $0.2 \, \text{g/cm}^3$, the classical exponent of $m=1/3$ was obtained. As the network concentration increases, the concentration dependence deviates from $m=1/3$, drastically. These data indicate that the concentration dependence of shear modulus can not be described by a single scaling exponent.

It is attempting to explain the deviation from classical rubber elasticity by glass transition. Since in general, the higher the polymer concentration, the higher the glass transition temperature. When the glass transition temperature is higher than room temperature, the polymer stiffening effect can increase the network elasticity. For poly(hydroxyethyl methacrylate) (PHEMA) network, the glass transition temperature drops from 125 °C for a dry gel to about 0 °C with 40% water content [7]. It had been reported that for poly(vinylpyrrolidone) the amount of "bound" water at given temperature is about one-third of the amount of water needed to reduce the polymer glass transition to the same temperature [8]. In the case of PHEMA gel, the factor is about half since the bound water of PHEMA is about 20% [9]. The bound water of swollen N-isopropyl-acrylamide (NIPA) gel is around 15% [10]. Therefore it is reasonable to assume that with about 30% water, the glass transition temperature of NIPA gel network is around 0 °C. Since acrylamide network is more hydrophilic than NIPA network, the reduction of glass transition at a given water content should be even higher. That is, the glass transition
Figure 6.1. Network concentration dependence of shear modulus for PAAM gels with different degrees of crosslinking. All data were collected at room temperature. The BIS concentration is represented by the number immediately following the symbols. For clarity, the data have been shifted by constant multiplication factors which are indicated by the numbers in parentheses: Circle 0.5 (16), triangle 0.75 (4), plus 1 (x1), Diamond 1.5 (1/3), star 2 (1/6), and open triangle 4 (1/16).

temperature of acrylamide gel network is expected to be below 0 °C for the network concentration below 0.7 g/cm³, which corresponds to 40% water content. At room temperature, the glass transition appears around 1g/cm³ at which the shear modulus increases sharply as shown in Figure 6.2 for gel samples with BIS=1. Therefore, the
observed room temperature elasticity for the acrylamide gel network concentration below 0.7 g/cm³ can not be explained by the glass transition effect.

Figure 6.2. Network concentration dependence of shear modulus for PAAM gel with BIS=1. The data were collected at room temperature. The glass transition point locates at around 1 g/cm³ as indicated by a dashed line.

The deviation of concentration dependence of gel shear modulus suggests that at high concentration, a different mechanism dominates the contribution to shear modulus. One likely mechanism is the compressional energy associated with the structural heterogeneity of the network. It is well known that the network structure of gels, in general, are highly heterogeneous [11-13]. These heterogeneities are mostly related to the gelation
processes, especially when the process is free radical polymerization [12]. For instance, when BIS is used as a hydrogel crosslinker, its hydrophobicity causes clustering of BIS in the network to form dense domains [11]. Intuitively, the network structure will be heterogeneous when the reaction rates involved are drastically different. When the chemical reaction involves ionic species (e.g., sodium acrylate), the electrostatic interaction generates lattice-like domain structure in the network, which has been observed by small angle neutron scattering [13]. Therefore, structure domains are characteristics of gel networks and are intrinsic properties. In our case, the domains are mostly due to the hydrophobicity of crosslinkers (BIS). These heterogeneities of gels, even the highly transparent ones, can be detected easily by light scattering techniques [14-17]. As a laser beam scans through a polyacrylamide gel sample, the scattered intensity changes dramatically with spatial correlation length around 25 microns [12-13]. The network heterogeneity has a direct impact on gel properties, including solvent permeability [11, 18]. It was also speculated that the gel heterogeneity has an impact on the measured critical exponents of its volume phase transition [19]. Figure 6.3 shows the two-phase heterogeneity model originally proposed by Weiss, Van Vliet, and Silberberg to explain their gel permeability data [11]. In this model, the network is assumed to have two phases: the dense phase and the dilute phase. The dense phase is highly crosslinked and has higher mechanical strength. As the gel is deswelled, the dilute (highly swollen) regions will be affected more than the dense regions. However, at high network concentration \( \phi \), the dense domains are getting closer and closer to each other. The compressional energy arising from the dense domain-domain repulsive interaction is related to the distance
Figure 6.3. A sketch of gel structure inhomogeneity with dense and dilute domains.

between them. This energy can therefore be written as,

$$F_3 \sim (\beta_i^+ \cdot \beta_j^+ \cdot \beta_k^+)$$  \hspace{1cm} (6.7)

where $\beta_i$ is the average distance between adjacent dense domains in the $i$-th direction (see Fig. 6.3). The power $t$ is a measure of the interaction. The $\beta_i$'s are related to both the network concentration $\phi$ and the compression ratio $\Lambda_i$,

$$\beta_i \sim \Lambda_i \phi^{-1/3}$$  \hspace{1cm} (6.8)

The total elastic free energy of a highly deswelled gel is therefore,
The elongational pressure is then,

\[ P = G_s \left( \frac{\phi}{\phi_c} \right)^{1/3} \left[ A - A^2 \right] + G_s \frac{tA_0}{2} \left( \frac{\phi}{\phi_c} \right)^{1/3} \left[ A^{3/2} - A^{-3/2} \right] \]  \hspace{1cm} (6.10)

To the first order of \( \Delta = (1+\Lambda) \),

\[ P = G_s \left[ \left( \frac{\phi}{\phi_c} \right)^{1/3} + A \left( \frac{\phi}{\phi_c} \right)^{1/3} \right] 3\Delta \]  \hspace{1cm} (6.11)

Where \( A \) measures the relative contribution between the two terms \( (A=\tau^2A^4) \). The shear modulus of a highly concentrated gel is therefore,

\[ G = G_s \left[ \left( \frac{\phi}{\phi_c} \right)^{m_1} + A \left( \frac{\phi}{\phi_c} \right)^{m_2} \right] \]  \hspace{1cm} (6.12)

where \( m_1=1/3 \) and \( m_2=1+\tau/3 \). The two terms in the bracket contribute to \( G \) equally at the crossover concentration \( \phi_c=\phi_c/A^{1/(m_2-m_1)} \). It was found that all of our data can be well fitted by Eq. (6.12). Table 6.1 lists the fitting parameters obtained from the data. No significant difference was found when the data were fitted with the value of \( m_1 \) fixed at 1/3. The two exponents \( m_1 \) and \( m_2 \) are plotted in Figure 6.4. As shown in this figure, the value of \( m_1 \) is approximately equal to \( 0.33 \pm 0.06 \), in agreement with the observations made by other groups [2-4]. The value of \( m_2 \) is \( 2.3 \pm 0.3 \). The values of exponents of BIS=4 series deviates significantly from values of other series and have not been used for statistical analysis. Figure 6.5 shows the fitting of Eq. (6.12) to BIS=1 samples. The contributions from the first term (dashed line) and the second term (solid line) are shown.
TABLE 6.1. Fitting parameters obtained by fitting the data to Eq. (6.12). The crosslinking concentration (BIS) is in the unit of 1.23 mol%. The unit of $\phi_e$ is g/cm$^3$. The parameters from the fitting with $m_1$ fixed at 1/3 are included as well.

<table>
<thead>
<tr>
<th>BIS</th>
<th>$\phi_e$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>100A</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>100A</th>
</tr>
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<tr>
<td>0.50</td>
<td>0.018</td>
<td>0.32</td>
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<td>0.25</td>
<td>(1/3)</td>
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<td>0.24</td>
</tr>
<tr>
<td>0.75</td>
<td>0.023</td>
<td>0.37</td>
<td>2.46</td>
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<td>(1/3)</td>
<td>2.39</td>
<td>0.35</td>
</tr>
<tr>
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<td>0.026</td>
<td>0.33</td>
<td>1.99</td>
<td>0.96</td>
<td>(1/3)</td>
<td>1.99</td>
<td>0.97</td>
</tr>
<tr>
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<td>0.27</td>
<td>2.15</td>
<td>1.00</td>
<td>(1/3)</td>
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<td>0.67</td>
</tr>
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<td>0.36</td>
<td>2.48</td>
<td>0.44</td>
<td>(1/3)</td>
<td>2.39</td>
<td>0.56</td>
</tr>
<tr>
<td>4.0</td>
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<td>0.37</td>
<td>3.38</td>
<td>0.062</td>
<td>(1/3)</td>
<td>3.27</td>
<td>0.083</td>
</tr>
</tbody>
</table>

Figure 6.4. The exponents $m_1$ and $m_2$ versus crosslinking concentration. The dashed line represents the classical exponent value of 1/3.
From this figure, it is clear that at low concentration, the first term, i.e., the classic rubber elasticity term, dominates. At higher concentration, the heterogeneity term becomes significant. The crossover concentration $\phi_c$ is plotted in Figure 6.6. The higher the crosslinking concentration, the higher the crossover concentration. This indicates that the higher the BIS concentration, the smaller, but denser, are the dense domains. The relative change of the crossover concentration, $\Delta \phi_c/\phi_c$, affected by $\Delta (m_2-m_1)$ is estimated to be about 40%.

Notice that the free energy term $F_3$ has an effect on isotropic swelling as well. The osmotic swelling pressure contribution from it is

$$\omega = \phi^2 \frac{\partial F_3}{\partial \phi} - \phi^{m_2}$$

(6.13)

The concentration dependent exponent of the osmotic pressure from the polymer solution term $F_3$ is 2.25, which is about the same as $m_2$. Therefore, the effect of $F_3$ can not be easily detected by analyzing the exponent of swelling osmotic pressure.

As a final note, Eqs. (6.3) and (6.6) deal with the entropy effect of polymer chain configuration change. In Eq. (6.6), the concentration is a manifestation of the shrinking of polymer "coils". This concentration effect is different from the concentration effects introduced by other ways, for example, by changing monomer [20] or crosslinker concentration [21] at the onset of polymerization. Furthermore, it is interesting to compare our system with other gel systems prepared in the limit of low cross-linker density but high polymer concentration [22]. In our case, the polymer chains have been forced into much
Figure 6.5. Detailed log-log plot of shear modulus versus polymer concentration for BIS=1 series. The solid curve is the least square fit to Eq. (12). The dashed and solid lines represent the first and second terms in Eq. (12), respectively.

smaller "coils" at high concentration by deswelling. In the other case, the polymers are still very much "Gaussian"-like but highly interpenetrated [22]. The theoretical treatment should be therefore different.

6.4 Conclusion

Measurement of shear modulus of PAAM gel has been performed over a very broad network concentration range. It has revealed that the classic term with an exponent of 1/3 can be applied only to the low concentration region, i.e., below 0.25g/cm³, in
Figure 6.6. The crossover network concentration of gels with different crosslinking concentrations. As shown, the crossover concentration increases as the crosslinking concentration increases.

agreement with available experimental and theoretical results. As the network concentration increases beyond this region, a new term based on a two phase inhomogeneity model starts to dominate. This inhomogeneity term can be characterized by an exponent $m_2$ with its value between 2.0 to 2.5. The comparison between the theory and experiments has been made for six series of samples which have different crosslink concentrations ranging from 0.61 to 4.91 mole percent. The agreement is excellent. New experiments with known built-in inhomogeneity would be interesting to further test the model proposed here.
CHAPTER 6 REFERENCES


5. P. J. Flory, *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953. We choose to use the simpler elasticity expression over other refined theories since these refined ones do not change the major conclusions of our study.


CHAPTER 7

THE PHASE TRANSITION AND SHEAR MODULUS OF
IONIC NIPA IN CONCENTRATED NaCl SOLUTIONS

7.1 Introduction

There are many external stimuli that can induce phase transition in polymer gels such as temperature, solvent composition, light, electric field, and pH value. Recently, thermal sensitive N-isopropylacrylamide (NIPA) gels have attracted great attention for their scientific interest [1-4] as well as for their technological potential in a variety of applications including drug delivery [5] and immobilized-enzyme reactors. [6]

Many potential applications of temperature-sensitive gels require incorporation of fixed ionizable groups within the gels. Particularly, the ionic gels in salt solutions are of interest. A nonionic NIPA gel exhibits a sharp volume phase transition at a critical concentration of sodium chloride solution (about 1 M) [7,8]. This kind of transition is not a "salting out" effect. On the other hand, ionic NIPA gels (NIPA copolymerized with methacrylamidopropyltrimethylammonium chloride simplified as MAPTAC) show a volume phase transition in dilute NaCl solution (less than 0.1 M) [9]. The phase transition of the ionic NIPA gel at such a low NaCl concentration can be explained by the Donnan-equilibrium argument.

In this chapter, swelling equilibria of the neutral and ionic NIPA (NIPA copoly-
merized by sodium acrylate) gels are investigated as a function of NaCl concentration in aqueous solutions. It is found that the ionic NIPA gels exhibit two phase transitions as the NaCl concentration increases at room temperature: One is in diluted NaCl solutions (NaCl less than 0.1 M), and the other is in concentrated NaCl concentration (NaCl greater than 0.8 M). The behaviors of the shear modulus and the turbidity of the NIPA gels in two phase transitions are also reported.

7.2 Experiment

The neutral NIPA gel samples were made by the same method as description in chapter 2. The NIPA and sodium acrylate (SA) copolymer ionic gel samples were made by incorporating 4, 8, 16, and 35 mM (SA) into the NIPA pregel solution, respectively. Nitrogen gas was bubbled through the solution to remove dissolved oxygen. Ammonium persulfate (0.169 mM) was added to the solution as an initiator. The pregel solution was then poured into cylindrical glass tubes with the diameters from about 5 mm to 10 mm, and the polymerization process was made in nitrogen environment. After polymerization, the gel samples were taken out of the tubes, and extensively washed with deionized and distilled water to wash away residual chemicals. The samples were then immersed in deionized and distilled water. It took approximately ten days for the diameters of the gels reaching an equilibrium value. The diameters and the heights of the gel samples used in the measurement were 8 to 12, and 10 to 15 mm in water, respectively.

The dimensions of the gel samples were measured using a caliber with the accuracy 0.05 mm in pure water and in aqueous sodium chloride solutions with the concentration range from $10^{-3}$ to 3.0 M at room temperature (about 22 °C). In the measurement of
swelling ratio, the gel samples were cut to thin strips. The swelling ratio $L/L_e$, i.e., the ratio of equilibrium length $L$ in various NaCl concentration to the length $L_e$ in water was calculated. The standard deviations of the measured swelling ratio were generally less than 5% of the mean.

The shear modulus was obtained in a uniaxial compression experiment. To keep a constant volume of the sample the time for performing the measurement was shorter than the characteristic deswelling time of the gels. In the experimental setup used in this study, the cylindrical gel was compressed by a glass plate attached to a calibrated digital force gauge. The displacements of the glass plate were controlled through a screw. For each displacement, the corresponding force $F$, was measured. When the volume of the gels was kept constant, one can obtain [10]

$$\frac{F}{S} = G(\lambda - \frac{1}{\lambda^2}) \quad (7.1)$$

where $G$ was the shear modulus, $S$ was the surface area of the undeformed gel and $\lambda$ was the z-direction elongation ratio of the gel. By plotting $F/s$ vs $(\lambda-1/\lambda^2)$, the slope $G$ was obtained. Values of $\lambda$ during the experiment were typically between 1 and 0.8. In order to decrease the sticky effect of the gel sample near the phase transition to the measurement, we put some vacuum oil on the gel surface which touched the glass plate. The error of the measurement was estimated to be less than 8%.

The optical absorption of the NIPA gels at various concentrations of sodium chloride solutions was determined by measuring the transmission at a 555 nm wavelength using a spectrophotometer (spectronic 301, Milton Roy Co.) at about 22 °C.
7.3 Results and discussion

7.3.1 Swelling Ratios

Figure 7.1 shows the swelling behavior of NIPA gels in NaCl solutions (from pure water to 3.0 M) at various SA concentrations at about 22 °C. Pure water is denoted on Figure 7.1 (a) as $10^{-7}$ M NaCl. The reduced swelling ratios are referring to the fully swollen equilibrium state of the gels in water. As the salt concentration increases above $10^{-3}$ M, the ionic gels shrink rapidly. The degree of deswelling highly depends on the strength of gel ionization (molar number of SA). The volume phase transition shown here is continuous and similar to one observed previously. [9] Such a behavior can be explained in terms of the Donnan-equilibria effect [9,11].

The reduced swelling ratio of NIPA gels in concentrated NaCl solutions is shown in Fig. 7.1 (b). When the NaCl concentration approaches about 1.0 M, the ionic gels undergo the second shrinkage. This second shrinkage indicates that there is a volume phase transition in concentrated NaCl solution. The second phase transition can not be explained in terms of either the "salting out" effect [7] or the Donnan-equilibria argument. [9,12] This kind of transition has been previously reported for a neutral NIPA gel. [7,8] To our knowledge, this is the first time that such a transition is observed in ionic NIPA gels. For convenience, we will call the phase transitions at NaCl ~ $10^{-3}$ M and NaCl ~ 1 M as the first transition, and the second transition, respectively.

For higher salt concentrations, the exclusion (Donnan effect) in ionic gels is less effective for two reasons: (i) the anions are pushed more strongly into the gel when more anions are present in environment, and (ii) the surplus of cations in the gel over the
Fig. 7.1 Swelling equilibria at 22 °C for NIPA/SA copolymer gels in water and in aqueous salt solutions as a function of NaCl concentration. The data at $10^{-7}$ M NaCl represent swelling in deionized and distilled water. (a) In diluted NaCl solutions, NaCl concentration from $10^{-7}$ to $10^{-1}$ M; (b) In aqueous salt solutions with NaCl concentration from 0 to 3.0 M.
bath becomes less pronounced. Therefore, the collapse of the gel in high salt concentration at room temperature is not a result of Donnan effect [12].

It is clear that the NIPA gel exhibits a lower critical solution temperature (LCST) in aqueous solution. The gel collapses above the LCST and reswells below that critical temperature. For the neutral NIPA gel, with increasing NaCl molality, the transition temperature is shifted to lower temperature [7,8]. The decreasing trend in the transition temperature is correlated with the viscosity coefficient (a measure of ion-water interaction) of ions, suggesting that water structure-making and breaking effects by ions may result in the LCST shift [7,13]. Thus, the LCST of the gel and the critical sodium chloride concentration are closely related. Even though the exact role of sodium chloride in lowering the LCST is not clearly understood [13], it seems that the driving force for the phase transition behavior of the neutral NIPA gel induced by either sodium chloride or temperature, is the same, i.e., via inter and intramolecular hydrophobic interactions [7].

When the NaCl concentration is greater than 0.1 M, the gel charge density has a minimal effect on swelling behavior. The ionized gels exhibit temperature-volume curves which are in near-quantitative agreement with those for uncharged NIPA gel [9]. That is to say, in the presence of a larger excess of salt, the screening effect is strong and the ionized gel should recover the behavior of a neutral gel [14]. Following this observation and that the LCST of the neutral NIPA gel can be shifted to lower temperature by increasing NaCl concentration [7,8], it is reasonable to suggest that the second phase transition of the ionic NIPA gels in aqueous NaCl solutions is the LCST of ionic NIPA gels, which undergo a similar shifting as their counterpart neutral gel.
To prove this argument, we chose a NIPA gel copolymerized with 8 mM SA as an example. The swelling ratio of ionic NIPA gels with 8 mM SA is measured as a function of temperature in various NaCl concentrations as shown in Figure 7.2 (a). The transition temperature is linearly proportional to the NaCl concentration as shown in Fig. 7.2 (b), where the transition temperatures $T_c$ are obtained by taking average variations of $\Delta (L/L_e) / \Delta T$ near the transition points. Analogous to that observed in a neutral NIPA gel in aqueous NaCl solution, [7,8] our results indicate that the concentrated NaCl solution can suppress LCST of ionic NIPA gels.

The transition concentration of sodium chloride, at which the second phase transition of ionic NIPA gels occurs at room temperature (about 22 °C), as a function of SA concentration in NIPA gels, is plotted in Figure 7.3. A good linear relationship can be obtained between the two, indicating that the critical NaCl concentration of the second transition increases with the increase of the ionic (SA) concentration of the NIPA gel. This is similar to that the higher critical temperature of the phase transition corresponds to higher SA concentration for the NIPA gel in pure water [15]. The critical NaCl concentration of the neutral NIPA gel is the lowest corresponding to the same temperature.

It is interesting to compare the amplitudes of variation of the swelling ratio of ionic NIPA gels at two transitions. Figure 7.4 shows the differences of the swelling ratios $\Delta L/L_e$ of ionic NIPA gels at two transitions as a function of SA concentration, where $\Delta L=L_a-L_e$. $L_a$ and $L_e$ are the lengths of the gel samples before and after the transition, respectively. It is clear that the amplitude of the swelling ratio increases with the increase of SA concentration at the first transition, in agreement with that obtained in NIPA gels copolymerized...
Fig. 7.2 (a) Swelling behavior for 8 mM SA ionic NIPA gel as a function of temperature in aqueous salt solutions with various NaCl concentration; (b) Effect of sodium chloride concentration on the critical temperature at which the 8 mM SA ionic NIPA gel exhibits a phase transition. The solid line is the best least-square fit to the data.
Fig. 7.3 The critical NaCl concentration of NIPA/SA copolymer gels in aqueous salt solutions, as a function of SA concentration in the NIPA gels at room temperature (about 22 °C). The solid line is the best least-square fit to the data.

Fig. 7.4 Comparison of the amplitudes of variation of the swelling ratio $\Delta L/L_e$ between the phase transitions in diluted NaCl (~ 0.1 M) and in higher NaCl concentration solutions (greater than 0.8 M) for ionic NIPA gels at 22 °C.
with methacryldopopyltrimethylammonium chloride (MAPTAC). [9] On the other hand, the amplitude of variation of the swelling ratio decreases at the second transition as the SA concentration increases.

7.3.2 Shear Modulus

Shear modulus plays an important role in determination of gel properties. In equilibrium state, the shear modulus $G_e$ and the swelling ratio $W_e/W_d$ ($W_e$ is the weight of the gel in water at room temperature and $W_d$ is the weight of the dry gel) of the NIPA gels with various SA concentration in water at room temperature are shown in Figure 7.5. From Fig. 7.5, one can see that the shear modulus $G_e$ decreases with the increase of the SA concentration initially, and then become flat. On the other hand, $W_e/W_d$ increases monotonically when the SA concentration increases.

![Graph showing shear modulus and swelling ratio vs SA concentration](image)

Fig. 7.5 In equilibrium state, the swelling ratio $W_e/W_d$ and the shear modulus $G_e$ of the NIPA gels in water at 22 °C as function of SA concentration.
Figure 7.6 shows the effect of sodium chloride concentration in aqueous salt solutions on the reduced shear modulus $G/G_e$ of the neutral NIPA and ionic NIPA gels at swelling equilibrium. For clarity, the data have been shifted vertically to different values as specified in the figure caption. The shear modulus as a function of NaCl concentration in diluted sodium chloride solution (NaCl concentration less than 0.1 M) is shown in Fig. 7.6 (a), and in aqueous salt solutions with higher NaCl concentration (until 3.0 M) is shown in Fig. 7.6 (b).

From Fig. 7.6 (a), one can see that the shear modulus of the ionic NIPA gels increases to a larger value when NaCl (about 0.1 M) induces the first phase transition. The increasing amplitude increases as the ionic (SA) concentration increases in the NIPA gel. It is noted that the shear modulus of the neutral NIPA gel almost keeps the same value because of no phase transition on it.

Figure 7.6 (b) shows that the shear modulus increases sharply for all NIPA gel samples including the neutral NIPA gel and ionic NIPA gel at the second transition. After the second phase transition, the shear modulus of all gels continuously increases with the increase of NaCl concentration. This may be due to the "salting out effect" and the glass phase transition.

Figure 7.7 shows the comparison of the variation of the reduced shear modulus of NIPA gels as a function of ionic concentration at the first and the second transitions. At the second transition, the variation of reduced shear modulus $\Delta G/G_e$ has no significantly change with increasing ionic concentration for the ionic NIPA gels. On the other hand, the $\Delta G/G_e$ values increase monotonically at the first transition as the SA concentration
Fig. 7.6 The effect of NaCl concentration on the shear modulus of the NIPA/SA copolymer gels with various SA concentrations in the gels at 22°C. The solid lines are a guide to the eye.

For clarity, the data have been shifted by constant multi-fication factors which are indicated by the number in parentheses. (a) NaCl concentration from $10^{-7}$ to $10^{-1}$ M, neutral (2), 4 mM SA (4), 8 mM SA (6), 16 mM SA (8), 35 mM SA (12); (b) NaCl concentration from 0 to 3.0 M, neutral (1), 4 mM SA (2), 8 mM SA (4), 16 mM SA (8), 35 mM SA (16).
increases in NIPA gels. This suggests that Donnan exclusion affects the shear modulus more in NIPA gels with higher ionic concentration than that in lower ionic concentration. The influence of the volume shrinking at the second phase transition to the elasticity of the gels is almost independent of the SA concentration.

It is noted that the shear modulus of the neutral NIPA gel at the phase transition increases about 2.5 times in 1.0 M NaCl aqueous solution than that in pure water at room temperature. This result is in good agreement with Hirotsu's observation that shear modulus increases also about 2.5 times near the critical temperature [16].

From Fig. 7.7, it is obvious that the effect of the second transition to the shear modulus is greater than that of the first transition for all gel samples. This may be qualitatively explained by Flory's theory. The shear modulus of the gel can be expressed as [16],

$$G = \frac{N_c}{2V_0}k_BT(\phi/\phi_0)^{1/2}$$  \hspace{1cm} (7.2)

where $N_c$ is the number of polymer chains, $V_0$ the volume of gel at the time of gelation in which the polymer chains obey Gaussian distribution, $k_B$ the Boltzmann constant, $T$ the absolute temperature, $\phi$ and $\phi_0$ the polymer concentration (volume fraction) corresponding to the value at time of measurement and gelation, respectively. Recently, we have found that when the polymer concentration is higher than about 0.3 g/cm$^3$, the shear modulus will deviate from equation 7.2. A possible cause is that the interaction between dense domains become stronger in high polymer concentration range. From phenomenological elasticity theory, by adding a compressional energy arising from the dense domain-domain repulsive interaction to the Flory theory of gels, the shear modulus
can be expressed as [17],

$$G = G_e \left( \frac{\phi_e}{\phi} \right)^{m_1} \cdot A \left( \frac{\phi_e}{\phi} \right)^{m_2}$$  \hspace{1cm} (7.3)

where $G_e$ and $\phi_e$ is the shear modulus and the polymer concentration of the gel fully swollen in equilibrium state in water at room temperature, respectively. $A$ is the structure constant of the gel and generally in $10^{-3}$ order, $m_1$ is 1/3, and $m_2$ is from 1 to 2.5 dependent on the gel structure. The first term is a classic elasticity and dominant in lower polymer concentration. The second term is negligible in low polymer concentration and becomes significant in high polymer concentration. Since the second transition takes place in higher

![Graph showing comparison of the amplitudes of variation of the reduced shear modulus $\Delta G/G_e$ between the phase transitions in diluted and higher concentrated NaCl aqueous salt solutions, for NIPA/SA copolymer gels with various SA concentrations at 22 °C.](image)

Fig. 7.7 Comparison of the amplitudes of variation of the reduced shear modulus $\Delta G/G_e$ between the phase transitions in diluted and higher concentrated NaCl aqueous salt solutions, for NIPA/SA copolymer gels with various SA concentrations at 22 °C.
polymer concentration than the first transition, the second term in Eq. (7.3) can not be neglected. As a result, the magnitude of variation of the shear modulus at the second transition should be greater than that of the first one. This is in good agreement with our experimental result as shown in Fig. 7.7.

7.3.3 Turbidity Measurement

In order to compare the influence of two phase transitions to the transparency of the NIP A gels to visible light, we measured the turbidity of NIP A gels in salt solutions with various NaCl concentration. The transmitted light intensity $I_t$ and the incident light intensity $I_0$ are related by the sample turbidity $\alpha$ and thickness $L$ [18],

$$I_t = I_0 \alpha^{\frac{-\alpha}{L}} \quad (7.4)$$

Therefore, the turbidity of the gels can be obtained from the ratio of the transmitted light intensity to the incident light intensity, $\alpha = -\frac{1}{L} \ln\left(\frac{I_t}{I_0}\right)$. Figure 7.8 (a) shows the turbidity $\alpha$ of the gel samples at wavelength 555 nm as a function of ionic concentration (SA) at various NaCl concentrations. It is clear that the values of $\alpha$ are very small (less than 0.5 cm$^{-1}$) and almost independent to SA concentration when the NIP A gels are in pure water or diluted NaCl solutions (NaCl concentration is less than 0.3 M). At 1.0 M NaCl solution, the neutral and 4 mM NaAc NIPA gels become opaque and the turbidity increase drastically, and the turbidity of the other ionic NIPA gels also increases. In our experiments, when turbidity $\alpha$ reaches about 4 cm$^{-1}$ the NIPA gels is defined in opaque state. The corresponding NaCl concentrations at which the turbidity of the NIPA gels reaches 4 cm$^{-1}$ is plotted as a function of ionic (SA) concentration in gels as shown in
Fig. 7.8 (a) The turbidity of NIPA gels in water and in aqueous salt solutions as a function of SA concentration in the gels at 22 °C; (b) The critical NaCl concentration, at which the NIPA gels become opaque, as a function of SA concentration in the gels. The solid line is the best least-square fit to the data.
Figure 7.8 (b). From Fig. 7.8 (b), one can see the opaque NaCl concentration increases with the increase of the ionic concentration of gels. The solid line is the best least-square fit to the data. The fitted result shows that the relationship between the critical NaCl concentration and SA concentration is closed to linear. All critical NaCl concentrations are higher than 1.0 M. It is interesting to note that only the second phase transition can obviously affect the turbidity of the NIPA gels. Turbidity is a good parameter to describe the spinodal decomposition of the NIPA gels. The high turbidity value means that the dense region and dilute region is separated, and a stable foam like structure is formed in gels [18].

7.4 Conclusion

The experimental results show there are two volume phase transitions in ionic NIPA (NIPA/SA copolymerized) gels induced by sodium chloride in aqueous solution at room temperature. One is in diluted NaCl solutions (~ 0.1 M) and can be explained by Donnan-equilibrium argument; the other is in higher NaCl solutions (greater than 0.8 M) and the cause is not clear now. One possible explanation of the second transition is that the LCST of ionic NIPA gels is shifted to lower temperature by the action of higher sodium chloride concentration. The shrinking magnitude increases with the increase of the ionic concentration, at the first transition, and decreases as the ionic concentration increases at the second transition for the NIPA gels. The shear modulus of the ionic NIPA gels jump to higher values at both phase transitions. The amplitude of variation of the shear modulus at the second transition is larger than that at the first one. The phase transition induced by Donnan effect in diluted NaCl solution does not affect the turbidity
of the ionic NIPA gel, but the second phase transition in aqueous salt solution with higher NaCl concentration can make the all NIPA gels become opaque. This phase transition behavior of neutral and ionic NIPA gels may have a wide range of potential applications such as chloride ion-sensitive biosensors and actuators.
CHAPTER 7 REFERENCES


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SYNTHESIS AND STUDY OF PAAM/NIPA INTERPENETRATING POLYMER NETWORK GELS

8.1 Introduction

Many polymer gels undergo volume change under an external stimulus such as temperature, solvent, pH, electric fields and laser light [1]. Such environmental sensitive gels have been explored for switches [2], chemical valves and actuators [3], and drug-delivery devices [4-5]. It is found that new [6-7] or drastically improved [8-10] physical properties of gels can be obtained by incorporating two or more polymer components into a single gel. For examples, the mechanical strength of membranes is increased by incorporating poly(vinyl alcohol) into either temperature sensitive N-isopropylacrylamide gel [8] or pH sensitive poly(acrylic acid) gel [9]. By controlling cooperative hydrogen bonding interactions between the molecules, the volume of the interpenetrating poly(acrylamide) and poly(acrylic acid) gel shrinks as the temperature decreases [6], which is opposite of the homo-NIPA gel. Recently, gel volume phase transitions that can be triggered with several different stimuli has attracted a growing attention [11-13]. The gels which are sensitive to more than one variable, in particularly temperature and pH, have been investigated [11-13] in drug delivery systems.

Previous experiments [14] on IPNs of poly(acrylamide) PAAM and poly(acrylic
acid) PAAc gels showed that the IPN exhibited rapid swelling changes, in contrast to random gels composed of the same monomer composition, which only exhibited gradual swelling changes near the transition temperature. Here, we report the synthesis and study of poly (acrylamide) and N-isopropylacrylamide interpenetrating polymer network gels, or PAAM-NIPA IPN. PAAM and NIPA polymers show good compatibility in aqueous solution [15]. Their hydrogels possess contractive swelling behavior [1], i.e., PAAM gel undergoes the volume phase transition in acetone/water mixture, while NIPA gel shrinks and eventually collapses with the increase of temperature. By interpenetrating PAAM gel with NIPA network, it is expected to form IPN gel whose volume change can be triggered by both acetone concentration and temperature. The swelling properties of the IPN system will be compared with that of its network components. From the application point of view, the elastic property of gels is one of the most important factors. This property can be modified by interpenetrating two kinds of networks [16]. Specifically, the shear modulus of the IPN gel will be measured as a function of network concentration and will be used to compared with that of homo-NIPA and homo-PAAM gels.

8.2 Experiment

The IPN samples were prepared in sequential steps. First, NIPA gel was made by same method as description in chapter 2. The NIPA gel was then dried slowly in sealed glass container so that they uniformly shrank. Second, the dried NIPA network was immersed into a pre-gel solution of the second polymer--PAAM. The PAAM solution was made using NIPA recipe with 7.8 g of N-isopropylacrylamide monomers replaced by 5.0 g of polyacrylamide monomers. The NIPA network swollen in the pre-gelation solution of NIPA gel for about 3 days. The polymerization of PAAM was then initiated
by immersing the sample in a T=70 °C thermal bath. The gelation was completed in about 4 hours, forming interpenetrating networks of PAAM and NIPA. The IPN sample exhibited milky color and was harder than either NIPA and PAAM gels. The samples showed isotropic swelling behavior in the temperature range used here (22 °C-35 °C).

To measure the temperature dependent swelling curve, the temperature of the samples was controlled by a circulation water bath (Brinkmam Lauda Super RM-6) and was stable to 0.1 °C over 24 hours. The shear modulus of samples was measured using the force-deformation method. The gel sample was compressed between two flat glass plates. A digital force meter was used to measure the force applied to the sample. The range of force applied was between 0 to 30 g. The deformation range was from 10% to 30%. The weight loss (<1%) was insignificant during the measurement. The experimental data were analyzed, under the condition of constant volume, according to the Mooney-Rivlin equation [17]:

\[
\frac{F}{S} = G(\Lambda - \Lambda^2)
\]

(8.1)

where F is the uniaxial force applied, S is the sample cross-section area before the deformation, \( \Lambda (=h/h_0) \) is ratio of the thickness before and after the deformation, and G is shear modulus. In the measurement, F and \( \Lambda \) were recorded during both force increase and force decrease process. The average value of G obtained from force-up and force-down curves was used. The accuracy of the digital force gauge used is ±0.2%. Considering the errors introduced in the measurement of sample size, the total accuracy of the measurement was estimated to be about ±3%.
8.3 Results and discussion

8.3.1 The volume phase transition in the PAAM-NIPA IPN gel

Figure 8.1 shows the shrinking ratio of final to initial diameters as a function of acetone concentration for the NIPA-PAAM IPN (square), NIPA (circle), and PAAM (triangle) gels. The PAAM gel collapses when the acetone concentration is above about 30%. The NIPA gel first shrinks upon increase of the acetone concentration increases. As the acetone concentration increases further, the NIPA gel swells. Such a re-entry-type transition has been previously observed for the NIPA gel in alcohol-water mixtures [18]. The shrinking behavior of NIPA-PAAM IPN gel is between the behavior of NIPA and PAAM gels.

The comparison of the shrinking ratio between the IPN and its components—the PAAM and the NIPA gels as a function of temperature is shown in Figure 8.2. The NIPA gel is sensitive to the temperature, in contrast to the PAAM gel. The resulting IPN gel exhibits a temperature induced phase transition, but its volume change is smaller than that of the NIPA gel. The transition temperature for the IPN gel is slightly higher than that for the NIPA gel. PAAM-NIPA copolymer solutions are also exhibits a higher lower critical solution temperature than that of the NIPA polymer solution [15]. The shift of the transition temperature in our case may be due to the internal constraint toward the NIPA network imposed by the PAAM network. It is known that the external constraint can causes a positive osmotic pressure and pushes the transition temperature toward a higher value [19].
Figure 8.1. The shrinking ratio of the PAAM-NIPA IPN (square), PAAM (triangle) and NIPA (circle) gels as a function of acetone concentration at room temperature. The initial thicknesses of samples were equal 2.0 mm.

Figure 8.2. The shrinking ratio of the PAAM-NIPA IPN (square), PAAM (triangle) and NIPA (circle) gels as a function of temperature. The initial thicknesses of samples were equal 2.0 mm.
Figure 8.3 shows the shrinking curves for the NIPA-PAAM IPN, PAAM, and NIPA gels in NaCl solution at 22 °C. The NIPA gel is sensitive to the salt concentration while the PAAM gel is not. The behavior of the IPN gel is again a summation of the properties of its components.

Figure 8.3. The shrinking ratio of the PAAM-NIAP IPN (square), PAAM (triangle) and NIPA (circle) gels as a function of NaCl concentration. The measurements were performed at 22 °C.

Figure 8.4 (a) shows the time dependent shrinking for the IPN and the NIPA gels in response to the sudden jump from water to 1.2 M NaCl solution at 22 °C. The corresponding swelling process is shown in Fig. 8.4 (b). The dimensions of the IPN and the NIPA gels are 13.05x1.57x1.35 mm³, and 14.50x1.43x1.25 mm³, respectively. The kinetic behavior of both IPN and the NIPA gels are very similar. It is noted that the
swelling process is faster than the shrinking process for both IPN and NIPA gels. This agrees with previous results, which were explained by considering the existence of a water diffusion barrier during the shrinking [11].

It is apparent that the PAAM-NIPA IPN has preserved the essential properties of individual components. The IPN has the unique property that it can undergo the volume phase transition triggered by multiple external stimuli including temperature, acetone, and salt concentration. Therefore, the IPN gel has a potential for device applications which simultaneously require temperature, acetone, and salt concentration sensitive.

5.3.2 Shear modulus of the PAAM-NIPA IPN gel

For many applications, the elastic properties of gels are some of the most important factors. Here, we particularly pay attention to shear modulus of the IPN gels. Theoretical analysis of the elastic modulus of a sequential IPN with respect to elastic modulus of its components has been developed previously [16, 21-22]. Following this model, before interpenetrating the shear modulus of a single network I can be written as [16]

\[ G_1^o = v_1 V_1 R T; \quad G_2^o = v_2 V_2 R T \] (8.2)

where \( v_1 \) and \( v_2 \) represents the number of moles of network I and II chains per cm\(^3\), and \( v_1 \) and \( v_2 \) are the volume fractions of the two polymers, respectively. The superscript \( o \) represents the equilibrium state. The quantities \( R \) and \( T \) stand for the gas constant and the absolute temperature, respectively. By interpenetrating process, the network I is swollen with the network II. This perturbation via network swelling changes the contribution to
Figure 8.4. (a) The shrinking kinetics of the PAAM-NIPA (square) gel and NIPA (circle) gel in response to the sudden jump from a pure water to 1.2 M NaCl solution at 22 °C. (b) The swelling kinetics of the PAAM-NIPA IPN (square) gel and NIPA (circle) gel in response to the sudden jump from 1.2 M NaCl solution to a pure water at 22 °C. Solid lines are the best fits with the exponential form.
the shear modulus. Specifically, the shear modulus of the network I is thus given by

\[ G_1 = v_{1}^{\frac{1}{3}} v_1 RT \]  

(8.3)

Assuming mutual network dilution and co-continuity, with no added internetwork physical crosslinks, the shear modulus, \( G \), of a sequential IPN can thus be written as [16]

\[ G = (v_{1}^{\frac{1}{3}} v_1 + v_2 v_2) RT \]  

(8.4)

Or,

\[ G = v_{1}^{\frac{2}{3}} G_1^0 + G_2^0 \]  

(8.5)

Since the volume fraction of the first network, \( v_1 \), is smaller than 1, \( G \) is expected larger than the simple summation of shear moduli of two individual networks.

Two series samples were prepared for shear modulus experiment. One series used a standard recipe, i.e., monomer concentrations for NIPA, PAAM, and NIPA-PAAM IPN, are 7.8 g, 5 g, and 7.8+5 g, respectively. Another series used a lower monomer concentrations for NIPA (5 g), PAAM (3 g), and NIPA (5 g)-PAAM (3 g) IPN gels. The shear modulus for different samples at room temperature are listed in Table 8.1 for comparison. The shear modulus of the IPN gel is higher than simple summation of those of individual PAAM and NIPA network components for both standard (left column) and the lower monomer concentration series samples (right column). Considering that the NIPA (network I) is swollen with PAAM (network II), we have used Eq. (8.5) to calculate the shear modulus of the IPN gel. Here, the volume fraction \( v_1 \) are 0.61 and
TABLE 8.1. Comparison of equilibrium shear modulus for PAAM, NIPA and PAAM-NIPA IPN gels at T=24 °C. The values in bracket indicate monomer mass in 100 ml water.

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<th>G (10^4 dyn/cm²)</th>
<th>Samples</th>
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<td>NIPA(5g)</td>
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</tbody>
</table>

0.63 for the IPN gels with standard and lower monomer concentration, respectively. The $G^0_1$ and $G^0_1$ are the equilibrium shear modulus values of homo-PAAM and homo-NIPA gels, respectively. The theoretical results are in good agreement in experimental values. The improvement of shear modulus of IPN gels may be due to the entanglement which increases the effective crosslinking density.

Figure 8.5 shows the polymer concentration dependence of the shear modulus of IPN, PAAM, and NIPA gels with standard compositions, i.e., monomer concentrations for NIPA, PAAM, and NIPA-PAAM IPN, are 7.8g, 5g, and 7.8g (NIPA)+5 g (PAAM), respectively. When the network concentration is less than about 0.2 g/cm³, the shear modulus as a function as network concentration for IPN, PAAM and NIPA can all be described using the classical elasticity theory with the scaling exponent equal to about 0.33
For the network concentration ranging from about 0.2 to about 0.6 g/cm$^3$, the curves deviated from the classical curve. The deviation of concentration dependence of gel shear modulus suggests that at high concentration, a different mechanism dominates the contribution to shear modulus. One likely mechanism is the compressional energy associated with the structural heterogeneity of the network. By adding compressional energy arising from the dense domain-domain repulsive interaction to standard Flory free energy of polymer network, the shear modulus of a highly concentrated gel may be expressed as

$$G = G_e [ (\frac{\phi}{\phi_0})^{m_1} + A (\frac{\phi}{\phi_0})^{m_2} ]$$

(8.6)

where $\phi$ and $\phi_0$ are polymer network concentrations and equilibrium one, respectively. $m_1 (=1/3)$ and $m_2$ are scaling exponents. $A$ measures the relative contribution between the two terms. The first term is a classic elasticity which is dominant in the low network concentration range. The second term is the contribution from inhomogeneity and becomes significant in high network concentration range. Table 8.2 lists the fitting parameters obtained from the data. The scaling exponent of $m_2$ for the IPN gel is smaller than that for the PAAM an NIPA systems. For the IPN gel studied here, the inhomogeneity may be caused mainly by the phase separation. By virtue of the unique method of interpenetration process, most of the IPNs exhibit microphase separation or partial miscibility [25].

8.4 Conclusion

The NIPA-PAAM interpenetrating polymer network gel has been successfully
Figure 8.5. The shear modulus of the PAAM-NIPA (square), NIPA (circle) and PAAM (triangle) gels as a function of network concentration. The solid lines are the best fit to data using Eq. (8.6).

TABLE 8.2. Fitting parameters obtained by fitting the data to Eq. (8.6) with $m_1$ fixed at 1/3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>A/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAAM(5g)</td>
<td>0.33</td>
<td>2.20</td>
<td>0.52</td>
</tr>
<tr>
<td>NIPA(7.8)</td>
<td>0.33</td>
<td>2.56</td>
<td>0.19</td>
</tr>
<tr>
<td>PAAM(5g)-NIPA(7.8) IPN</td>
<td>0.33</td>
<td>1.40</td>
<td>0.24</td>
</tr>
</tbody>
</table>
synthesized. The IPN samples have preserved the essential properties of individual components and undergo the volume phase transition in response to multiple external stimuli including acetone concentration, temperature and salt solution. It is found that the shear modulus of IPNs is higher than simple summation of shear moduli of its two individual network components. The entanglements formed by interpenetration are assumed to be responsible for the increased strength of the IPN samples. This effect has been explained in terms of a thermal dynamic model. Shear modulus of the IPN, PAAM and NIPA gels has been measured with the network concentration ranging from 0.02 to 1.0 g/cm$^3$. In the low concentration region, the shear modulus is a scaling function of network concentration with the exponent equal to 1/3, which is expected by classical rubber elasticity theory. As the concentration increases, the behavior of shear modulus deviates from the classical theory significantly. A two-phase inhomogeneity network structure model was proposed to explain the results. For the IPN gel studied here, the inhomogeneity may be caused mainly by the phase separation.
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CHAPTER 9

CONCLUSION

This dissertation involves the study of the synthesis and physical properties of polymer gels including: infrared induced phase transition and bending effect in the NIPA gel; the visible light transmission in NIPA gel controlled by CO$_2$ laser; synthesis of modulated gels and their application; the quantitative analysis of bending of bi-gels; non-classical elasticity of the PAAM gel; the behavior of ionic NIPA gels in concentrated NaCl solution; the synthesis of multi-functional gels by interpenetrating technique. The major conclusion can be summarized into seven points:

1. A volume phase transition of NIPA gels can be induced by a CO$_2$ laser. Under the influence of a CO$_2$ laser, the gel not only shrinks, but also bends toward the laser beam. The degree of bending depends on CO$_2$ laser power and on the sample cell temperature. After blocking the CO$_2$ laser, the gel restores its original shape with a relaxation time about 8.5 min. The bending phenomenon can be explained in terms of a thermally-induced volume phase transition in gels. The bending of a gel in this fashion may have application in photon-response devices, which can convert laser energy into mechanical energy.

2. The transmission of He-Ne light through a gel sample can be controlled by a CO$_2$ laser. The switching time from 90% to 10% relative transmission is about 15 s and from 10% to
90% is about 0.5 s. The sample cell temperature during the transmission cycles remains almost unchanged. The CO₂ laser acts like a strong local heating source, which makes the gel surfaces decompose into two different concentration domains: one is swollen (dilute) and the other is in a condensed state. The visible light is strongly scattered by such domains when their sizes are comparable with the size of the optical wavelength. Since the switch time from the transparent to opaque is very fast, such effects may lead to the development of fast-response gel devices.

3. A new class of environmentally responsive materials based on spatial modulation of the chemical nature of gels has been proposed and demonstrated. The modulation is achieved by interpenetrating only part of one gel network with another gel network. Therefore, these gels have an internally heterogeneous, or modulated, structure. The difference of the thermal coefficients between two gels can be much larger than that between two metals. For example, the difference of expansion coefficients for a typical bimetallic strip of brass and steel is about 7x10⁻⁶ °C⁻¹. However, for the PAAM-NIPA bi-gel, such difference can be as high as 0.5 °C⁻¹. The bi-gel strip bends almost to a circle when its temperature or solvent is changed. The shape memory gel changes its shape from a straight line to a pentagon, to a quadrangle at different temperatures. The gel hand in water can grasp or release an object simply by adjusting the temperature.

4. The bending of a bi-gel strip (IPN-PAAM) can be induced by temperature, acetone and water mixture, and salt solution. The maximum strain values in the IPN side and in the PAAM side are about 0.25 and 0.60 respectively. At 37 °C the restoring relaxation time of a 3 mm bi-gel is 34.3±2.5 minutes in pure water. In 1 M NaCl solution the restoring
relaxation time of a 2 mm bi-gel linearly increases with the increase of temperature within 20–34 °C ranges. At about 22 °C, the restoring relaxation time of a 2 mm bi-gel shows no obvious change from salt solution to pure water. The collective diffusion coefficients of ionic IPN gels in pure water at 37 °C and 39 °C are about $1.1 \times 10^{-7}$ cm$^2$/s and $0.50 \times 10^{-7}$ cm$^2$/s, respectively. They are the same order as ionic NIPA in water. The bending effect of a bi-gel, may have applications in biological engineering or the biomedical field.

5. Measurement of the shear modulus of PAAM gel has been performed over a very broad network concentration range. It has revealed that the classic term with an exponent of 1/3 can be applied only to the low concentration region, i.e., below 0.25 g/cm$^3$, in agreement with available experimental and theoretical results. As the network concentration increases beyond this region, a new term based on a two phase inhomogeneity model starts to dominate. This inhomogeneity term can be characterized by an exponent $m_2$ with its value between 2.0 to 2.5. The comparison between the theory and experiments has been made for six series of samples which have different crosslink concentrations ranging from 0.61 to 4.91 mole percent. New experiments with known built-in inhomogeneity would be interesting to further test the model proposed here.

6. The experimental results show there are two volume phase transitions in ionic NIPA (NIPA/SA copolymerized) gels induced by NaCl in aqueous solution at room temperature. One is in diluted NaCl solutions (less than 0.1 M) and can be explained by Donnan-equilibrium argument; the other is in higher NaCl solutions (greater than 0.8 M) and can explained by the suppression of the LCST of the ionic NIPA gels by the action of concentrated NaCl solutions. The shrinking magnitude increases with the increase of the
ionic concentration at the first transition, and decreases as the ionic concentration increases at the second transition for the NIPA gels. The shear modulus of the ionic NIPA gels increases at both phase transitions. The amplitudes of variation of the shear modulus at the second transition are larger than that at the first one. The second phase transition can make all NIPA gels become opaque. This phase transition behavior of neutral and ionic NIPA gels may have a wide range of potential applications such as chloride ion-sensitive biosensors and actuators.

7. The double functional gel, i.e., NIPA-PAAM interpenetrating polymer network gel has been successfully synthesized. The IPN samples have preserved the essential properties of individual components and undergo the volume phase transition in response to multiple external stimuli including acetone concentration, temperature and salt solution. It is found that the shear modulus of IPNs is higher than simple summation of shear moduli of its two individual network components. This effect has been explained in terms of a thermal dynamic model. Shear modulus of the IPN, PAAM and NIPA gels has been measured with the network concentration ranging from 0.02 to 1.0 g/cm$^3$. The results can be explained by the two-phase inhomogeneity network structure model described in chapter 6. For the IPN gel studied here, the inhomogeneity may be caused mainly by the phase separation.

The study in this dissertation provides a better understanding of polymer gels and opens the door for further improving the properties of the gels. This study also shows that the research of polymer gels is an exciting area and has bright future for wide applications in various fields.
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