SYNTHESIS AND CHARACTERIZATION OF MONODISPERSED MICROGEL

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by

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DECLARATION

I hereby declare that the work carried out in this thesis is entirely original. It was carried out at Department of Physics, National Institute of Technology, Rourkela. I further declare that it has not formed the basis for the award of any degree, diploma, or similar title of any university or institution.

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CERTIFICATE

This is to certify that the thesis entitled, **"Synthesis and Characterization of Monodispersed Microgel"** submitted by Ritu Choudhary in partial fulfilment of the requirements for the award of Master of Science in Physics at the National Institute of Technology, Rourkela is an authentic experimental work carried out by her under my supervision. To the best of my knowledge, the experimental matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

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ABSTRACT

Monodispersed Poly [*N*-isopropylacrylamide] (PNIPAM) micro gel has been synthesised by free radical polymerisation reaction. NIPAM, MBA, SDS and KPS were used in proportionate amount for synthesis of PNIPAM microgel. The morphology, shape and size of the prepared monodispersed PNIPAM microgel are characterized by UV-Spectroscopy (UV), Scanning Electron Microscopy (SEM) and Dynamic Light Scattering (DLS) Experimental techniques. The SEM images reveal the particles to be spherical in nature with size of ~ 90 \pm 5 nm. The DLS experiments gives the particles size to be ~ 100 \pm 5 nm with a polydispersity parameter of 0.157.

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<u>CHAPTER 1</u>

INTRODUCTION

1.1 <u>GELS</u>

The term gel (colloidal system) was introduced by Thomas Graham in 1861. He proposed that gel is a continuous solid state extending throughout the liquid and forming a frame work of liquid [1].

Derived from the Latin word "gelatus" meaning "frozen or immobile", gels are defined as the jelly-like materials exhibiting no flow in steady state. Gels have remarkable features. Even though they are mostly thought to be liquids, they do exhibit solid-like behaviour owing to the crosslink's present among the polymer chains extending throughout the systems. Thus these are the dispersion of particles within a liquid, with solid as discontinuous phase and the liquid as continuous phase [1]. The cross link networks present help the gels to attain a particular structure. Gels exhibits both fluidity and elasticity and hence shows viscoelastic properties [2]. There are several ways to identify a true gel.

Herman defined a gel as: 'A coherent system of at least two components, which exhibits mechanical properties characteristic of a solid, where both the dispersed component and the dispersion medium extend throughout the whole system'.

According to Ferry, 'it is a substantially diluted cross linked system which exhibits no steady state flow'. The cross linked networks in the solvent gives it's the hardness.

In polymerization if more than two functional groups (number of binding sites) are present then the formation of three-dimensional interconnected giant molecular structure as shown in the figure below is possible. These structures do not always possess all the features of a gel. Usually, long-chain polymers are cross linked chemically in the solvent medium to produce a chemical gel, which are rigid and can sustain significant amount of compression and shear deformations [2].



Fig.1 (A) A branched polymer, (B) A grafted polymer, (C) A network cluster, and (D) A gel state.

There are numerous examples of applications of gels. Bio-polymeric gels are present in abundance in living organisms; the cornea, the vitreous, and the connective tissues are all gels. Gels serve as excellent surfaces of the internal tracts such as stomach, lungs, kidney basement, and blood vessels [2]. In industries they are used as storage and separation medium [3].

1.2 <u>CLASSIFICATION OF GELS</u>

Gels are classified on depending on the following

- ✓ Source
- ✓ Internal structure
- \checkmark Size of the particles

Depending upon source the gels are of two types

Natural gel: Natural gels are the viscous substance that exists in the nature. It is gelatinous and assumed to be 'sticky'.

Ex: - aloe Vera, Jelly fish, sea algae, clay and in human body it is the cytoplasm which is a typical example of the hydro gels.

> Artificial gel: These are the gels which are synthesised in industries.

Ex: - Cosmetic products, hair gels, ointments etc.

Based on the internal structure

- Physical gel: These are formed by formation of weak bonds like hydrogen bond, vanderwaals forces, hydrophobic and ionic interactions. These are also known as weak gels [2].
- Chemical gel: These are formed by chemical reaction such as co-polymerisation, poly condensation, and vulcanization. The chemical reaction leads to the formation of branched network made up of linear flexible chains attached by covalent bonds and surround by large quantity of solvents. These are also known as strong gels [2].

According to particle size

- Macrogels: Particles are visible by naked eye. They take the shape of the container in which they are placed.
- > Microgels: Particles diameter lies within the range of $1nm-1\mu m$.
- ▶ **Nanogels:** The gels with the particle size of 100 nm or less are placed under this category.

1.3 APPLICATIONS OF GELS

Gels have a wide range of applications in numerous fields of which few are given below.

In personal care

- Hair gel used for setting hair styles
- Shower gel used as a cosmetic body wash
- Face wash, toothpaste, shaving creams, shampoos, body lotions and other cosmetic products.

In pharmaceutics and physical chemistry

➢ Gel capsule, drug delivery, etc.

In biochemistry

Gel Electrophoresis, a method of separation of deoxyribonucleic acid, ribonucleic acid and protein through an electric charge.

- Gel-filtration chromatography, which is used for fractionation of proteins and other watersoluble polymers.
- Gel permeation chromatography is used to analyze the molecular weight distribution of organic-soluble polymers [1].

Colloidal microgel have numerous attractive properties such as good morphology, high porosity and adjustable dimensions that can respond to changes in temperature, pH, solvent quality and the ability to act as carriers for drugs, bio molecules, synthetic polymers or inorganic nanocrystals. Thus these materials are being increasingly used for their potential applications in drug and gene delivery, catalysis, sensing, fabrication of photonic crystals, separation and purification technologies.

Particles having uniform size and shape are monodispersed in nature. Monodispered gels make good crystal structure because of their uniform size and shape. These crystals are used in photonic crystals and photonic band gap structures. Photonic crystals are the periodic array of particles consisting of both high and low dielectric regions. The periodicity or the spacing determines the relevant light frequiences that they allow to pass through [4].

Photonic Band Gap (PBG) materials have a band gap due to a periodicity in the materials having dielectric properties. The band gap in photonic crystals represents the forbidden energy range where photons cannot be transmitted through the material. The size of the band gap is determined by the difference in dielectric constant between the materials used.

PBG structures have many applications which include their use in optical devices as lowloss waveguides, resonant cavities, optical switches, filters and beam shaping for LEDs [5].

Besides the above applications monodispersed gels are considered important as the study of phase transition in them is easier because of weak interactions among the particles. The crystals formed by monodispersed gels have weaker bond stength as compared to that of the solids. So the force required for breaking the bonds is easierr than in solids. Hence the transition study becomes convenient in case of monodispersed gels.

1.4 APPLICATIONS OF NIPAM

> Poly (*N*-isopropylacrylamide) (PNIPAM) microgel is a well-known soft nanomaterial.

Being stimuli responsive PNIPAM microgels have numerous biomedical applications such as drug delivery, bio sensing and catalysis.

✓ In drug delivery:

Synthetic microgels consist of a cross linked polymer network that provides a depot for loaded drugs. The water content in the hydrogels and cross linking density can determine the drug transfer in and out of the gel. They have the unique property of undergoing volume changes in response to environmental factors such as temperature, ionic strength and pH. Thus the controlled release of a drug depends on properties of the drug and polymer design of the microgels [6,7].

\checkmark In catalysis:

The inverse temperature-dependent solubility feature of PNIPAM makes it an attractive polymer substrate for synthesis and catalysis. PNIPAM polymer supports solubility in water at low temperature and solubility lowers down as temperature increases. Such catalysts can be recovered by heating the aqueous solution and then reused after adding fresh water. This behaviour of PNIPAM helps to prepare many recoverable homogeneous substrates [8].

✓ In bio sensing:

PNIPAM hydrogels are used in bio sensing as the hydrogels provide a three dimensional environment for biological interactions. The hydrogels provide inert surfaces that prevent non-specific adsorption of proteins. Biological molecules can be easily bonded to the hydrogels. These gels change property in response to external environmental conditions like temperature, pH, ionic concentration, and solvent composition [9].

✓ In photonic crystals:

PNIPAM micro/nanogel colloidal particles can assemble into crystalline arrays. These crystalline arrays undergo volume phase transition at ~ 35° C, the micro/nanogels exhibit shrinkage resulting in the increase in diffraction and consequently decrease in light transmission in these arrays. This phenomenon has been exploited by the photonic switches and optical filters [10].

1.5 LITERATURE SURVEY

Polymer gels are polymer network, which lose its identity when the polymer chains are cross linked. They show varying physical properties with change in external environmental conditions like pH, temperature, solvent compositions, ionic strength, etc. Due to their varying properties they have been an important area of research [3]. Gels show volume transition when subjected to external stimulus. Gels are often used to immobilise enzymes and are used as carriers of functional groups. The structures of gels are responsible for its shrinking and swelling properties [11].

Gilanyi and his co workers prepared PNIPAM microgels particles by emulsion polymerisation. PNIPAM nanogel particles were synthesised in the presence of inert atmosphere at a temperature of 60°C. The prepared samples were purified by dialysis with distilled water. The samples were cleaned from dust particles using a glass filter of 0.8µm pore size for characterisation. These PNIPAM microgels were characterised by static and dynamic light scattering. The particles were found to be monodispersed. The electrophoretic mobility of the microgel particles was determined using a laser Doppler electrophoretic equipment. The measurements were performed at different ionic strength adjusted by NaCl solution. The total analytical charge of the gel particles were determined by conductometric titration of the sample with NaOH solution. Before titration the sample were purified by mixed anion – cation exchange. The gels were found to be negatively charged [11].

Xiaohu Xia and his co partner Zhibing Hu synthesised PNIPAM microgel by *Jones and Lyon's* method by controlling the reaction time. The microgels showed inverse thermoreversible gelation. The surfactant concentration was seen to have a significant effect on the particle size and on increasing the surfactant concentration smaller particles of microgels could be synthesized. The turbidity measurements were made by UV-Vis spectrometer. The kinetics of particle formation was obtained by measuring the turbidity variation. The particles were also characterised with static and dynamic light scattering. From the light scattering experiments it was found that the hydrodynamic radius of the particle varied as a function of time [12].

Kratz and his partners prepared NIPAM microgels with different cross linker density by surfactant free emulsion polymerisation. Hydrodynamic radius of the colloidal particles was determined by DLS measurement in swollen state at low temperatures. The SEM analysis of the samples was done to determine the shape of the microgel particles. The dried micro gel reveals a spherical shape and order structure on the surface [3]. The morphology of the micro gel particles with different cross linker density were determined by SANS. The temperature dependent measurement provides information of structural changes due to volume phase transition. AFM

studies gave the roughness of the particle interface [3]. The physical parameters were studied by static light scattering and the dynamics by dynamic light scattering [2].

Brijitta group synthesised PNIPAM nanogel particles by free radical precipittion polymerisattion reaction at a temperature of 70 0 C. The samples were purified using celluose bags before characterising by SLS and DLS. The volume phase transition was observed occur at ~ 32.4 0 C. At higher particle concentration PNIPAM nanogels were found to be in the crystalline state [13].

1.6 **OBJECTIVES**

The objectives of this project work are

- > Preparation of monodispersed PNIPAM microgels.
- > Characterization of the sample using UV, SEM and DLS techniques.

1.7 THESIS ORGANISATION:

The thesis has been covered in five chapters.

Chapter 1 describes about the gels and gives some basic idea about it. It focuses on the classification of the gels based on its source, size of the particle and internal bonding. It covers some of the application of gels ranging from day –to day life to industrial uses. It also tells about the applications of NIPAM gels. The chief objectives of this work has also been discussed in this chapter.

Chapter 2 gives a brief idea about the chemicals that has been used in addition to the exact procedure to synthesize the samples required for the SEM and DLS characterization

Chapter 3 covers the experimental techniques used for characterization of the sample. It brings out the basic working principles of UV, SEM and DLS.

Chapter 4 presents the results obtained from the experimental section.

Chapter 5 gives the concluding remarks of the project work.

CHAPTER 2

SAMPLE PREPARATION

2.1 DESCRIPTION OF CHEMICALS FOR MICROGEL PREPARATION

> <u>N-isopropylacrylamide (NIPAM)</u>

Molecular weight – 113.16 gm Molecular formula – (-CH₂CHCONH₂-)



Fig.2 Chemical Structure of NIPAM

NIPAM is a temperature responsive polymer. It forms a three dimensional hydrogel when cross linked with N, N'-Methylene bisacrylamide (MBA). PNIPAM gels have negative thermo sensitivity i.e. they exhibit a remarkable shrinking with increasing temperature. A non continuous collapse transition occurs around 34°C which is called volume phase transition in gels (VPT). These gels are often used to immobilise enzymes and as carriers of certain functional group important for biochemical or biomedical applications. The gels are heated either by a surrounding heat source or internally by an electromagnetic field to control the degree of swelling, consequently controlling the release rate.VPT is caused by molecular interaction i.e. hydrogen bonding, electrostatic repulsion and hydrophobic interaction. In micro phase separation the hydrophilic (swollen) part and part is due hydrophobic (shrunken) part co-exists. It undergoes a phase transition from a swollen hydrated state to shrunken dehydrated state by loosing 90% of its mass [7,10].

Methylene bisacrylamide (MBA)

Molecular weight- 154.17 gm Molecular formula – $C_7H_2N_{10}O_2$



Fig.3 Chemical Structure of MBA

It is acts as a crosslinker. It is used as cross linking agent for acrylamide gel and NIPAM microgel. The two double bonds present at the either ends are responsible for crosslinkage with the acrylamide.

Pottasium persulphate (KPS)

Molecular weight- 270.31 gm Molecular formula- K₂S₂O₈

Fig.4 Chemical Structure of KPS

It acts as an initiator. It initiates the polymerization reaction by radical formation.

Sodium dodecyl sulphate (SDS)

Molecular weight-288.38 gm

Molecular formula-C₁₂H₂₅SO₄Na



Fig.5 Chemical Structure of SDS

It is the surfactant helps in formatation of microgel.

2.2.1 SAMPLE PREPARATION FOR THE SEM CHARACTERISATION

Appropriate amounts of the required chemicals (NIPAM, MBA, SDS, KPS) were weighed. NIPAM was added to 89 ml of double distilled water while MBA and SDS solutions were prepared separately in 10 ml of double distilled water. The reaction mixture was then left for overnight stirring by a magnetic stirrer. The mixture was again stirred for about an hour the following day maintaing a constant temperature 70 ^oC. The whole experimental set-up was kept under an inert atmosphere achieved by passing of the argon gas thrugh the triple necked glass flask. After about an hour 1 ml of freshly prepared KPS solution was added to the reaction mixture. The stirring was continued for next 4 hrs at the above mentioned temperature in the presence of argon gas to obtain the microgels. The experimental set-up is shown in the figure below.



Fig.6 (A) Before Polymerization

(B) After Polymerization



Fig.7 Sample prepared after 14 hrs of stiring

2.2.2 SAMPLE PREPARATION FOR DLS CHARACTERISATION

DLS characterization requires clean and dust free sample, so extra care has been taken in preparing the sample. The milli-Q water used was filtered twice using syringe filters with a pore size 0.22μ . The chemicals of required concentration were dissolved in the filtered milli-Q water. The filtration and mixing of the samples procedure was carried out inside the Horizontal Laminar Flow (Model # CP- HLAF) maintaining ultraclean environment. The rest of the procedure of the sample preparation remains same as that of the SEM sample. Later the prepared sample was again filtered inside the Horizontal Laminar Flow using the syringe filters with same specifications before the DLS characterization to ensure that it is clean and dust free.



Fig.8 Horizontal Laminar Flow



Fig.9 Sample prepared with total of 5 hrs stirring

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 UV SPECTROSCOPY:

Spectroscopy is the study of the electromagnetic spectrum as emitted or reflected by various materials. Ultraviolet-Visible (UV) spectroscopy is useful to study the absorption, transmission and reflectivity in a variety of materials. It measures the intensity of light (I) passing through the sample against the initial light intensity (I_o). This I/ I_0 ratio are known as transmission coefficient.

$$T = I/I_0$$

The absorption coefficient can be determined from the transmission coefficient by using,

$$A = -\log T = -\log (I / I_0) = \log (I_0 / I)$$

where A is absorbance.

UV spectrophotometer is used to measure the extent to which the samples under consideration absorbs, reflects or transmits light at different wavelengths. The instrument automatically records absorbance, reflectance, and transmittance for wavelengths within the specified spectral range.



Fig: 10 Schematic Diagram of UV spectrophotometer

The basic parts of a spectrophotometer are a light source, a sample holder, a diffraction grating, a monochromator or a prism to separate the different wavelengths of light, and a detector. The sources of light is generally a deuterium arc lamp which provides light in ultraviolet region (190 to 350 nm) and Tungsten-Halogen lamp for visible and near infrared region (350 to 1100nm). The detector is generally a photodiode or a CCD camera. Light passing through the cuvette containing sample falls on the mirror one (M_1). The reflected light from the M_1 is incident on the grating and the diffracted light from the grating is directed towards the second mirror (M_2). The detector picks up the signal and displays it as a transmittance/absorbance versus wavelength spectra.

3.2 SCANNING ELECTRON MICROSCOPE

Scanning Electron Microscope is an electron microscope using high energy beam of electrons to scan the sample surface. The incoming electrons interact with the atoms of the sample to emit signals that contain information about the morphology and composition of the sample under scan. Different signals produced due to the electron-matter interaction such as the back scattered, secondary electrons, x-ray carry different information regarding the sample. The figure following the text shows the schematic of a typical SEM instrument.



Fig.11 Schematic diagram of SEM

3.3 DYNAMIC LIGHT SCATTERING

Light scattering takes place whenever an electromagnetic wave interacts with the matter. The incident light is redirected after interaction which is better known as the scattered light. The incoming incident light tends to induce electric dipoles in the matter it passes through. As the em wave is oscillating the dipoles induced oscillates thus resulting in the scattered radiations. The following figure describes the phenomena of scattering of light.



Fig. 12 Scattering of Light

The light scattering is classified as the elastic or inelastic scattering depending on the whether energy changes takes place or not. Besides a different classification of light scattering: static and dynamic light scattering is also provided under the elastic depending on the properties it measures. The static light scattering is so called as it measures the static properties like the molecular weight, second virial coefficient and radius of gyration of polymers under study. Unlike the static light scattering, the dynamic light scattering measures the dynamic properties and diffusion coefficient of the polymer solutions, colloidal suspensions, biopolymers and gels. From the diffusion coefficient one can measure the particle size (hydrodynamics radius) and polydispersity parameter of the system under study. In the text below the DLS characterization technique is described briefly.

DLS is also known as the 'Photon Correlation Spectroscopy' and 'Quasi-Elastic Light Scattering'. DLS is based on the fact that the particles in the solution undergo Brownian motion induced by their bombardment with the solvent molecules which are themselves moving because of their thermal energy [14]. The motion of the particles is random and they keep colliding with the other suspended particles, while doing so they tend to impart momentum to the suspended particles whose magnitude and direction fluctuates with time. This randomness actually is responsible for the experimental realization of this technique. The figure below shows the schematic of the DLS set-up.



Fig. 13 Schematic of DLS set up

When a laser beam is shined through such a solution the beam is scattered in all directions with the particles acting as the scattering centres resulting in scattering angle dependent intensity. As the particles experience the Brownian motion the scattered intensity pattern also fluctuates, the rate of which depends on the size of the particle, as the smaller particles are scattered more than compared to the heavier ones. So the DLS is quite efficient method in determining the size and shape of the particle and the size profile. Even though the dynamic light scattering is a remarkable technique for characterization it is very sensitive to dust and hence extra care has to be taken during sample preparation.

In order to determine the diffusion coefficient one needs to know the field-field autocorrelation, $g_1(q,\tau)$ function given by [14]

$$g_{1}(q,\tau) = \frac{\langle E_{S}(t)E_{S}^{*}(t+\tau) \rangle}{\langle |E_{S}(t)|^{2} \rangle}$$

However the experimental measurement of the field-field correlation function is not possible and so one need to measure the intensity-intensity correlation function, $g_2(q,\tau)$ given by the equation below [14]

$$g_{2}(q,\tau) = \frac{\langle I_{s}(t)I_{s}^{*}(t+\tau) \rangle}{\langle |I_{s}(t)|^{2} \rangle}$$

The intensity-intensity correlation function is related with the field-field correlation function by the Siegert's relation given by the following equation.

$$g_2(q,\tau) = 1 + \beta |g_1(q,\tau)|^2$$

Where β is the coherence factor, depends on the instrumental set-up.

So from the intensity-intensity correlation function one can extract the field-field correlation function using the above equation. The field-field auto correlation function is related to decay constant (Γ) by

$$g_1(q,\tau) \sim \exp(-\Gamma \tau)$$

The decay constant, Γ is given by

$$\Gamma = Dq^2$$

Where D is the diffusion coefficient and q is the scattering wave vector given by,

$$q = \frac{4\pi n \sin \frac{\theta}{2}}{\lambda}$$

Where n is the refractive index of the solution, θ is scattering angle, λ is the wave-length of light.

From the diffusion coefficient, D it is possible to determine the hydrodynamic radius of the particles by using Stokes-Einstein relation given by

$$D = \frac{k_B T}{6\pi\eta r_H}$$

where k_B is the Boltzmann constant, η is the viscosity of the solution and r_H is the hydrodynamic radius of the particle.

CHAPTER 4

RESULTS

4.1 <u>RESULTS OF UV SPECTROSCOPY</u>

The UV analysis was done for both the unreacted monomers and the polymer gels. The absorbance vs. wavelength curve is shown in the figure below.



Fig.14 UV spectrometer Schimadzu, Model # UV-2450



Fig. 15 Graph showing UV-Vis curves

The absorbance maximum occurs between 200-300 nm. Moreover it can be inferred from the graph that the absorption maximum tends to decrease with the dilution of the sample. The minimum absorbance was observed for the unreacted sample.

4.2 RESULTS OF SEM



Fig.16 SEM JEOL, Model # T-330

The SEM characterization was done with a JEOL (Model # T-330) experimental set-up.

SEM characterisation was done samples with different dilutions. The diluted samples were mixed in ultrasonic vibrator for half an hour. Then slides of samples having different concentration were made and are left to dry for an hour at a temperature of 70°C. The sample slides were coated with platinum before the characterization was done on them.



Fig. 17 SEM Images of the Sample

From SEM images it can inferred that the particles are nearly spherical in shape and of sizes ~ 90 ± 5 nm. The bigger particles are due to aggregation of the microgels during the slide preparation for SEM Images.

4.3 <u>RESULTS OF DLS</u>



Fig.18 DLS Malvern ZS-90

The DLS measurements were done with a Malvern (Model # ZS-90) experimental set-up.

Before the DLS characterization the prepared samples were filtered with the syringe filter with the pore size 0.22 μ to remove the dust that might interfere with the results. The filtered sample was then diluted to 1% and 5% of the initial concentration. The diluted samples were again filtered to ascertain it is dust free and suitable for DLS characterization. The experiment was carried out a constant temperature of 35 0 C.



Fig.19 Field-Field Auto Correlation Function

Figure 19 shows the field-field auto correlation function extracted from the intensityintensity auto correlation function using Siegert's relation. The correlation function decays from ~ 1 at t = 0 (short time) to 0 at t = 1 ms (Long-time).



Fig.20 Field-Field Auto Correlation Function fitted to cumulant equation

Figure 20 shows the cumulant fit to the field-field auto correlation function, $g_1(q, \tau) = e^{-\Gamma \tau}$. The solid line is the cumulant fit to the crosses (experimental data). It can be seen a good agreement between the experimental points and the fitting.



Fig.21 Graph showing particle size

Figure 21 shows the particle size distribution. The particle size distribution has a peak around 100 nm with a polydispersity of 0.157.

CHAPTER 5

CONCLUSION

In the present work, we have prepared monodispersed PNIPAM microgel and studied the particle size, shape and morphological properties using different experimental techniques. The following are the conclusion drawn from experimental measurements.

- > SEM results show the PNIPAM microgel particles to be spherical in shape.
- > The particle size obtained from SEM is ~ 90 ± 5 nm.
- > The DLS shows particle size of ~ 100 ± 5 nm.
- The polydispersity index obtained from the DLS results are 0.157, indicating the synthesized microgel is fairly monodispersed in nature.

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