Carbon Dioxide and Nitrogen-Modulated Shape Transformation of Chitosan-Based Composite Nanogels

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ABSTRACT: Chitosan/poly[N-(3-(dimethylamino)propyl) methacrylamide]/poly(acrylic acid) (CS/PDAMPA/PAA) composite nanogels (CPACNGs) were fabricated in the solution of chitosan by surfactant-free emulsion polymerization. N-(3-(Dimethylamino)propyl)methacrylamide (DAMPA) and acrylic acid (AA) were initiated by 2,2′-azobis-2-methyl-propanimidamide to graft from the backbone of chitosan. Nanogels were formed by noncovalent forces, including of hydrogen bonds, hydrophobic, and electrostatic interaction. Nanogels were characterized by transmission electron microscopy, scanning electron microscope dynamic light scattering, X-ray photoelectron spectroscopy, Fourier transform infrared spectrometer spectra, and 1H NMR. Spherical nanoparticles were observed in the latex system. Nanogels exhibited an excellent CO2 responsivity and CO2/N2 reversible response and switchability and had a faster response rate. The morphological shape transformation of nanogels was modulated by bubbling with CO2 and N2. The responsive mechanism was explored by determining the pH and electrical conductivity. In addition, nanogels were successfully emulsified by bubbling with CO2, and then a phase transition was achieved by bubbling with N2 in the organic solvent/water mixture.

1. INTRODUCTION

Over the years, stimulus-responsive materials have received increasing attention with a high potential value in many fields.1 Stimuli-responsive nanogels have rapidly developed for potential applications, such as controlled release, oil recovery, water treatment, and Pickering emulsion2−6. Under stimulation, the chemical properties of these “smart” nanogels can be reversibly altered by interactions between polymer chains and solvent molecules, leading to significant phase-volume changes that make them valuable switchable materials.7−8

The most widely studied highly effective stimuli are temperature, pH, and light.9−10 In particular, carbon dioxide (CO2)-responsive materials were widely applied in CO2 capture and separation.11 CO2 is a weak gaseous acid that can interact with amine, amine, and carboxyl groups to change molecular hydrophilic or hydrophobic properties.12

CO2-responsive polymers have been used as a novel and valuable type of stimuli-responsive polymer over recent years.13,14 They are a new type of polymer with reversible change of properties after purging and releasing CO2. Compared with the traditional triggers, such as pH, temperature, and light, CO2-responsive polymers showed some unique advantages.15 For instance, they showed reversible responses via purging and releasing CO2 without substance accumulation and could be repeated in more responsive cycles with low sensitivity depletion.16 In addition, CO2-switchable latexes could be reversibly coagulated by N2 bubbling and redispersed by CO2 bubbling.17,18 CO2-controllable responsive polymeric nanoparticles exhibit excellent thermal properties and unique temperature/pH responsiveness as well as the ability to switch CO2/N2, which has made them attractive multifunctional polymer nanoparticles with wide application prospects.19

In recent years, a lot of natural polymers have been used to fabricate CO2-responsive shape memory hydrogels.20−22 Compared with traditional shape memory hydrogels, CO2-responsive shape memory hydrogels have many advantages. For example, after several reversible cycles, the performance does not fade and there is no accumulation, which has a great potential application.23

Previously reported systems based on synthetic polymer had many disadvantages, such as the use of a cross-linking agent and surfactant in the preparation process, which limits their further application. Chitosan is the only alkaline polysaccharide in nature that is rich and easy to gain, renewable, naturally nontoxic, biodegradable, and biocompatible. Chitosan contains a large amount of primary amine (−NH2) and is a potential candidate for CO2-responsive polymers.24−27 Moreover, chitosan could be used as an emulsifying agent in the surfactant-free emulsion polymerization process to ensure emulsion stability in the preparation process. Chitosan (−NH2) exhibited a good CO2-responsive cross-linking/de-cross-linking by purging/removing CO2 in the response process to achieve the purpose of shape memory. There are a few studies on the preparation of chitosan into a CO2-responsive shape memory.

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In the current paper, a new type of CO₂-responsive composite nanogel based on chitosan was fabricated. N-(3-(Dimethylamino) propyl)methacrylamide (DMAPMA) and acrylic acid (AA) were functionally incorporated into the nanogels of CS using CO₂-responsive 2,2′-azobis-2-methylpropanimidamide (VA-044) as the initiator. CS/PDMAPMA/PAA composite nanogels (CPACNGs) were prepared by the self-assembly surfactant-free emulsion polymerization in the chitosan solution (Scheme 1). Through noncovalent forces, such as hydrogen bond, hydrophobic, and electrostatic interaction, physical cross-linking is generated by the combination within chains. The effects of AA and DMAPMA content on the stability of composite nanogels and their morphologies were investigated to further explore their effects on the CO₂ response performance. In addition, the responsive mechanism was explored by determining the pH and electrical conductivity. Emulsification and phase transition of nanogels were further investigated in the organic solvent/water mixture.

### 2. RESULTS AND DISCUSSION

#### 2.1. Preparation and Characterization of Nanogels (CPACNGs)

In the current paper, monomers AA and DMAPMA were initiated by VA-044 to fabricate CS/PDMAPMA/PAA composite nanogels (CPACNGs) in the chitosan solution. CS/PDMAPMA/PAA composite nanogels were formed by the physical and chemical cross-linking among CS, AA, and DMAPMA. Table 1 shows that composite nanogels (CPACNGs) were prepared by varying the concentration of monomers (i.e., DMAPMA and AA) in the chitosan solution.

The amino groups (−NH₂) on the backbone of chitosan have a high reactivity to form a chitosan-based grafting copolymer.  

As shown in Scheme 1, the initiator VA-044 generates an activated free radical on the amino group (−NH₂) of chitosan and then introduces monomers AA and DMAPMA grafting from the main chain of chitosan. In general, latex was commonly prepared by emulsion polymerization. Chitosan with a hydrophobic backbone chain and hydrophilic side group was used as an emulsifier in the surfactant-free emulsion polymerization process. Therefore, chitosan is beneficial for the formation of nanogels and makes the latex more stable due to its emulsifier properties. Then, DMAPMA can be protonated under acidic conditions. Combining DMAPMA and AA into the nanogels of CS can form physical cross-linking through noncovalent forces, such as hydrogen bonds, hydrophobic piles, and electrostatic interactions, and through association within and between chains to form a semi-interpenetrating polymer network (semi-IPN).

In the present paper, composite nanogels (CPACNGs) were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectrometer spectra (FTIR), and ¹H NMR. As shown in Figure 1, in the FTIR spectrum of composite nanogels (CPACNGs), the characteristic peak (C═O) occurred at 1740 cm⁻¹, −COOH of PAA occurred at 1462 cm⁻¹, C−N occurred at 1261 cm⁻¹, and the characteristic peaks occurred at 2800–3000 cm⁻¹ for −CH₂ and −CH₃.

As shown in Figure 2, ¹H NMR (D₂O/trifluoroacetic acid-d) (95:5, v/v) of CPACNGs: δ = 0.68 ppm (−CH₃ of PDMAPMA), 1.6–1.93 ppm (−CH₂− of PDMAPMA and PAA), 1.95 ppm (−COCH₃ of CS), 2.55 ppm (−N(CH₃)₂ of PDMAPMA), 3.01 ppm (CH of CS), 3.05–3.21 ppm (CH₂ of PDMAPMA), 3.44–4.00 ppm (CH and CH₃ of CS), 4.70 ppm (CH of CS). Compared with the ¹H NMR spectrum of CS, CPACNGs showed new proton peaks, which were attributed to PDMAPMA and PAA.

### Table 1. Preparation of CS/PDMAPMA/PAA Composite Nanogels (CPACNGs)

| Sample   | DMAPMA (g) | AA (g) | Gelation | CS/PDMAPMA/AA | Amine/Acid Mole |
|----------|------------|--------|----------|---------------|-----------------|
| CPACNGs4-1 | 1.00       | 0.05   | Transparent | 12.5:25:2     | 1.42            |
| CPACNGs4-2 | 1.00       | 0.10   | Transparent | 15:30:1       | 1.85            |
| CPACNGs4-3 | 1.00       | 0.15   | Transparent | 15:30:2       | 1.66            |
| CPACNGs5-2 | 1.25       | 0.10   | Latex     | 15:30:3       | 1.49            |
| CPACNGs6-1 | 1.50       | 0.05   | Latex     | 17.5:35:2     | 1.89            |
| CPACNGs6-2 | 1.50       | 0.10   | Latex     | 17.5:35:2     | 1.89            |
| CPACNGs6-3 | 1.50       | 0.15   | Latex     | 17.5:35:2     | 1.89            |
| CPACNGs7-2 | 1.75       | 0.10   | Latex     | 17.5:35:2     | 1.89            |

Note: Composite nanogels (CPACNGs) were prepared by varying the concentration of monomers (i.e., DMAPMA and AA) in the chitosan solution.
The morphology of the CS/PDMAPMA/PAA composite nanogels was investigated by SEM (Figure 3). CPACNGs were spherical nanoparticles with a diameter of 100 nm. The TEM image revealed that most nanogels with a diameter of about 100 nm were of uniform size and gathered together, and a few nanogels with a diameter of about 200 nm were also observed (Figure 4).

The size distribution and zeta potential of CPACNGs-3 were measured by DLS. The DLS results showed a large number of nanogels in the diameter peaks at 272 nm with a width of 22 nm (Figure 5). The zeta-potential results are shown in Figure 6. The zeta potential of CPACNGs-3 is 59 mV with a width of 7 mV. It was reported that the larger the absolute value of the zeta potential, the greater the repulsive force between colloids than the attractive force. The data of DLS revealed that the latex of composite nanogels was stable and uniform in size in the present system, and the surface of composite nanogels carried a large of positive charges.

The XPS of CPACNGs is shown in Figure 7. It can be found that the carbon spectrum is an asymmetrical peak (C 1s), that is, 286.35, 284.88, and 284.35 eV. The peak of 284.35 eV is attributed to sp² C−C in the nanogels, the peak of 284.88 eV is attributed to the carbon atom in sp³ C−C in the nanogels, and the peak of 286.35 eV is attributed to a small number of carbon atoms of C=O. The nitrogen spectrum (N 1s) was also fitted to the following three peaks: 399.1, 399.7, and 400.35 eV. The peak of 399.1 and 399.1 eV is assigned to −NR−C=O and R−NH−R from PDMAPMA. The peak of 400.35 eV is attributed to the nitrogen atom in the amino groups (−NH₂) from the chitosan. The oxygen spectrum was similarly fitted to the following peak at 531.6 eV. This peak is assigned to the oxygen atom in C=O.

2.2. CO₂-Responsivity of CS/PDMAPMA/PAA Composite Nanogels (CPACNGs). In the current paper, the mass ratio of chitosan to monomers influencing the CO₂-response
performances of nanogels was studied. The effect of the DMAPMA monomer quantity on the response performance was investigated, as shown in Figure 8a. CPACNGs5-2, CPACNGs6-2, and CPACNGs7-2 were prepared by varying the mass of DMAPMA and keeping the contents of AA. As shown in Figure 8a, when CPACNGs5-2 and CPACNGs6-2 were prepared at a low concentration of DMAPMA, the nanogels exhibited an excellent CO2 responsivity. However, CPACNGs7-2 was prepared at a higher concentration of DMAPMA and noticeable CO2 responsivity cannot be observed.

Figure 8a shows that another monomer, AA, also influenced the CO2 responsivity of composite nanogels. CPACNGs6-1, CPACNGs6-2, and CPACNGs6-3 were prepared by varying the mass of AA and keeping the contents of DMAPMA. The nanogels exhibited an excellent CO2 responsivity when CPACNGs6-2 and CPACNGs6-3 were prepared at a higher concentration of AA.

CPACNGs5-2, CPACNGs6-2, and CPACNGs6-3 have more complete response and a faster response rate. CPACNGs5-2 reaches the response equilibrium within 3 min. CPACNGs6-2 reaches the response balance in about 4 min. CPACNGs6-3 reaches the response balance in about 2 min, which is an improvement compared with our previous work, a response balance of about 5 min, indicating that the physically cross-linking CS/PDMAPMA/PAA composite nanogels have a faster response rate and better reversible response effect.

CPACNGs5-2, CPACNGs6-2, and CPACNGs6-3 also have good reversible responsiveness (Figure 9). The reversibility of the response with CO2 treatment was further examined to explore if the gas-switchable process could be reversed by purging the system with inert gas N2. The gas-replacement process was repeated by gas aeration for 3 cycles in the order "CO2 → N2 → CO2 → N2 → CO2 → N2". As shown in Figure 9, multi-cycling CO2 and N2 aeration was carried out for 3 cycles, and no loss in the gas responsivity was observed. The result demonstrated that nanogels have a good reversible response.

Figure 7. XPS spectrum of CPACNGs: (a) the full spectrum of CPACNGs, (b) the nitrogen spectrum of CPACNGs, (c) the carbon spectrum of CPACNGs, and (d) the oxygen spectrum of CPACNGs.

Figure 8. Transmittance of the nanogels latex with the change of the weight ratio of DMAPMA to AA [(a) 5:2, 6:2, 7:2 and (b) 6:1, 6:2, 6:3] by passing CO2.
Figure 10 shows the appearance of the nanogels latex after CO$_2$ and N$_2$ treatment. The original nanogels latex (left) was creamy white. After purging with CO$_2$ (middle) for 10 min, the creamy white latex became clear gradually. The nanogels latex remained as a stable dispersion after being treated with CO$_2$, and particle coagulation was not observed. A turbidity measurement confirmed the optical changes. The transmittance of the original nanogels latex was 6.58%. After purging with CO$_2$ for 10 min, the transmittance increased to 91.49%. After purging with N$_2$ for 20 min, the system was returned to the original latex state (right) and the transmittance decreased to 12.12%.

From the SEM image, the morphology of CS/PDMAPMA/PAA composite nanogels before and after CO$_2$/N$_2$ treatment was observed (Figure 11). Figure 11a shows that the nanogels are spherical nanoparticles with a diameter of 50 nm. After purging with CO$_2$ for 5 min, the morphology of the nanogels changed dramatically (Figure 11b). The regular sphere was destroyed and became an irregular microstructure. This could be attributable to chitosan (−NH$_2$) reacting with CO$_2$ in the presence of water to form carbamate, which acted as cross-linking points to cause the association of the chitosan chains. Meanwhile, the tertiary amine groups of PDMAPMA, the carboxyl groups of PAA, and a large number of initiator residues, including imidazole groups presented in the structure of nanogels, were easily protonated/unprotonated by CO$_2$ in an aqueous solution. In order to balance the osmotic pressure generated by the charges, water molecules swelled into the nanogels network, which reduced the system’s light-scattering index and led to the creamy-to-transparent conversion. Thus, optical changes in the nanogels suspension took place via the CO$_2$-responsive behavior.

Figure 11c shows that the morphology of the nanogels was returned to original spherical nanoparticles after purging with N$_2$ for 20 min. It was clear that the morphology of the nanogels returned to its original state. It was hypothesized that the dissolved CO$_2$ molecules could be easily washed off by N$_2$. Figure 9. Transmittance of the nanogels latex with the different weight ratio of DMAPMA to AA (DMAPMA: AA (m/m) = 5:2, 6:2, and 6:3, respectively) by 3 cycles passing CO$_2$/N$_2$.
bubbling to recover the original state of the nanogels. The results indicated that the nanogels had a good morphological switchability by CO₂ and N₂ bubbling.

Figure 12 shows that the transmittances of the nanogels system were treated by bubbling CO₂ for different times. When bubbling CO₂ for 30 s, the transmittance of the nanogels suspension increased slowly. Subsequently, it was rapidly increased within 1 min. It reached the equilibrium by bubbling CO₂ for 2 min. This was result to the initial reaction of chitosan chain (−NH₂) with carbon dioxide leading to the aggregation of nanogels. When CO₂ was further introduced, the transmittance increased rapidly, because the nanogels expanded rapidly. Then it reached the equilibrium of swelling gradually.

2.3. Effect of the CO₂-Responsive Process on the pH Value of CS/PDMAPMA/PAA Composite Nanogels. Figure 13 shows that the pH of CS/PDMAPMA/PAA composite nanogels latex was influenced in the process of CO₂ injection at a constant rate of 16 mL/min. At the beginning, the pH value of the original latex was determined as 7.3. When CO₂ was injected within 0.5 min, the pH value decreased rapidly and was determined to be 6.2. Afterward, the pH value decreased slowly. After 2 min, the pH value remained basically unchanged, indicating that the response balance was achieved, and the pH value remained basically unchanged after CO₂ was continuously injected. When N₂ was introduced, the nanogels system returns to its original state, and the pH value was 7.3, which is consistent with the pH value of the original latex. Figure 14 shows that the pH value of the nanogels system did not change by multi-cycling CO₂ and N₂ aeration, which further indicates that the response behavior of nanogels was reversible.

The nanogels consisted of CS, PDMAPMA, and PAA. CS and PDMAPMA contained the free amino groups, and PAA contained the carboxyl groups. All these functional groups were considered CO₂-responsive groups and were introduced into the skeleton of the polymers to fabricate CO₂-responsive composite materials. The pKₐ of PDMAPMA, CS, and PAA were 8.8, 5.5–6.5, and 4.5, respectively. At pH 7.3, the amino groups of PDMAPMA should be protonated before the CO₂ addition. Meanwhile, the carboxylate groups from PAA should not be protonated at a pH of 6.2. Therefore, when the pH decreased from 7.3 to about 6.2 by CO₂ injection, it was attributed to the presence of the free amino groups from CS in the nanogels. In addition, it cannot be ignored that the free amino groups reacted with CO₂ to form carbamate in the presence of water.

2.4. Effect of the CO₂-Responsive Process on the Conductivity of CS/PDMAPMA/PAA Composite Nanogels. CO₂ or N₂ was injected into the CS/PDMAPMA/PAA composite nanogels suspension in the order "CO₂ → N₂ → CO₂ → N₂ → CO₂ → N₂" at a constant rate of 16 mL/min, and the conductivity was measured at room temperature. The conductivity of the nanogels suspension depends on the ionic strength. The dielectric constant of the CS/PDMAPMA/PAA composite nanogels suspension was studied to detect the change in ionic strength during CO₂ and N₂ cycling. Figure 15a shows that the conductivity of the nanogels suspension was increased gradually by CO₂ injection within 2 min. It can be found that the conductivity remains unchanged after 2 min. When the nanogels suspension was increased gradually by CO₂ injection, this rule of the change in conductivity was in accordance with that of pH.

Afterward, N₂ gas was infused to the nanogels suspension treated by CO₂. Figure 15b shows that the conductivity was first decreased and was then increased with the passage of N₂ gas. Because CO₂ in the nanogels system is easy to be driven out by N₂, it results in the decrease of its charged particles. Figure 16 shows the change of conductivity in the 3 cycling of CO₂/N₂, and the results further indicate that the nanogels system has good reversibility.

2.5. Emulsification and Phase Transition of CS/PDMAPMA/PAA Composite Nanogels in the Organic Solvent/Water Mixture. Figure 17 shows the CO₂/N₂ switching emulsification performance of CS/PDMAPMA/PAA composite nanogels in the mixture 1:4 (v/v) of n-hexane to nanogels system. When n-hexane was added into the...
nanogels system and was shook, the mixture was divided into 2 layers, consisting of the transparent n-hexane solution in the upper layer and the suspension in the lower layer (Figure 17a,b). Subsequently, when CO₂ was injected into the mixture, the suspension in the lower layer became transparent, and the n-hexane solution was still in the upper layer, while the nanogels suspension responded to CO₂ gas in the lower layer (Figure 17c). The amino groups of nanogels were protonated by CO₂ bubbling in water and increased the hydrophilicity of nanogels. The latex became a transparent solution. The whole mixture was shook and then became an unlayered suspension (Figure 17d). On further infusing N₂ gas, the nanogels suspension divided into a white suspension in the upper layer and a transparent solution in the lower layer (Figure 17e). After bubbling N₂, CO₂ was driven out of the mixture, and nanogels gradually acquired a hydrophobic state, allowing it to disperse in the oil phase, that is, n-hexane. The results indicated that nanogels were successfully emulsified by bubbling with CO₂, and then a phase transition was achieved by bubbling with N₂ in the n-hexane/water mixture.

The experimental results show that CS/PDMAPMA/PAA composite nanogels have a good switching emulsification performance of CO₂/N₂, and the system is expected to have a great application prospect in the field of oil and water separation, drug carrier, and so on. In addition, it also proves once again that the proposed response mechanism is correct, providing a theoretical basis for the further development of new intelligent CO₂ materials in the future.

3. CONCLUSIONS

In the current work, chitosan-based nanogels, consisting of chitosan (CS), PDMAPMA, and PAA, were successfully prepared by surfactant-free emulsion polymerization. Composite nanogels exhibited an excellent stimuli responsivity, and their microstructures were controlled by the addition or removal of CO₂ as an external stimulus. The nanogels had a good morphological switchability by the CO₂-responsive cross-linking/de-crosslinking of chitosan (−NH₂) and the protonation/deprotonation of other CO₂-responsive groups in aqueous solutions. Emulsification and phase transition of nanogels were achieved in the organic solvent/water mixture by cycling of CO₂ and N₂ bubbling. It is expected that chitosan-based composite nanogels have broad application prospects as intelligent devices, biosensors, CO₂-adsorbent materials, and drug carriers.

4. EXPERIMENTAL SECTION

4.1. Materials. DMAPMA (98%, Aldrich), chitosan (CS, 95%, Sangon Biotech), AA (99%, Sinopharm Group), 2,2′-azobis-2-methyl-propanimidamide (VA-044, AR, Aldrich), and acetic acid (AA, 99.5%, Shanghai Chemical Industry) were used as received. Other chemical reagents were of analytical grade and were used as received. Distilled water was used in the present experiment. CO₂ and N₂ gases were controlled by LZB-3WB flow meters to maintain a constant gas flow of 16 mL/min.

4.2. Preparation of Chitosan/Poly[DMAPMA/Poly(acrylic acid)](CS/PDMAPMA/PAA) Composite Nanogels (CPACNGs). 0.25 g CS was dispersed in 50 mL 0.6% of acetic acid solution under stirring at room temperature, until dissolved completely. CS/PDMAPMA/PAA composite nanogels with different compositions were prepared by surfactant-
free emulsion polymerization using 2,2′-azobisisobutyronitrile (VA-044) as the initiator. 50 mL chitosan solution and 0.7 mL DMAPMA were added into a 100 mL three-neck flask. The reactor was magnetically stirred at 300 rpm and purged with nitrogen for 5 times. Then, VA-044 solution (50 mg/1 mL) was injected into the reactor until the reactor was gradually heated to 60°C. 0.8 mL of monomer (i.e., DMAPMA) and 0.15 mL of monomer (i.e., AA) was dissolved in 9.7 mL of water prior to the preparation of 10 mL mixture solution of monomers. After stirring for 2 hours, 10 mL mixture solution of DMAPMA and AA was added dropwise within 25 min. Subsequently, the polymerization was continuously carried out for 5 h. The reaction was stopped by exposing the latex to air and cooling down to room temperature, and the creamy-white latex was obtained. The powder was obtained by centrifugation at 9000 rpm on the centrifuge (TGL-20M, Changsha Pingfan Instrument Co. Ltd.) for 5 min and dried under vacuum at room temperature for 3 days.

4.3. Characterization. CPACNGs powder was combined with KBr crystals and was then pressed into a pellet. FTIR was recorded by an FTIR spectrometer (VERTEX 70, Bruker, Switzerland) and scanned from 4000 to 400 cm⁻¹. CPACNGs powder was dissolved in the mixed solvent (D₂O/trifluoroacetic acid-d) (95:5, v/v) at 25°C to prepare the sample for the measurement of ¹H NMR spectra. ¹H NMR spectra were performed at 500 MHz using an AVANCE III 500 spectrometer (Bruker). The surface electronic state of CPACNGs was determined by XPS (PHI-5702). The original latex was diluted 15 times to prepare the sample for the measurement of SEM, TEM, and DLS. The morphology of CPACNGs was observed by SEM (JSM-6701F, JEOL Ltd., Tokyo, Japan). TEM was performed on a JEM-1200EX microscope (Japan Electron Optics Lab. Co. Ltd. (JEOL), Tokyo, Japan). The size distribution and zeta potential were measured by DLS (Mastersizer 3000).

4.4. CO₂ Responsivity Tests of CS/PDMAPMA/PAA Composite Nanogels (CPACNGs). 6 mL CPACNGs latex was moved into the CO₂-response device. The nanogels latex was purged by CO₂/N₂ gas in the order CO₂ → N₂ → CO₂ → N₂ → CO₂ → N₂ at a constant flow rate of 16 mL/min for 3 cycles. CO₂ and N₂ gas aeration was continued for 10 and 20 min, respectively. Then, the transmittance of the nanogels suspension was recorded at 550 nm by a UV–vis spectrophotometer (UV-2012PC/PCS). The conductivity of the nanogels latex was recorded by a conduct meter (DDS-11A). The pH of the nanogels suspension was recorded by a digital pH meter (PHS-2S).

4.5. Test of Emulsifying Properties of CS/PDMAPMA/PAA Composite Nanogels (CPACNGs). 4 mL CPACNGs latex was mixed in 1 mL n-hexane. Phase separation was observed in the bottle. After purging CO₂ at a constant rate of 16 mL/min for 5 min, the change of suspension was recorded with a camera. Then, N₂ was purged at a constant rate of 16 mL/min for a continuous time of 20 min, and the change of suspension was recorded with a camera.

Author Contributions
The paper was written through contributions of all authors. All authors have given approval to the final version of the paper.

Notes
The authors declare no competing financial interest.

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Abbreviations

1H NMR, nuclear magnetic resonance; AA, acrylic acid; CO₂, carbon dioxide; CPACNGs, chitosan/poly[N-(3-(dimethylamino)propyl)methacrylamide]/poly(acrylic acid)-(CS/PDMAPMA/PAA) composite nanogels; CS, chitosan; D₂O, deuterium oxide; DLS, dynamic light scattering; DMAPMA, N-(3-(dimethylamino)propyl)methacrylamide; FTIR, Fourier transform infrared spectrometer; PAA, poly(acrylic acid); PDMAPMA, poly[N-(3-(dimethylamino)propyl)methacrylamide]; SEM, scanning electron microscope; TEM, transmission electron microscopy; UV–vis, ultraviolet–visible; VA-044, 2,2′-azobisisobutyronitrile; XPS, X-ray photoelectron spectroscopy

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