SYNTHESIS AND CHARACTERIZATION OF CRYSTALLINE ASSEMBLY OF
POLY(N-ISOPROPYLACRYLAMIDE)-CO-ACRYLIC ACID
NANOPARTICLES
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Dissertation Prepared for the Degree of
DOCTOR OF PHILOSOPHY

UNIVERSITY OF NORTH TEXAS
December 2004

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Zhou, Bo, Synthesis and characterization of crystalline assembly of poly
Nisopropylacrylamide)-co-acrylic acid nanoparticles. Doctor of Philosophy (Materials
Science and Engineering), December 2004, 95 pp., 1 table, 29 illustrations, references,
99 titles.

In this study, crystalline poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAm-co-
AAc) nanoparticle network in organic solvents was obtained by self assembling
precursor particles in acetone/epichlorohydrin mixture at room temperature followed by
inter-sphere crosslinking at ~98 °C. The crystals thus formed can endure solvent
exchanges or large distortions under a temporary compressing force with the
reoccurrence of crystalline structures. In acetone, the crystals were stable, independent
of temperature, while in water crystals could change their colors upon heating or
changing pH values. By passing a focused white light beam through the crystals,
different colors were displayed at different observation angles, indicating typical Bragg
diffraction. Shear moduli of the gel nanoparticle crystals were measured in the linear
stress-yield ranges for the same gel crystals in both acetone and water. Syntheses of
particles of different sizes and the relationship between particle size and the color of the
gel nanoparticle networks at a constant solid content were also presented.

Temperature- and pH- sensitive crystalline PNIPAm-co-AAc hydrogel was
prepared using osmosis crosslinking method. Not only the typical Bragg diffraction
phenomenon was observed for the hydrogel but also apparent temperature- and pH-
sensitive properties were performed.

The phase behavior of PNIPAm nanoparticles dispersed in water was also
investigated using a thermodynamic perturbation theory combined with lightscattering
and spectrometer measurements. It was shown how the volume transition of PNIPAM particles affected the interaction potential and determined a novel phase diagram that had not been observed in conventional colloids. Because both particle size and attractive potential depended on temperature, PNIPAM aqueous dispersion exhibited phase transitions at a fixed particle number density by either increasing or decreasing temperature.

The phase transition of PNIPAm-co-AAc colloids was also studied. The results from the comparison between pure PNIPAm and charged PNIPAm colloids showed that the introducing of carboxyl (-COOH) group not only contributed to the synthesis of three-dimensional nanoparticle network but also effectively increased the crystallization temperature and concentration range. The phase transitions at both low and high temperatures were observed from the turbidity change by using UV-Vis spectrometer.

Centrifugal vibration method was used to make crystalline PNIPAm-co-AAc dispersion at high concentration (8%). The turbidity test proved the formation of iridescent pattern.
ACKNOWLEDGMENTS

I sincerely thank my major advisor Dr. Zhibing Hu for his enthusiastic guidance and friendly encouragement. I am not only impressed and stimulated by his hard-working spirit during the whole work but also benefited a great deal from his many unique ideas. Additionally, he is such a nice person that working with him is really a pleasure.

I also give thanks for the help of Prof. Jianzhong Wu (University of California), Dr. Jun Gao (Postdoctoral, Department of Physics), Gang Huang (Ph.D., group member), Tong Cai (Ph.D., group member), Jun Zhou (Ph.D., group member), Shijun Tang (Ph.D., group member) and Jie Lin (Ph.D., Department of Physics). Without their warm-hearted favor I could not have finished my projects so well.

I also give my sincere thanks to all the committee members who give my dissertation a careful reading. I appreciate their suggestions very much.

Last but not least, I want to thank my wife, Yinghua Wang. Her encouragement and care contributed a lot from the beginning to the finishing of this dissertation.
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CHAPTER 1

BACKGROUND INTRODUCTION

1.1. Polymer Gels

A polymer gel is a form of matter intermediate between a solid and a liquid, which is created by polymer chains that are cross-linked either chemically or physically. It is a tangled network immersed in a liquid medium. The properties of the polymer gel depend strongly on the interaction between these two components. The liquid prevents the polymer network from collapsing into a compact mass; the network prevents the liquid from flowing away. Depending on chemical composition and other factors, gels vary in consistency from viscous fluids to fairly rigid solids but typically they are soft and resilient or, in a word, jellylike [1].

Under certain conditions, such as by altering the temperature, the gel composition, the pH [2], the pressure on the gel [3], the electric signal [4], the light [5] or the ionic strength [6] of the solvent, drastic changes can be brought out to the gel, the gel will shrink or swell by a factor of as much as several hundred. These stimuli-responsive aspects make polymer gel become a unique field in materials science nowadays. The varied responses of the gel to changes in external conditions can be understood in the context of phase transitions and
critical phenomena. Just as many substances can exist as a liquid or as a vapor under different circumstances, so can a gel sometimes have two phases, which are distinguished by different configurations of the polymer network. The discontinuous change in the volume and other properties of the gel constitutes an abrupt transition between the phases, analogous to the boiling of a liquid. At higher temperatures or under various other conditions (pH, magnetic field, light, electric field etc.), the two phases of the gel can no longer be distinguished; in a similar way the distinction between liquid and vapor disappears at high temperature and pressure. The physical mechanisms underlying these changes of state are peculiar to the structure of a gel and can be understood only through an analysis of the forces acting on the polymer network.

1.2. Polymer Hydrogels

As the most important branch in polymer gels, stimuli-responsive polymer hydrogels are widely studied due to its special liquid medium-water. Stimuli-responsive hydrogels are fascinating materials with potential applications in biomedicine and the creation of "intelligent" materials system, for example, as media in drug delivery [7-9], separation processes [10]. Especially hydrogels as chemical sensors have obtained more and more attention in the recent decades. Several terms have been coined for hydrogels, such as 'intelligent gels' or 'smart hydrogels' [11]. The smartness of any material is the key to its ability to receive, transmit or process a stimulus, and respond by producing a useful effect [12]. Once acted on, stimuli can result in changes in phases, shapes, optics,
mechanics, electric fields, surface energies, recognition, reaction rates and permeation rates. Hydrogels are ‘smart’ or ‘intelligent’ in the sense that they can perceive the prevailing stimuli and respond by exhibiting changes in their physical or chemical behavior like a live organ. Here, we should notice that the difference between the term ‘gel’ and ‘hydrogel’. As polymeric networks, both of them might be similar chemically, but they are physically distinct. Technically, gels are semi-solid systems comprising small amounts of solid, dispersed in relatively large amounts of liquid, yet possessing more solid-like than liquid-like character [13]. Hydrogels then are a cross-linked network of hydrophilic polymers. They possess the ability to absorb large amounts of water and swell, while maintaining their three-dimensional (3D) structures [14]. This definition differentiates hydrogels from gels, which are polymeric networks already swollen to equilibrium, and the further addition of fluids results only in dilution of the polymeric network. The feature central to the functioning of a hydrogel is its inherent cross-linking. Conventional gels can also develop small levels of cross-links as a result of a gain in energy under the influence of shear forces, but this is reversible because of the involvement of weak physical forces. So hydrogels can be described as a more rigid form of gel. The cross-link inside the hydrogels can be provided by covalent bonds, hydrogen bonding, van der Waals interactions or physical entanglements. Hydrogels have found many significant applications in many areas due to their special environmental-sensitive property. Tanaka Miyata studied antigen-responsive hydrogel [15]. They used reversible
binding between an antigen and an antibody as the crosslinking mechanism in the Semi-Interpenetrating network hydrogel. They suggest that this approach might permit drug delivery in response to a specific antigen. Also in recent years, with regard to the polymer film, a lot of work had been performed. Hoitz and Asher [16] studied the polymerized colloidal crystal hydrogel films as intelligent chemical sensing materials. They reported the preparation of a material that changes color in response to a chemical signal by means of a change in diffraction properties. Because of the excellent bio-compatibility of them, hydrogels have been studied more and more in medicine, biotechnology [17, 18] etc. fields.

Like talked above, according to the different environment stimuli, hydrogels can usually be classified as the following several categories:

1.2.1. Temperature-sensitive Hydrogels

Not like most polymers which increase their water-solubility as the temperature increases, polymers with lower critical solution temperature (LCST) decrease their water-solubility upon increasing the temperature. When the temperature increases above the LCST, Hydrogels made of LCST polymers shrink. This type of behavior is known as inverse (or negative) temperature-denpendence. This kind of hydrogels are made of polymer chains that either possess moderately hydrophobic groups or contain a mixture of hydrophilic and hydrophobic segments. At lower temperatures, hydrogen bonding between hydrophilic segments of the polymer chain and water molecules are dominates,
leading to enhanced dissolution in water. As the temperature increases, however, hydrophobic interactions among hydrophobic segments become strengthened, while hydrogen bonding becomes weaker. The net result is shrinking of the hydrogels due to inter-polymer chain association through hydrophobic interactions. In general, as the polymer chain contains more hydrophobic constituent, LCST becomes lower [19]. So the LCST can be changed by adjusting the ratio of hydrophilic and hydrophobic segment of the polymer. Poly(N-isopropylacrylamide) is a very popular example in this category.

1.2.2. pH-sensitive Hydrogels

All the pH-sensitive polymers contain pendant acidic (e.g. carboxylic and sulfonic acids) or basic (e.g. ammonium salts) groups that either accept or release protons in response to changes in environmental pH. Hydrogels made of crosslinked polyelectrolytes (polymers with a large number of ionizable groups) display big differences in swelling properties depending on the pH of the environment. The pendant acidic or basic groups on polyelectrolytes undergo ionization just like acidic or basic groups of monoacids or monobases. The presence of ionizable groups on polymer chains results in swelling of the hydrogels much beyond that can be achievable by nonelectrolyte polymer hydrogels. Since the swelling of polyelectrolyte hydrogels is mainly due to the electrostatic repulsion among charges present on the polymer chain, the extent of swelling is influenced by any condition that reduce electrostatic repulsion, such
as pH, ionic strength, and type of counterions [20]. Poly(acrylic acid) is a good example falling into this category.

1.2.3. Electric Signal-sensitive Hydrogels

Hydrogels sensitive to electric current are usually made of polyelectrolytes, as are pH-sensitive hydrogels. Electro-sensitive hydrogels undergo shrinking or swelling in the presence of an applied electric field. Sodium acrylic acid-co-acrylamide copolymer is a good example here [21].

1.2.4. Light-sensitive Hydrogels

This kind of hydrogels has big potential applications in developing optical switches, display units, and ophthalmic drug delivery devices. Since the light stimulus can be imposed instantly and delivered in specific amounts with high accuracy, light-sensitive hydrogels may possess special advantages over others. They can be divided into UV-sensitive and visible light-sensitive hydrogels. Unlike UV light, visible light is readily available, inexpensive, safe, clean and easily manipulated. Leuco derivative molecules are good examples for UV-sensitive hydrogels [22]. By introducing light-sensitive chromophore to some hydrogels, we can also get Visible light-sensitive hydrogels. [23]

1.2.5. Pressure-sensitive Hydrogels

The concept that hydrogel may undergo pressure-induced volume phase transition came from thermo-dynamic calculations based on uncharged hydrogel theory. According to the theory, hydrogels which are collapsed at low pressure
would expand at higher pressure. Experiments with poly(N-n-propylacrylamide) is one of the examples. The pressure sensitivity appeared to be a common characteristic of temperature-sensitive gels. It was concluded that the pressure sensitivity of the temperature-sensitive gels was due to an increase in their LCST value with pressure [24].

1.2.6. Other Stimuli-sensitive Hydrogels

There are also specific ion-sensitive hydrogels [25], specific antigen-responsive hydrogels [15], glucose-sensitive hydrogels [26] etc.

1.3. Poly (N-isopropylacrylamide)

PNIPAm as the most known temperature-sensitive microgel was first prepared by Philip Chibante, a high school summer student with aspirations to become a dentist, under the supervision of Dr. Robert Pelton [27]. The resulted microgel was a monodisperse, colloidal dispersion. The structure of PNIPAM was illustrated below:
As shown above, the PNIPAm has both hydrophilic –NH- group and hydrophobic –CH₃CHCH₃- group. At room temperature, its hydrophilic part will dominate the property. PNIPAm’s macromolecular transition from a hydrophilic to a hydrophobic structure occurs rather abruptly once above its LCST. Most importantly, PNIPAm’s LCST usually lies between 30°C and 38°C (the exact temperature will be a function of the detailed microstructure of the macromolecule). The existence of LCST that is close to body temperature makes PNIPAM a unique species whose growth over the past few years has become rather explosive especially in the biotech field.

1.4. Laser Light Scattering

The phenomenon of light scattering is encountered widely in everyday life. For example light scattering by particles in the atmosphere gives rise to the blue color of the sky and the spectacular colors that can sometimes be seen at sunrise and sunset. These are all examples of static light scattering since the time-averaged intensity of scattered light is observed.

In general, the interaction of light with matter can be used to obtain important information about the structure and dynamics of the matter. When light is shined on matter, it will be scattered. The scatter light can give us important information of molecular structure and motion in the matter. According to the semi-classical light scattering theory, when light impinges on matter, the electric field of light induces an oscillating polarization of electrons in the molecules, then the molecules serve as the secondary source of light and subsequently radiate
light. The frequency shifts, the angular distribution, the polarization and the intensity of light are determined by the size and shape of the material and also the interaction in the material. Thus from the light scattering characteristics of a given system it should be possible, with the aid of electrodynamics and theory of time dependent statistical mechanics, to obtain the information about the structure and molecular dynamics of the material.

![Fig.1.1 Laser Light Scattering Experimental Setup](image)

**Fig.1.1 Laser Light Scattering Experimental Setup**

Laser Light Scattering (LLS) methods (Fig.1.1) are widely used to characterize polymers or colloidal particles in dilute solutions (dispersions) with laser as incident light. It includes two categories: Static Light Scattering and Dynamic Light Scattering.
1.4.1. Static Light Scattering

This method was mainly used to give the information of the intramolecular properties of the molecular weight $M_w$ and root-mean-square z-average radius of gyration $<R^2_g>_z$, as well as the intermolecular property of the second virial coefficient $A_2$ which shows the affinity between polymers and water, and possibly higher order virial coefficients. In static light scattering experiments the time-averaged (or 'total') intensity of the scattered light is measured, and for solutions is related to the time-averaged mean-square excess polarizability which in turn is related to the time-averaged mean-square concentration fluctuation. The reduced integrated scattering intensity $KC/R_{vv}(q)$ is calculated from the absolute photon count which is recorded simultaneously with the measurement of the time-correlation functions (TCF). For a dilute solution, there exists the following relationship between $KC/R_{vv}(q)$ and the weight molecular weight ($M_w$) [28]:

$$
\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w} \left( 1 + \frac{1}{3} <R^2_g>_z q^2 \right) + 2 A_2 C
$$

$K$ is an optical constant, $K = (4\pi^2/N_A\lambda^4)\{n(dn/dC)\}^2$, it depends on the square of the refractive index increment ($dn/dC$) of the solute and the square of the refractive index ($n$) of the solvent, $\lambda$ is the wavelength of the incident light in vacuum, $C$ is the mass concentration of the solution, and $R_{vv}(q)$ is the Rayleigh ratio, $q$ is the modulus of the scattering vector ($q = (4\pi n/\lambda) \text{sin} (\theta/2)$, $\theta$ is the scattering angle)), $N_A$ is the Avogadro constant.
From the above equation, the relationship between $KC/R_\theta$ and $(\sin^2\theta/2 + KC)$ can be built by extrapolating both the concentration $C$ and the scattering angle $\theta$ to zero. The resulted graph is called Zimm-plot (Fig.1.2). The molecular weight, the second virial coefficient and the radius of gyration can be deducted from it.

![Diagram](image)

Fig.1.2 Measurement of the weight average molecular weight using Zimm-plot, $c$ is the concentration of polymer dispersion, $\theta$ is the scattering angle, $K$ is an optical constant, $R_\theta$ is the hydrodynamic radius of the polymer particles.

The reason that extrapolation of both concentration and scattering angle to zero is because there usually exist two non-ideal effects in polymer solutions: non-ideal solution effect and large particle size effect. Extrapolating the concentration to zero can remove the non-ideal solution effect; and extrapolating
the scattering angle to zero can remove the large particle size effect. We can also get the second virial coefficient ($A_2$) from the slope of concentration's extrapolation, while get the radius of gyration ($R_g$) from scattering angle’s extrapolation.

1.4.2. Dynamic Light Scattering

As we know, there exists well-known Brownian motion for the solute molecules in the polymer solution. Usually the Brownian motion of the solute molecules will give rise to a Doppler effect and so the scattered light possesses a range of frequencies shifted very slightly from the frequency of the incident light (this phenomenon is called quasi-elastic scattering). These frequency shifts yield information relating to the movement (i.e. the dynamics) of the solute molecules. A very popular means of monitoring the motion of solute molecules is to record the real-time fluctuations in the intensity of the scattered light in terms of the intensity TCF which is recorded with an ALV-5000 correlator. The TCF ($G^{(2)}(t,q)$) can be expressed as [29]:

$$G^{(2)}(t,q) = \langle I(t,q)I(0,q) \rangle = A(1 + \beta |g^{(1)}(t,q)|^2)$$

where $t$ is the decay time, $A$ is a measured baseline, $\beta$ is the coherence factor, and $g^{(1)}(t,q)$ is the normalized first-order electric field time correlation function $E(t,q)$ and is related to the line width distribution $G(\Gamma)$ by [29]:
\[ g^{(1)}(t, q) = \langle E(t, q) E^*(0, q) \rangle = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma \]

\( G(\Gamma) \) can be obtained from inverse Laplace transformation of \( g^{(1)}(t, q) \). Both the CONTIN program provided by Provencher [30] and CUMULANT analysis has been employed to get the average line width \( \Gamma \). In general, \( \Gamma \) is a function of both \( C \) and \( q \) and can be expressed as [29]:

\[ \frac{\Gamma}{q^2} = D(1 + k_d C)(1 + f < R_d^2 > q^2) \]

Where \( k_d \) is the diffusion second virial coefficient, and \( f \) is a dimensionless number depending on the chain conformation, solvent and internal motions. The extrapolation of \( \Gamma/q^2 \) to \( C = 0 \) and \( q = 0 \) led to the translational diffusion coefficient \( (D) \). Further, \( G(\Gamma) \) can be converted to the translational diffusion coefficient distribution \( G(D) \) and to the hydrodynamic radius distribution \( f(R_h) \) by using the Stokes-Einstein equation [29,31]:

\[ R_h = \frac{k_B T}{6\pi \eta D} \]

where \( k_B, T, \) and \( \eta \) are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.
Chapter 1 References


CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF CRYSTALLINE POLY(N-ISOPROPYLACRYLAMIDE)-CO-ACRYLIC ACID GELS IN ORGANIC SOLVENT

2.1. Introduction

Since Kuhn and Katchalsky’s pioneering work [1], polymer gels have gained extensive attention in recent decades because they can behave as smart materials in many fields, such as drug-delivery systems [2-4], biosensors [5], biotissues [6,7]. As the newest emerging branch in the polymer gels field, nano-scale photonic polymer crystal is studied more and more due to its unique optical property, namely Bragg diffraction. Some applications such as designing narrow band optical rejection filters [8,9], nanosecond nonlinear optical switching and limiting devices [10] and chemical sensing devices [11] have already been performed. However, most studies in this field focus on polymer hydrogels hitherto, no work has been done on the three-dimensional nano-scale crystalline polymer gel in organic solvent.

Monodisperse nano-scale colloidal particles can self-assemble into body-centered cubic (bcc) or face-centered cubic (fcc) crystalline arrays under the effect of certain interactions, i.e. interparticle screened Coulombic repulsion [12] for hydrogels, polar interaction between particles and solvent molecules for polymer gel in organic solvent [13]. The various refractive indexes caused by the
difference of dielectric constant between colloidal particles and surrounding medium contribute to the typical Bragg diffraction. Emulsion polymerization is the most often used process which can produce exceedingly uniform spheres of polymer colloids such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) [14]. This is also the polymerization method used in our experiment.

Poly(N-isopropylacrylamide) (PNIPAm) became one of the mostly studied polymer gels due to its typically thermo-sensitive property and good monodispersity since it was prepared in 1986 [15]. The mechanism of swelling and shrinking of PNIPAm gel had also been widely studied [16, 17]. Tanaka [16] proposed that three forces, rubber elasticity, polymer-polymer affinity and the hydrogen-ion pressure, had been identified as the driving forces contributing to the swelling and shrinking of polymer gels. Based on the study of collapse of gels by Tanaka, acetone can behave as a good sedimentary agent in the colloidal suspensions at certain concentration under room temperature. Acetone is also a good solvent for PNIPAm nanoparticles due to the existence of both hydrophobic functional groups and hydrophilic functional groups in PNIPAm.

Two types of mechanisms are believed attributing to the iridescence of monodisperse latex, one is believed to occur due to the specific diffraction of visible light by ordered layers of the substances, i.e. Bragg diffraction; the other type is believed to occur due to the specific scattering of particles randomly suspended in a solvent. When the radius of particles in a monodisperse colloid is roughly comparable to or larger than the wavelength of the light and the indexes
of refraction of the dispersed and continuous phases differ appreciably, iridescent coloration can be observed. Iridescent coloration phenomena of amorphous polymer gel without specific ordered structure in organic solvent had also been observed [13].

In this experiment, crystalline poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAm-co-AAc) nanoparticle network in organic solvent was obtained by self-assembling narrowly distributed precursor particles in acetone/epichlorohydrin mixture followed by curing them through inter-sphere crosslinking. Here, what we need to mention is that the “crystals” we got is different from conventional crystals: it is in an amorphous state inside the nanoparticles, but periodic structure is got from the self-assembling of the particles. The crystals formed are stable and elastic such that they can endure solvent exchanges or big distortions under a temporary compressing force with the reoccurrence of crystal structures. In acetone, the crystals are stable and independent of temperature; while in water, crystals can change their colors upon slightly heating below the phase transition temperature of PNIPAm or upon changing pH values. By passing a strongly focused white light beam through the crystals, different colors were displayed at different observation angles, indicating typical Bragg diffraction. Shear moduli of the gel nanoparticle crystals were measured in the linear stress-yield ranges for the same gel crystals in both acetone and water. Series synthesis of gel nanospheres of different sizes as well as the relationship
between size and the color of the synthesized gel nanoparticle networks at the same solid content was also discussed.

2.2. Experimental Section

2.2.1. Materials

N-isopropylacrylamide (NIPAAm) (Polysciences Inc.) monomer, N,N’-Methylene-bis-acrylamide (BIS) (Bio-Rad Laboratories), Acrylic acid (AAC), Dodecyl sulfate, sodium salt (SDS), Potassium persulfate (KPS) and Epichlorohydrin (EPO) (Aldrich Chemical Company, Inc.) were used as received.

2.2.2. Preparation of PNIPAm-co-AAc Nanoparticles

The experiment was conducted in a 500 ml reactor under a nitrogen atmosphere with gentle stirring. In our experiment, 3.80g N-isopropylacrylamide (NIPAm), 0.0665g N,N’-Methylenebis-acrylamide (BIS), 0.11g Acrylic acid (AAC) and a certain amount of Sodium dodecyl sulfate (SDS) were added into the reactor, diluted with deionized water to 250 ml solution. The reactor was incubated in a water bath and heated to 70 °C. The solution was stirred for 30 minutes with a nitrogen purge to remove the oxygen inside the solution, 16.6g 1% potassium persulfate (KPS) was added to start the reaction. The reaction was carried out at 70 °C for 4 hours.

2.2.3. Synthesis of Crystalline PNIPAm-co-AAc Nanoparticle Network

The particle water dispersion was cooled to room temperature. Acetone was added to precipitate the PNIPAm-co-AAc nanoparticles. The precipitates were
washed with acetone/water mixtures and dried for 2 days before being re-dispersed in acetone to an aimed concentration. Epichlorohydrin (EPO) (5 wt% of the dispersion) was added for intersphere crosslinking. The dispersion was vortexed, centrifuged to eliminate inhomogeneity. Crystalline was formed after standing for a couple of hours depending on different concentrations. The chemical cross-linking was conducted by incubating the sealed crystalline acetone dispersions at 98 °C for 6 hours.

2.2.4. Characterization of the Nanoparticles and Network

The particle size and its distribution were measured using light scattering technique. Our light scattering hardware setup consists of a commercial equipment for simultaneous static and dynamic experiments by ALV-Laservertriebgesellschaft (Langen, Germany). A He-Ne ion laser (632.5nm) was used at a power output of 0.1 to 200 mw. The primary beam’s intensity and position were monitored by means of a beam splitter and a four-segment photodiode. The thermostated sample cell is placed on a motor-driven precision geniometer.

The turbidity of the PNIPAM-co-AAc nanoparticle dispersions as a function of the wavelength was measured using a UV-Visible Spectrophotometer (Agilent 8453).

The shear modulus of the resulted PNIPAm-co-AAc gels was measured using a Digital Force Gauge (Shimpo, Japan).
2.3. Results and Discussion

2.3.1. The Nanoparticles Size Distribution

Dynamic laser light scattering characterization gives the size distributions of PNIPAm-co-AAc nanoparticles both in water and in acetone. Very narrow particle size distributions of PNIPAm-co-AAc nanoparticles (PDI < 0.1) with different average hydrodynamic radii ($<R_h>$) in water were shown in Fig. 2.1(i), which contributed to the formation of crystalline PNIPAm-co-AAc gels. PNIPAm-co-AAc nanoparticles with different $<R_h>$ can be obtained by adjusting the amount of SDS added in the syntheses. In addition, $<R_h>$ of PNIPAm-co-AAc nanoparticles is obviously smaller in acetone than in water, as shown in Fig. 1(ii), consistent with previous report [18]. This is because of the amphilicity of PNIPAm-co-AAc nanoparticles, the more hydrophilic property of PNIPAm-co-AAc nanoparticles made them have higher tendency to contract in acetone but swell in water. This result is also uniform to the phenomenon observed later during solvent exchanging process.

The recipe for synthesizing PNIPAm-co-AAc nanoparticles is shown in table 1.
Fig. 2.1 (i) Hydrodynamic radius distributions $f(R_h)$ of the precursor PNIPAm-co-AAc gel nanoparticles (Batches I to VII from left to right) synthesized by using different amounts of surfactant SDS (mass ratio in the parentheses).

(ii) Particle size distribution of the PNIPAm-co-AAc gel nanoparticles (Batch II) at 25 °C in water ($<R_h> = 232$ nm) and in acetone ($<R_h> = 142$ nm).
Table 1. Synthesis conditions of PNIPAM-co-AAC nanoparticles

<table>
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<tr>
<th>Batch</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
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<td>3.80</td>
<td>3.80</td>
<td>3.80</td>
<td>3.80</td>
<td>3.80</td>
<td>3.80</td>
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<tr>
<td>BIS (g)</td>
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<td>0.066</td>
<td>0.066</td>
<td>0.066</td>
<td>0.066</td>
<td>0.066</td>
<td>0.066</td>
</tr>
<tr>
<td>SDS (g)</td>
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<td>0.2083</td>
<td>0.1547</td>
<td>0.1232</td>
<td>0.1016</td>
<td>0.0634</td>
<td>0</td>
</tr>
<tr>
<td>AAC (g)</td>
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<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>KPS (mg)</td>
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<td>166</td>
<td>166</td>
<td>166</td>
<td>166</td>
<td>166</td>
<td>166</td>
</tr>
<tr>
<td>$R_h$ (nm)</td>
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<td>161</td>
<td>213</td>
<td>295</td>
<td>360</td>
<td>524</td>
<td>720</td>
</tr>
</tbody>
</table>

2.3.2. Reaction Mechanism

The cross-linking reaction mechanism, as previously reported [19] is shown in Scheme 1. The emulsion polymerization was carried out and PNIPAm-co-AAc nanospheres were obtained (Scheme 1(a)). The carboxyl group on the surface of nanospheres can be further cross-linked in acetone by epichlorohydrin (EPO) at temperatures near 98 °C to form three-dimensional nanoparticle network (Scheme 1(b)). This method has an advantage over intersphere crosslinking in water since the nanoparticle network thus formed has a much higher solid density due to the lower swelling ability of the precursor nanospheres in acetone. As a result, shear modulus of the nanoparticle network is much higher, as will be discussed later.
For crystalline nanoparticle networks formation, crystals were formed in acetone at the concentration of ~ 10 wt%, much higher than ~ 3 wt% that is for
the formation of crystalline in water [19]. These values are consistent with precursor particle sizes as are shown in Fig.2.1 (ii), according to Pusey’s criteria that the effective volume fractions for the formation of the crystals are between 0.494 and 0.545 [20]. It can be noted that the crystals still exist after intersphere crosslinking at such high temperatures as of about 98 °C, because acetone becomes a better solvent for PNIPAm-co-AAc gel spheres at a higher temperature, as was visualized by the increase in viscosity of the acetone dispersions at higher temperatures. As temperature increases, the nanospheres swell until they reach a very close-packed state: they become more acetone hungry. The swelling of the spheres occurs so rapidly that they soon squeeze against each other and the periodic crystalline structure is maintained. This structure is “permanently” set upon chemical intersphere crosslinking.

2.3.3. Polymer Gels with Different Particle Size

PNIPAm-co-AAc gel nanoparticles with different sizes can form gel nanoparticle networks with different colors, as shown in Fig.2.2 (i). The smaller precursor size corresponds to a color with a shorter wavelength due to the Bragg phenomena. Crystalline PNIPAm-co-AAc gel is formed from the precursor particles (Batch III) with $<R_n>$ of 320 nm in water in a fully swollen state. The picture was taken after transferring gel nanoparticle networks into bigger vials containing acetone (by injecting acetone into the bottom of the original vials to push them out) and then washing for a few days until an equilibrium state was reached. Crystalline PNIPAm-co-AAc gels can typically Bragg diffract the visible
light due to their suitable intersphere distance and the slightly difference in refractive indices between PNIPAm-co-AAc nanoparticles and interstitial environment.

2.3.4. Bragg-Diffraction of the Crystalline Gels

Fig.2.2 (ii) shows the Bragg diffraction of crystalline PNIPAm-co-AAc gel (Batch III) suspended in EPO. By passing a strongly focused white light beam through the crystals, different colors were displayed at different observation angles, indicating typical Bragg diffraction. The iridescent patterns originate from Bragg diffraction [20-23]. Constructive interference occurs if Bragg condition of $2nd\sin\theta = m\lambda$, is satisfied, where $d$, $\theta$, $n$, $\lambda$, and $m$ are the lattice spacing, diffraction angle, refractive index of the gel medium, wavelength of light in vacuum and diffraction order, respectively.

The above self-assembled crystalline structures can be better revealed by turbidity measurements using UV-Visible spectrometer, the results are as shown in Fig.2.3 for samples of Batches 1, 2 and 3 with various particle sizes, where all dispersions contain polymer concentration of 10 wt%. The turbidity curves exhibit a sharp peak (batch III) or a “shoulder” like peak (batches I and II). A sharp peak indicates a long-ranged order structure, while the “shoulder”-like shape in the spectra indicates a short-ranged, less well-organized order. It can be seen from the figure that the peak position shifts to short wavelength as the particle size decreases. This is because the decreasing in particle size of
nanoparticle spheres reduces the inter-particle distance so that $\lambda_c$ shifts to a lower wavelength.

Fig. 2.2 (i) (Top) PNIPAm-co-AAc gels with different colors in acetone: Hydrodynamic radius ($<R_h>$) from left to right is 188 nm (blue, Batch I), 232 nm (light green, Batch II), 320 nm (crystalline, Batch III) and 410 nm (white opaque, Batch IV) respectively. The solid contents are 10 wt%.

(ii) (Bottom) Bragg diffraction of crystalline PNIPAm gel (Batch III) suspended in EPO. Different colors can be seen from different observation angles: from left to right, orange red at (a) 15°, yellow-green at (b) 35° and blue-purple at (c) 95°.
Fig. 2.3 UV-Visible absorbance spectra of the PNIPAM-co-AAc nanoparticles in acetone at 10% polymer concentration from particles prepared in Batch I (122 nm), Batch II (161 nm), Batch III (213 nm). The particle sizes were measured in water at room temperature using dynamic light scattering method.
2.3.5. Solvent Exchange Experiment

The solvent exchange process was also performed in this experiment. Pictures were taken at different stages and shrinking-swelling kinetics was recorded as the function of gel size. Crystals can be observed clearly from acetone soaked crystalline gel matrix (Fig.2.4a). After immersing the gel into large amount of water, water-acetone exchange process started rapidly. The gel became turbid and shrank into smaller size in a few minutes (Fig.2.4b). This process slowed down and the gel reached its smallest size in about 60 minutes (kinetics curve in Fig.2.4). After then, the surface of the gel begins to swell, resulting in a shimming colored shell (Fig.2.4c). The swelling continued and the gel retrieved its crystalline state in water (Fig.2.4d). Note the dimension of the gel increase by ~ 30% after the solvent exchange and the color of crystal changed from shorter (green in Fig.2.4a) to longer (pink in Fig.2.4d) wavelength accordingly.

The kinetics of the solvent exchange process was shown in Fig.2.4. A critical phase transition point was observed at time equals to 60 minutes, the collapse of the crystalline gel at this point could be explained as the result of changing the fluid composition inside the polymer gel [24]. The shrinking process follows an exponential
Fig. 2.4 (Top) Solvent exchange (acetone-water) process (Batch III):
(a) 0 min (b) 15 min (c) 120 min (d) 900 min. The height of crystalline
PNIPAm gel is 15mm, the gel was immersed into a glass cultural dish
with 120 ml water. (Bottom) The shrinking and swelling kinetics during
solvent exchange process. A critical point appears at 60 minutes.
decay, the average decay period is ~3 minutes; the following swelling process is an exponential growth process, the average growth period is ~254 minutes. The swelling speed depends on elastic force from macroscopic view and on the affinity between polymer chain network and solvent water from microscopic view. The remnant acetone inside the gel, though the concentration is low, may partially destroy the hydrogen bond between PNIPAm and water, which is the major driven force for gel to swell, and this may explain the slow swelling rate.

2.3.6. Shear Modulus Measurement

The crystalline gels synthesized also show good resilient properties. When a certain force is applied perpendicular to the surface of the gel, as is shown in Fig.2.5, the crystals temporarily disappear because of the gel distortion, but the colors of the gel still exist and change to bright yellow (of higher wavelengths). This is because the gel extended under the force, the interplanar spacing of the lattice plane doesn’t changed much. After the force was removed, the gel recovered its original form and the crystals appeared again. The existence of the crystals further confirms that the crystals had been fixed in their positions. This “elastomer” property may have potential applications in the future.

For the rubber composed of ideal polymer chains, both the energy of intermolecular interaction and contributions from deformation of valence bonds are neglected. Thus, \( \frac{\partial E}{\partial L} \) would be exactly equal to zero [25]. Under the
condition, the stress-strain response of ideal networks under uniaxial compression or extension is characterized as follows:

\[ \tau = \frac{F}{A_0} = G_0(\lambda - \lambda^{-2}) \]  

(1)

Fig. 2.5 (Top) Crystalline gel (Batch III, after solvent exchange) elastic test (Bottom) Shear modulus (G) measurement of the crystalline PNIPAm gels (Batch III) in acetone (Δ) (G_{acetone} = 1.3 \times 10^3 \text{ dyn/cm}^2) and in water (●) (G_{water} = 0.2 \times 10^3 \text{ dyn/cm}^2).
Where $G_0 = N_0k_BT$ ($G_0$ shear modulus), $\tau$ engineering stress, $F$ applied force, $A_0$ undeformed cross-sectional area of swollen polymer, $\lambda = L/L_0$, $L$ sample length under stress and $L_0$ undeformed sample length. At low strains, a plot of stress versus $\lambda - \lambda^{-2}$ will yield a straight line whose slope is the modulus.

However, for a nanoparticle network, considering the contribution of both internal energy and entropy changes associated with crosslinked nanoparticles, the shear modulus could be described by:

$$G = k_BT N_0 (\gamma n_s + 1)$$  \hspace{1cm} (2)

Here $G$ is closely related to the number of nanoparticle’s sphere between cross-linking points $n_s$, crosslinking intensity $\gamma$ and the number of chains per unit volume $N_0$.

The shear modulus of the gels synthesized is also measured. As shown in Fig.2.5 (bottom), the crystalline gel has much higher modulus in acetone than in water. This is mainly due to the higher crystallization concentration in acetone than in water. From Equation 2, one can see that the shear modulus increases as the value of $n_s$ increases. The good linear relationship also shows the good resilient property.

2.4. Conclusion

In conclusion, high solid content (10 wt.%) three-dimensional crystalline PNIPAm-co-AAC acetone gel nanoparticle networks were first-time synthesized. The colored crystal gels can be finger-held, played, compressed to have a big
distortion or undergo a solvent exchange. Because of the similar mechanical properties as that of a bulk gel and its optical features, this colored gel may find its way as a sensor or decoration material. It may also be used as a special matrix for separation purposes.
Chapter 2 References


CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF POLY(N-ISOPROPYLACRYLAMIDE)-CO-ACRYLIC ACID NANOPARTICLE NETWORKS IN WATER

3.1. Introduction

Monodispersed colloidal spheres have been widely studied as a scientific target because of a number of reasons: first, their spherical figures represent the simplest form that colloidal particles can adopt and are just right for the theoretical analysis and treatment, such as treated with Mie theory [1]; second, it is easy to control the properties of the colloidal particles by adjusting the size, surface functional group and the chemical composition of the particles [2,3]; furthermore, they can significantly self-assemble to form periodic structures or mesoscopic crystal structures which attract more and more attention recently [4-6]. Applications in this field are also found in optical devices and biosensors [7,8].

Poly(N-isopropylacrylamide) (PNIPAm) has become one of the mostly studied polymers in the hydrogel field due to its thermal sensitive property since it was found in 1986 [9]. Its LCST (lower critical solution temperature) is at 32\degree C, and also functionalized PNIPAm can increase or decrease its LCST according to the different relative hydrophilic or hydrophobic content of the PNIPAm hydrogel, both of these make PNIPAm a much popular object of research in medical field as carrier for control-release system and drug-delivery systems [10,11]. The very
narrow polydispersity of PNIPAm nanoparticles in colloidal solutions also contributes to the formation of photonic crystals. Photonic crystals based on hydrogels have gained more and more attention recently [4, 6, 8, 12]. However, hydrogel opals of nanoparticle network are still seldom studied. The opals having been synthesized in our group before [13] had the disadvantage of very weak strength and reproducibility which strongly limited its possible applications in the future, so different ways must be taken in order to improve the mechanical property of the crystalline hydrogel. In this paper, a new synthesizing method was introduced, the resulted three-dimensional (3D) nanocrystalline PNIPAm hydrogels have much better strength and reproducibility, the typical Bragg diffraction were observed, also as an “intelligent polymer”, the thermo- and pH-sensitive properties of the crystalline hydrogel were studied in detail.

Emulsion polymerization is the most popular method that is used to get narrow-distributed polymer nanoparticles [14]. In our experiment, a water-soluble sulfate radical initiates a water-soluble NIPAACm monomer which then grows in solution until it reaches a critical chain length after which the growing chain collapses to become a colloidally unstable ‘precursor particle’. The precursor particles follow one of two competing processes. Either they deposit onto an existing colloidally stable polymer particle or they aggregate with other precursor particles until they form a particle sufficiently large to be colloidally stable. At the polymerization temperature (70°C) which is well above the LCST (lower critical soluble temperature) of PNIPAm, the growing PNIPAm particles are colloidally
stabilized by electrostatic stabilization originating from sulfate groups introduced by the persulfate initiator and carboxyl groups by the Acrylic Acid. In the process of emulsion polymerization, surfactant also plays a significant role. The interaction between a surfactant and a polymer can affect the overall properties of the system in a number of ways depending on the nature of the polymer and surfactant involved. For nonionic polymers, ionic surfactants can enhance polymer solubility by forming aggregate on the polymer thereby reducing repulsive interactions between the head groups of the surfactant molecules when in micellar form. In the case of ionic polymers attractive interactions between the polyelectrolyte and surfactants of opposite charge are known to result in precipitation. These interactions are predominantly electrostatic and can be reversed by the addition of electrolyte. With regard to the polymer particles, the interactions between anionic PNIPAm microgel and Sodium Dodecyl Sulfate (SDS, anionic surfactant) was also studied [15,16]. In this experiment, SDS was used to control the size of PNIPAm nanoparticles by adjusting its amount (Fig.3.1). After the colloidal particles were synthesized, SDS was removed by means of dialysis. The formation of hydrogel opals includes three building blocks. One was Poly(N-isopropylacrylamide)-co-Acrylic acid (PNIPAm-co-AAc) nanoparticles, another one was 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), the third one was adipic acid dihydrazide (AADD). Considering the hydrolysis of EDC, the reaction was performed in the refrigerator (4°C) for 24hrs.
3.2. Experimental Section

3.2.1. Materials

N-isopropylacrylamide (NIPAAm, Polysciences Inc.), N,N'-Methylene-bis-acrylamide (BIS, Bio-Rad laboratories), Acrylic acid (AAC, 99%, Aldrich Chemical Company, Inc.), Dodecyl sulfate, sodium salt (SDS, 98%, Aldrich Chemical Company, Inc.) and Potassium persulfate (KPS, 99%, Aldrich Chemical Company, Inc.), 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC or EDAC) (Research Chemicals Ltd.) and Adipic Acid Dihydrazide (AADD) (Sigma Chemicals Co.) were used as received.

3.2.2. Preparation of PNIPAm-co-AAc Nanoparticles

The experiment was conducted in a 500 ml flask with a nitrogen bubbling tube and a PTFE stirrer. 3.80g NIPAAm, 0.0665g BIS, 0.11g AAc and certain amount of SDS (In our experiment, we prepared PNIPAm-co-AAc nanoparticles with different sizes by adjusting the amount of the surfactant SDS, the detailed latex recipe is listed in Table I) were added into the flask, diluted with deionized water to 250 ml solution. The flask was immersed into a water-bath with temperature 70 °C. The solution was stirred at 300 rpm for 30 minutes with a nitrogen purge to remove the oxygen inside the solution. 16.6g KPS (1%) was added and the reaction was executed for 4 hours.
3.2.3. Synthesis of Crystalline PNIPAm-co-AAc Nanoparticle Network

The latex above was concentrated under 50°C for two days. Crystalline PNIPAm-co-AAc can be obtained at solid content ~3.1%. The latex was held in a special cylindrical apparatus with a large amount of holes in the wall and the bottom, the size of the holes is 0.5 mm (Fig.3.1). The apparatus is half-immersed into EDC and AADD solution (5%). Keep them at 4°C for 24 hours, then exchange with EDC and AADD solution (7%) for another 24 hours.

3.2.4. Characterization of Particle Size using Dynamic Light Scattering

The hydrodynamic radii of the synthesized nanoparticles were characterized using dynamic light scattering technique. Our light scattering hardware setup consists of a commercial equipment for dynamic experiments by ALV-Laservertriebsgesellschaft (Langen, Germany). A He-Ne ion laser (632.5nm) was used at a power output of 0.1 to 200 mw. The primary beam’s intensity and position were monitored by means of a beam splitter and a four-segment photodiode. The thermostated sample cell is placed on a motor-driven precision geniometer.

3.2.5. Temperature-sensitivity and pH-sensitivity Test

Upon changing the temperature and pH value, the sensitivity experiment of the nanoparticle network was performed.
3.3. Results and Discussion

3.3.1. Reaction Mechanism

A scheme (Scheme 2) was developed to show the crosslinking reaction mechanism. It includes two steps. The first step is the synthesis of PNIPAm-co-AAc nanoparticles with carboxyl group on the particle surface. NIPAAm monomer, N, N’-methylene-bis-acrylamide (BIS) and Acrylic Acid (AAc) took part in this step; the second step is the formation of PNIPAm hydrogel. In the second step, EDC react with carboxyl group on the surface of PNIPAm particles to form a highly reactive intermediates, this active species can then react with two primary amines of AADD to form two amide bonds. The two active amine groups attribute to the formation of the final network.
3.3.2. Crystalline Colloids with Different Concentration and Particle Size

Under certain concentrations, the PNIPAm-co-AAc nanoparticles can self-assemble into periodic structure arrays, the size of crystal domains can be adjusted by controlling the concentration (Fig.3.2). In a limited concentration
range, the more dilute the colloid, the bigger the crystal domain. The crystalline colloid solution can be further cross-linked to result the nanocrystalline hydrogel. Osmosis mechanism was adopted in this experiment; the crosslinking reaction rate was controlled by poring the reactor and wrapping it with a dialysis film.

There exist many factors that can affect the crystal growth of monodispersed PNIPAm-co-AAc colloid solutions: concentration, temperature and also particle size. The influence of first two factors on the PNIPAm system has been already reported in our previous paper [17]. With regard to the particle size, we found crystallization could usually happen when particle size was between 190nm and 450nm for PNIPAm-co-AAc colloids under fitable concentration and temperature. The refractive index difference between water

Fig.3.2 Nanocrystalline PNIPAm colloids with different solid content: (a) 2.8%; (b) 3.0%; (c) 3.1%. Here the hydrodynamic radius of PNIPAm nanoparticles: $R_h = 220$nm, measured with ALV-5000 light scattering at $90^\circ$C. The pictures showed the size of the crystal decreases with the increasing solid content at a certain temperature, the pictures here were taken at room temperature.
Fig. 3.3 (Top) Different PNIPAm nanoparticle size can result different-colored colloid gels with the same concentration (~3%) (a) $R_h = 190$ nm (b) $R_h = 220$ nm. (Bottom) Hydrodynamic radii distribution for both a and b.
and PNIPAm-co-AAc nanoparticle contributes to the color of the colloidal solutions, so PNIPAm-co-AAc with different particle size will show different colors. When particle size is at the lower end (~190nm), only green and blue light can be reflected on the crystal domain, so the color of the crystal in the colloid solutions will be blue-green (Fig.3.3a); when particle size is above 200nm, crystal with red color can also be obtained (Fig.3.3b).

3.3.3. Bragg-Diffraction of the Crystalline Gel

Crystals can also typically Bragg diffract the light, Fig.3.4 showed crystalline PNIPAm-co-AAc hydrogel with different colors at three different angles: red at 30°, green at 90° and blue at 120°.

3.3.4. Thermal Sensitivity of the Crystalline Hydrogel

The existence of both hydrophilic and hydrophobic groups makes PNIPAm hydrogel show the remarkable temperature-sensitive property. For the crystalline 3D PNIPAm-co-AAc hydrogel, this phenomenon still holds (Fig.3.5). When the temperature was increased above 34°C (here we can notice that the phase transition temperature is a little bit higher than pure PNIPAm due to the existence of carboxyl group), crystals disappeared and the hydrogel became blurry. Increasing the temperature further (35°C), the PNIPAm-co-AAc hydrogel obviously started to shrink. This was because the water inside the hydrogel had been expelled out of the network due to the strengthened hydrophobic effect. Keeping increasing the temperature would make the hydrogel become smaller.
and smaller until all the water inside the hydrogel was expelled out of the network. When the temperature was decreased back to the room temperature, the crystals could still come back and the hydrogel could recover its original figure. This memory effect also confirmed that the periodic structures had been well positioned.

3.3.5. pH-Sensitivity of the Crystalline Hydrogel

The resulted crystalline PNIPAm-co-AAc hydrogel also showed pH-sensitive property in basic environment (Fig.3.6). When the basicity of solution increased, the hydrogel would become blurry and also shrank. As talked before, PNIPAm-co-AAc hydrogel had both hydrophilic and hydrophobic properties. For PNIPAm-co-AAc hydrogel, in basic solution, the hydrophilic property of PNIPAm was lessened due to the deprivation of active hydrogen (H⁺) in the –NH- part, which correspondingly resulted the increasing of hydrophobic aspects, the hydrogel became blurry (Fig.3.6 d). When the basicity was high enough, the hydrophobic parts would play the main role, water would be expelled out of the PNIPAm network, so the hydrogel obviously shrank (Fig.3.6 e). But in acidic solution, the hydrophilic property would be strengthened, which made the hydrogel clearer (Fig.3.6 a). Increasing the acidity of the solution further couldn’t get much change. Additionally, all processes above are reversible, which make the crystalline PNIPAm a potential object in the sensor fields.
3.4. Conclusion

In summary, we have successfully synthesized 3D crystalline PNIPAm-co-AAc nanoparticle network by a new route that can result PNIPAm hydrogel with much higher strength. The crystalline hydrogel has both thermo- and pH-sensitive property. Future work will be focused on both the optical properties and control-release function of the crystalline hydrogels.
Fig.3.4 The typical Bragg Diffraction of crystalline PNIPAm-co-AAc hydrogel at different angles ($R_h = 220$ nm, solid content is $\sim 3\%$): (a) $30^\circ$, red (b) $90^\circ$, green (c) $120^\circ$, purple.

Fig.3.5 Thermo-sensitivity of crystalline PNIPAm hydrogel ($R_h$ is 190nm). (a) $25^\circ$C (b) $30^\circ$C (c) $35^\circ$C. Phase Transition happens around $34^\circ$C, crystals disappeared, the hydrogel became turbid and shrunk at $35^\circ$C. The whole process is reversible. (The length of the marker is 10mm)
Fig. 3.6  pH-sensitivity of nanocrystalline PNIPAm hydrogel (R_h is 190nm).  (a) pH=2  (b) pH=6  (c) pH=9  (d) pH=11  (e) pH=12.  The hydrogel showed obvious shrinking phenomenon when pH is bigger than 11.  This process is also reversible.  The grid on the background is 15mm × 15mm.
Chapter 3 References


CHAPTER 4

THE STUDY OF PHASE BEHAVIOR OF THERMALLY RESPONSIVE MICROGEL COLLOIDS

4.1 Introduction

In many aspects, colloidal particles suspended in a liquid behave similar to large idealized atoms that exhibit liquid, glass, and crystal phases similar to those observed in atomic systems [1–6]. Phase transitions in colloidal systems have been intensively studied over the past decade not only because of the theoretical interest for addressing fundamental questions about the nature of liquids, crystals, and glasses, but also for many practical applications of colloids, especially for the fabrication of nanostructured materials [7–11]. Previous investigations on the phase behavior of colloidal dispersions, however, are primarily focused on hard-sphere-like particles such as polymethylacrylate, silica, or polystyrene; little attention has been given to those colloids where the interparticle potential is a strong function of temperature. In this Letter, we consider specifically aqueous dispersions of poly-N-isopropylacrylamide (PNIPAM) microgel particles that exhibit a reversible and continuous volume transition in water around 34°C [12–28]. We synthesized PNIPAM microgels using an emulsion polymerization method [12]. We show that the lower-critical-solution-temperature–like behavior of a PNIPAM microgel could affect the
interparticle forces between microgels, resulting in drastic different phase behavior from those of conventional hard-sphere-like colloidal systems.

4.2 Experimental Section

4.2.1 Materials

NIPA (N-isopropylacrylamide, Polysciences Inc.) monomer, BIS (N, N'-methylene-bis-acrylamide, Bio-Rad Laboratories), SDS (Dodecyl sulfate, sodium salt, 98%, Aldrich Chemical Company, Inc.), KPS (Potassium persulfate, 99%, Aldrich Chemical Company, Inc.)

4.2.2 Preparation of PNIPAM Nanoparticles

1.54 g N-isopropylacrylamide (NIPA) monomer, 0.0262 g N, N-methylene-bis-acrylamide as cross-linker, 0.0439 g sodium dodecyl sulfate as surfactant, and 90 ml deionized water were mixed in the flask. The solution was stirred at 300 rpm for 30 min under nitrogen. 0.0624 g potassium persulfate dissolved in 10 ml of deionized water was added to start the reaction. The reaction was carried out at 70 °C for 4 h. The PNIPAM particle dispersion was concentrated using an ultracentrifuge with a speed of 40 000 rpm for 3 h.

4.2.3 Characterization of PNIPAM Nanoparticles

The average hydrodynamic radius and the radius distribution of microgel particles were characterized using a dynamic light scattering technique, while the radius of gyration, osmotic second virial coefficient, and the molecular weight of
microgels in the aqueous dispersions were obtained using static light-scattering measurements (ALV-5000, Germany).

4.2.4 Turbidity Measurement

The phase behavior of the PNIPAM microgels was characterized using UV-Vis spectrometer mentioned in previous chapters. The crystalline PNIPAM specimens used were made from the concentrated PNIPAM colloids.

4.3 Results and Discussion

Typically, the hydrodynamic radius of the PNIPAM particles was narrowly distributed with a polydispersity less than 5% (Fig.4.1).

![Graph showing PNIPAm hydrodynamic radius distribution](image)

Fig.4.1 PNIPAm hydrodynamic radius distribution measured by dynamic light scattering, $R_h$ is 133nm.
Fig. 4.2 (a) presents the particle size in an average of the radius of gyration and hydrodynamic radius \([(5/3)^{(1/2)}R_g+R_h)/2\]. This average value is used to reduce the particle inhomogeneity effect on calculations.

Fig. 4.2 (b) shows the reduced osmotic second virial coefficient \((B_2/B^{HS}_2)\) as functions of temperature. Here, \(B^{HS}_2\) is calculated from the particle average radius assuming that they are hard spheres. The phase transitions in aqueous dispersions of PNIPAM particles are easily observable from their appearances. Fig. 4.3(a) shows the iridescent patterns when nearly monodispersed PNIPAM particles with the polymer concentration of 16.9 g/L self-assemble into a crystalline phase. Here, the temperature is 21 °C and the microgel spheres are fully swollen. At 26 °C, the iridescent grains disappear completely and the dispersion becomes a homogeneous liquid with small turbidity [Fig. 4.3(b)]. When the temperature is raised further to 35 °C, the sample becomes white and opaque, indicating a second phase separation [Fig. 4.3(c)]. While at low temperature the solid phase exhibits apparent characteristics of a colloidal crystal, the phase-separated state at high temperature is probably related to the metastable fluid-fluid equilibrium that will be discussed later.

A quantitative phase diagram of PNIPAM dispersions can be constructed by measuring the UV-visible absorbance spectra on a diode array spectrometer (Hewlett-Packard, Model 8543) with the wavelength ranging from 190 to 1100 nm. The turbidity of the samples was obtained from the ratio of the transmitted light intensity \((I_t)\) to the incident intensity \((I_0)\) as \(\alpha = -(1/L)\ln(I_t/I_0)\), where \(L\) was the
Fig. 4.2 (a) The size of PNIPAM microgel spheres in water as a function of temperature. Here the symbols represent the averages of the hydrodynamic radius and the radius of gyration, and the line is calculated from the Flory-Rehner theory. (b) Reduced osmotic second virial coefficient from the static light scattering (symbols) and from the calculation using Eq. (1) (line).
Fig. 4.3 Color pictures of the PNIPAM microgel dispersion with polymer concentration of 16.9 g/L at various temperatures: (a) 21 °C, (b) 26 °C and (c) 35 °C. The average hydrodynamic radius of PNIPAM microgel spheres in water at $T = 25$ °C is 133 nm. The diameter of the vial is 1 cm.
sample thickness (1 cm). In the crystalline phase, the UV-VIS spectrum exhibits a sharp attenuation peak due to the Bragg diffraction arising from ordered colloidal structures [14]. Above the crystalline melting temperature, the peak disappears. On the other hand, as the temperature rises to the phase separation temperature, the turbidity increases sharply in the entire range of visible light wavelengths (Fig.4.4 (a)). The melting temperature is determined by observing the disappearance of the turbidity peak (Fig.4.4 (b)).

Fig.4.5 presents the phase diagram of a PNIPAM microgel dispersion determined from the turbidity measurements. Below the volume phase-transition temperature, the PNIPAM dispersion exists as a clear liquid at low polymer concentration, and a crystalline solid at high polymer concentration. Above the volume transition temperature of the microgel particles, a sharp increase in turbidity (shown later) designates a second phase transition. In this case, no crystals are observed and the dispersion becomes opaque. No macroscopic phase separation was observed; even when the dispersion had been preserved at constant temperature for over a few weeks [Fig.4.3(c)]. The phase behavior of microgel dispersions can be semiquantitatively represented by a simple thermodynamic model. The pair potential between neutral microgel particles includes a short-range repulsion that is similar to the interaction between two polymer-coated surfaces, and a longer-ranged van der Waals-like attraction that
arises from the difference in the Hamaker constants of the particle and the solvent [29]. An analytical expression for the interparticle potential that

![Graph](image)

Fig.4.4 (a) Turbidity change vs. temperature (b) The melting temperatures of the crystals are determined by the disappe-
Fig. 4.5 The phase diagram of aqueous dispersions of PNIPAM particles determined from turbidity measurements (symbols) and from the thermodynamic perturbation theory with an empirical correction of temperature (lines). The filled and open circles represent, respectively, the melting and the second phase-separation temperatures. The inset shows the predicted phase diagram without any adjustable parameters.

covers the entire temperature range of microgel swelling is yet to be developed. Because the phase diagram is not sensitive to the detailed function of the short-range forces [30], we assume in this work that the potential between microgel particles can be *effectively* represented by the Sutherlandlike function (Eq. 1):

\[
\frac{u(r)}{kT} = \begin{cases} \infty & r \leq \sigma \\ -\frac{T_0}{T}\left(\frac{\sigma_0}{\sigma}\right)^6 + n\left(\frac{\sigma}{r}\right)^n & r \geq \sigma \end{cases}
\]
where $\sigma$ is the effective diameter, $r/\sigma$ denotes the reduced center-to-center distance, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $T_0$ is an empirical proportionality constant that has the unit of temperature, and $\sigma_0$ is the particle diameter at a reference temperature where the conformation of the network chains is closest to that of unperturbed Gaussian chains. Introduction of $T_0$ and $\sigma_0$ in Eq. (1) is solely for the purpose of dimensionality. The dependence of the particle diameter $\sigma$ as a function of temperature can be represented by, as shown in Fig.4.2(a), the modified Flory-Rehner theory for volume-transition equilibrium of temperature-sensitive polymer gels [26]. This theory takes into account the heterogeneity of microgels and has been successfully applied to describe the volume transition of bulk PNIPAM gels. The inverse power in Eq. (1) is assumed to be $n = 8$, in considering that the van der Waals attraction between colloidal particles is short ranged in comparison to that between atomic molecules (relative to the particle size) [31]. We find that $n = 8$ gives optimum results for fitting the osmotic second virial coefficients of microgel dispersions. The temperature-independent parameters $\sigma_0 = 251.6$ nm and $T_0 = 1.884 \times 10^2$ K are obtained from the average radius of microgel particles and the osmotic second virial coefficients of the microgel dispersions as shown in Fig.4.2.

Once we have the interaction potential between microgel particles, the phase diagram can be calculated using thermodynamic models for the fluid and the solid phases. The reduced Helmholtz energy $F_f / NkT$ for the fluid phase includes a hard-sphere contribution that depends only on the particle volume
fraction $\eta = \frac{\pi \rho \sigma^3}{6}$, and a perturbation that takes into account the short-range attraction $u_A(r)$ [33] (Eq.2)

$$
\frac{F_f}{NkT} = \ln(\eta) - 1 + \frac{4\eta - 3\eta^2}{(1 - \eta)^2} + 12\eta \int_1^\infty x^2 g_f^{HS}(x) \frac{u_A(x)}{kT} dx,
$$

where $x = r/\sigma$, $N$ stands for the total number of particles, $\rho$ is particle number density, and $g^{HS}_f(r)$ is the hard sphere radial distribution function that was calculated from the Percus-Yevick theory [2] using the analytical direct correction function, and the integral was evaluated numerically. The Helmholtz energy for the solid phase is similarly given by (Eq.3)

$$
\frac{F_s}{NkT} = \frac{F^{HS}_s}{NkT} + 12\eta \int_1^\infty x^2 g^{HS}_s(x) \frac{u_A(x)}{kT} dx,
$$

where the reference Helmholtz energy $F^{HS}_s$ and the radial distribution function of the hard-sphere solid $g^{HS}_s(r)$ can be calculated from a modified cell model [32].

Like that in a hard-sphere system, an aqueous dispersion of PNIPAM microgel particles is at low cross-linking density ("softer" particles) [33]. The first-order perturbation theories for both fluid and solid phases are sufficient in this work because, when the attractions are short ranged, higher order terms make only a negligible contribution to the total Helmholtz energy [34]. The chemical potential
and osmotic pressure as required in the phase-equilibrium calculations can be directly derived from Eqs. (2) and (3) following standard thermodynamic relations.

The phase diagram calculated with the thermodynamic perturbation theories is also shown in Fig.4.5. The inserted plot shows the predicted results using the size and energy parameters obtained from the osmotic second virial coefficients. It can match almost perfectly with experimental data if the calculated temperature is rescaled empirically by $T' = T \left(\frac{15}{R_g}\right)^{0.005}$. The discrepancy is probably because the effect of osmotic pressure on the particle size is neglected in the perturbation theory or because of the slight size difference (~2 nm) between the microgel samples used in light scattering and in turbidity measurements. Nevertheless, the theory and experiment give the same interesting phase diagram that has not been reported before. In addition, the calculated results clearly indicate that the second phase transition is due to the metastable liquid-liquid phase transition of the microgel dispersion. That explains why crystallization is not observed at high temperatures.

The phase diagram shown in Fig.4.5 is perceivably different from that for a typical hard-sphere-like colloid or that for an atomic system. First, the metastable fluid-fluid coexistence curve (the dashed line) shows a low critical temperature instead of an upper critical temperature (as observed in conventional colloids) [32]. Second, at low temperatures, the coexisting liquid and solid phases have close particle densities, similar to those observed in a hard-sphere system;
however, at high temperatures, the fluid-solid transition spans over a wide range of particle concentrations. At low temperatures, the PNIPAM particles are in the swollen state and they contain up to 97% of water by weight. In this case, the van der Waals attraction between colloidal particles is negligible due to the close match in the dielectric constants of the particle and the water. As a result, the PNIPAM particles behave essentially like hard spheres as shown in Fig.4.2(b). However, at high temperatures, the PNIPAM particles collapse and the polymer density within each particle rises significantly, leading to strong van der Waals attractions. The phase behavior of PNIPAM dispersion at high temperatures resembles that for strongly attractive colloids. The phase-separated state is probably related to the metastable fluid-fluid equilibrium: Fast kinetics of fluid-fluid transition leads to an amorphous fluid phase of high particle concentration. Most interestingly, Fig.4.5 shows that, as observed in experiments, a microgel dispersion exhibits phase transitions by either increasing or decreasing temperature. For instance, according to Fig.4.5, a microgel dispersion with 17 g/L polymer concentration is in the fluid state at 32 °C, it becomes a solid of similar particle density when the temperature drops to about 25 °C, and it will be phase separated into a dilute phase and a solid of much higher density (about 200 g/L) at about 34 °C. Whereas a conventional colloid exhibits a hard-sphere-like phase behavior at high temperature, the opposite is true in an aqueous dispersion of PNIPAM particles.
4.4 Conclusion

In summary, we have investigated the volume transition equilibrium and the interaction potential between neutral PNIPAM particles dispersed in water using spectrometric and light-scattering experiments. We found from experiments and thermodynamic perturbation theory that aqueous dispersions of PNIPAM particles exhibit phase transitions at both high and low temperatures. The phase behavior of microgel dispersion resembles that for hard spheres at temperatures below the volume-transition temperature. However, at higher temperatures, the phase separation is driven by van der Waals attractions and metastable liquid-liquid equilibrium exists within the fluid-solid coexistence.
Chapter 4 References


CHAPTER 5

THE PHASE BEHAVIOR OF PNIPAm-CO-AAc COLLOIDS

5.1 Introduction

Crystalline arrays have attracted considerable interest in recent years due to their unique chemical, optical and mechanical properties designed in the building blocks so that control over the properties of the resulted arrays can be reached. The factors influencing the self-assembly as a function of particle shape and surface chemistry have been elucidated [1-3]. These assemblies have already been applied in optical devices [4, 5], biosensors [6] and genomics [7]. Among those methods that can produce ordered arrays, three representative approaches have been summarized [8]: Sedimentation in a force field; Crystallization via repulsive electrostatic interactions; Self-Assembly under physical confinement. The first method involves a strong coupling of several complex processes such as gravitational settling, translational diffusion and crystallization. The success of this method relies on tight control over several parameters such as the size and density of the spheres, as well as the rate of sedimentation. Usually this method is good for hard-sphere colloids but having the disadvantages of both hard-to-control morphology of the top surface and relatively long time (weeks or months). The second method is good for those highly charged colloidal spheres suspended in a dispersion medium. By
minimizing repulsive electrostatic interaction between them, the colloidal spheres can spontaneously self-assemble into ordered structures. This method has strict requirement on the experimental conditions: temperature, monodispersity in size, density of charges on the surface, number density of spheres and concentrations of counterions in the dispersion medium. The third method is a faster approach to form the crystalline structures but need certain physical confinement, such as continuous sonicaton.

In this experiment, the carboxyl group (-COOH) was introduced to the building block of the PNIPAm nanoparticles due to their highly polydispersity (<0.1). The crystalline PNIPAm-co-AAc colloidal spheres could be obtained via the second method mentioned above. Ultraviolet-visable spectrometer method was used to monitor the phase behavior of resulted crystalline PNIPAm-co-AAc colloids. Comparison between the phase behavior of pure PNIPAm microgel and charged PNIPAm microgel has been researched. The results showed the introducing of the charge could not only greatly increased the crystallization concentration range but also improved the particle size range for self-assembling.

5.2 Experimental Section

5.2.1 Materials

N-isopropylacrylamide (NIPAm, Polysciences Inc.), N,N’-Methylene-bis-acrylamide (BIS, Bio-Rad laboratories), Acrylic acid (AAc, 99%, Aldrich Chemical
Company, Inc.), Dodecyl sulfate, sodium salt (SDS, 98%, Aldrich Chemical Company, Inc.) and Potassium persulfate (KPS, 99%, Aldrich Chemical Company, Inc.)

5.2.2 Synthesis of PNIPAm-co-AAc Nanoparticles

The experiment was conducted in a 500 ml flask with a nitrogen bubbling tube and a PTFE stirrer. 3.80g NIPAAm, 0.0665g BIS, 0.11g AAc and 0.10g SDS were added into the flask, diluted with deionized water to 250 ml solution. The flask was immersed into a water-bath with temperature 70 °C. The solution was stirred at 300 rpm for 30 minutes with a nitrogen purge to remove the oxygen inside the solution. 16.6g KPS (1%) was added and the reaction was executed for 4 hours.

5.2.3 Preparation of Crystalline PNIPAm-co-AAc Colloid

The resulted colloidal dispersion from 5.2.3 was centrifuged to get concentrated colloids. Three different concentrations (15.2 g/L, 17.3 g/L, 20.1 g/L) were made for further use.

5.2.4 Dynamic Light Scattering Experiment

The colloidal particle size distribution and molecular weight were measured using light scattering technique. The experimental setup was as talked in previous chapters.
5.2.5 UV-Vis Spectrometer Measurement

The absorbance of the PNIPAm-co-AAc colloids for each sample at a certain temperature range (5\(^{\circ}\text{C}~35^{\circ}\text{C}) was measured using a UV-Visible Spectrophotometer (Agilent 8453). The stabilizing time at each temperature is 1 hour.

5.3 Results and Discussion

The dynamic light scattering result dictated the average hydrodynamic particle size of the synthesized PNIPAm-co-AAc \( R_h \) was around 200nm (Fig.5.1). The light scattering result showed a very narrow particle size distribution, i.e. small polydispersity, which contributed to the further crystallization of the nanoparticles.

![Fig.5.1 PNIPAm-co-AAc Nanoparticle size measured by dynamic light scattering](image_url)
light scattering, the average hydrodynamic particle size $R_h$ is 206 nm, polydispersity < 0.1.

The molecular weight of the particles was calculated by the static light scattering method (Fig.5.2). Three different concentrations were used in the experiment ($1.1 \times 10^{-4} \text{ g/L}$, $2.3 \times 10^{-4} \text{ g/L}$, $3.5 \times 10^{-4} \text{ g/L}$). The results showed the same weight-average-molecular-mass ($M_w$) was got from the extrapolation of either concentration or scattering angle. The second virial coefficient for the PNIPAm-co-AAc nanoparticles is $2.047 \times e^{-8} \text{ dm}^2/\text{g}^2$.

Fig.5.2 PNIPAm–co-AAc weight average molecular weight was characterized using static light scattering method. The concentration of the three samples used (black points, from
left to the right) was $1.1 \times 10^{-4}$ g/L, $2.3 \times 10^{-4}$ g/L, $3.5 \times 10^{-4}$ g/L respectively. $R_h$ is 206nm. The colored points were the extrapolation result.

The temperature sensitivity of the synthesized nanoparticles was also measured using the UV-Vis spectrometer. Two very interesting phase transitions at both low and high temperatures were observed for three samples we made (Fig.5.3). At lower temperature, the nanoparticles self-assembled into ordered structures under the repulsive electrostatic interaction, the existence of the crystal peaks proved this judgement; when the temperature increased, the thermal vibration of the molecules would destroy the equilibrium formed between the nanoparticles. The crystals started to melt until all of them disappeared to form a clear solution (crystal peaks attenuated to flat showed the evidence according to Fig.5.4) so that the first phase transition (crystal to liquid) was completed; keep increasing the temperature, when the temperature was above $32^0C$, the abrupt jumping of the absorbance (Fig.5.4) showed the second phase transition (liquid to solid). Fig.5.5 showed the appearance change upon heating. At $20^0C$, the crystals could be seen clearly; when the temperature increased to $26^0C$, some of the crystals melted, also the crystal size decreased; at $29^0C$, the crystals totally disappeared, the clear liquid was obtained; when the temperature reached $34^0C$, the solution became completely turbid which was the abrupt jump of the absorbance shown in Fig.5.3.
Fig. 5.3 Turbidity measurement of the PNIPAm-co-AAc colloids with three different concentrations: (a) 15.2 g/L (b) 17.3 g/L (c) 20.1 g/L. The curves shown above dictate the two phase transitions happened upon heating from low temperature to high temperature.
Fig. 5.4 Crystal peaks disappeared upon heating. The melting temperature of the crystals are (a) $17^\circ C$ at 15.2 g/L; (b) $20^\circ C$ at 17.3 g/L; (c) $28^\circ C$ at 20.1 g/L, respectively.
Fig. 5.5 Phase behavior appearance upon heating at concentration 20.1 g/L: (a) 20°C (b) 26°C (c) 29°C (d) 34°C. The diameter of the vial is 1cm.

The change of crystal peak positions vs. the temperature was also plotted in Fig. 5.6. When the temperature increased, the crystal peaks started to move to the smaller-wavelength direction. This is because the particle size decreased when temperature increased which was shown in Fig. 5.7.

Fig. 5.5 Phase behavior appearance upon heating at concentration 20.1 g/L: (a) 20°C (b) 26°C (c) 29°C (d) 34°C. The diameter of the vial is 1cm.

Fig. 5.6 Crystal peak positions vs. temperature for crystalline PNIPAm-co-AAc colloids: (a) 15.2 g/L (b) 17.3 g/L (c) 20.1 g/L.
Fig. 5.7 The nanoparticle size decreased upon increasing temperature. Critical point appeared at $T=33^0\text{C}$.

The phase diagram of the PNIPAm-co-AAc colloid was plotted according to the consequences deduced from the UV test of a series of samples that had different concentration. The result was shown in Fig. 5.8a. From the experimental results, we saw that the PNIPAm-co-AAc colloids could go through four phases: Glass, Crystal, Liquid and Solid. The phase transition among those four phases was understandable. At low temperature, the nanoparticles keep on their positions to form a glass state; when the temperature increases, the thermal action of the particles increases, which can effectively assemble themselves into an ordered structure at certain temperature range, i.e. the crystal phase; at higher temperature, when the thermal action is strong enough to break the equilibrium formed during crystallization process, the crystals melt and then a liquid phase is approached; when the temperature is above the LCST of
PNIPAm-co-AAC colloid (around 34°C), the hydrophobic property of PNIPAm will dominate the micro-structure, this will lead to another phase transition to form the solid phase. Correspondingly the phase diagram for pure PNIPAm colloid was shown in Fig.5.8b [9]. By comparison, we could conclude that the introducing of the charge to the building block of PNIPAm would effectively enhance the crystallization temperature range and increase the crystallization concentration by electrostatic repulsive interaction between the nanoparticles. Another important advantage of introducing functional groups to the building blocks was that three dimensional crystalline nanoparticle network could be prepared by crosslinking the nanoparticles, as we have already made in the previous chapters.

![Phase Diagram](image.png)
Fig. 5.8 (a) Phase behavior of PNIPAm-co-AAc colloids, the hydrodynamic radius ($R_h$) is 206 nm. (b) Phase behavior of pure PNIPAm colloids, the hydrodynamic radius ($R_h$) is 133 nm.

5.4 Conclusion

The phase behavior of PNIPAm-co-AAc colloids was studied using UV-Vis spectrometer measurement. The turbidity results showed that the microgel colloids would undergo two observable phase transitions: Crystal to Liquid, Liquid to Solid. Comparison of the phase behavior between carboxyl-group charged colloids and pure PNIPAm colloids was also performed. The introducing of charge on the building blocks of PNIPAm could remarkably increase the crystallization range by repulsive electrostatic interaction. The introduction of carboxyl group could also lead to the formation of 3D crystalline PNIPAm-co-AAc hydrogel.
Chapter 5 References


CHAPTER 6

ADDITIONAL EXPERIMENTAL RESULTS

6.1 Vibrational Crystallization of Concentrated PNIPAm-co-AAc Colloids

Normally there are three factors which will affect the self-assembling of microgel nanoparticles: particle size ($R_h$), temperature ($T$) and concentration ($C$). Based on the diagram we did from the experiment, concentrated ($C>5\%$ in water) PNIPAm dispersions can only self-assemble into ordered structures at higher temperature. However, the existence of LCST will make the microgel more turbid at high temperature than that at room temperature. In order to get more transparent crystalline dispersions, vibration method was tried for the dispersions with concentration higher than 5\% (Fig.6). The resulted dispersions with iridescent pattern were shown in Fig.6.1i-(b). The turbidity test shown in Fig.6.1(ii) also proved the formation of ordered structure after vibration with the appearing of crystal peak at ~500nm.
Fig. 6.1 Vibration formed crystalline concentrated PNIPAm-co-AAc colloids (a) before vibration (b) after vibration. The cell diameter is 1 cm. Rh is 240 nm, the solid content is 8%.

Fig. 6.2 Turbidity Measurement before and after vibration. Rh is 240 nm, the solid content is 8%.
6.2 Bragg Diffraction of Teared Crystalline PNIPAm-co-AAc Hydrogel

We measured the Bragg-diffraction of teared PNIPAm-co-AAc crystalline hydrogel (Fig. 6.3). Different color could be observed at different angles. This is due to the wavelength ($\lambda$) change resulted from the observation angle $\theta$ according to the formula $2nd\sin\theta = m\lambda$, $n$ and $m$ are integers, $d$ is the layer distance respectively. From the intercept of crystalline hydrogel, we found the crystals were distributed the whole dispersion. It also showed the crystals had been fixed in their positions.
Fig. 6.3 Bragg diffraction of teared crystalline PNIPAm-co-AAc Hydrogel: (a) red, 15° (b) red-green 60° (c) green 90° (d) purple, 120°. $R_h$ is 205 nm, solid content is 3%.
CHAPTER 7

RESEARCH SUMMARY

High solid content (10 wt.%) three-dimensional crystalline PNIPAm-co-AAC acetone gel nanoparticle networks were first-time synthesized. The colored crystal gels can be finger-held, played, compressed to have a big distortion or undergo a solvent exchange. Because of the similar mechanical properties as that of a bulk gel and its optical features, this colored gel may find its way as a sensor or decoration material. It may also be used as a special matrix for separation purposes.

Three-dimensional crystalline PNIPAm-co-AAc nanoparticle networks were prepared by a new route which could result PNIPAm hydrogel with much higher strength. The crystalline hydrogel also has both thermo- and pH- sensitive property.

We further investigated the volume transition equilibrium and the interaction potential between neutral PNIPAM particles dispersed in water using spectrometric and light-scattering experiments. We found from experiments and thermodynamic perturbation theory that aqueous dispersions of PNIPAM particles exhibit phase transitions at both high and low temperatures. The phase behavior of microgel dispersion resembles that for hard spheres at temperatures below the volume-transition temperature. However, at higher temperatures, the
phase separation is driven by van der Waals attractions and metastable liquid-liquid equilibrium exists within the fluid-solid coexistence.

The phase behavior of PNIPAm-co-AAc colloids was also studied using UV-Visible spectrometer measurement. The turbidity results showed that the microgel colloids would undergo two observable phase transitions: Crystal to Liquid, Liquid to Solid. Comparison of the phase behavior between carboxyl-group charged colloids and pure PNIPAm colloids was also performed. The introducing of charge on the building blocks of PNIPAm could remarkably increase the crystallization range by repulsive electrostatic interaction. The introduction of carboxyl group could also lead to the formation of 3D crystalline PNIPAm-co-AAc hydrogel.

Centrifugal vibration method was used to deal with PNIPAm-co-AAc colloidal dispersions at higher concentration. The result showed it was possible to get crystalline hydrogel at high concentration (>5%). More detailed work would be further performed.
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