

Synthesis and Investigation of Stimuli-Responsive Amphiphilic Latex Nanoparticles by the Seeded Emulsion Polymerization

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ABSTRACT

Stimuli-responsive amphiphilic core-shell polymer nanoparticles are important categories of smart materials which have been studied due to their advantages of changing physical or chemical properties in response to stimuli. In this study, poly[2(dimethylamino)ethyl methacrylate] (PDMAEMA) as the hydrophilic core with hydrophobic layer polystyrene (PS) as shell were synthesized by the seeded emulsion polymerization to achieve dual-sensitive core-shell nanoparticles (CSNP). Temperature and CO₂ dually-responsive CSNPs were investigated as two important smart behaviors. The CSNPs were characterized by dynamic light scattering (DLS) and scanning electron microscopy (SEM). In addition, two essential parameters including the polymerization conversion and stability of latex polymers were investigated. Obtained results showed that the hydrophilicity-hydrophobicity balance of the latex nanoparticles could be changed by the variation of temperature and the induction of CO₂ gas flow, as a result of temperature and CO₂ dual-responsivities of the PDMAEMA core. The particle size of the CSNP was increased when the temperature rised above the lower critical solution temperature (LCST) of the PDMAEMA. It is due to the formation of hydrogen bonds between water molecules and the tertiary amine group which leads to swelling in PDMAEMA below the LCST, and deswelling by losing water above the LCST of the PDMAEMA. Furthermore, the size of the latex nanoparticles was increased from 696 nm to 853 nm after CO₂-bubbling which led to increasing hydrophilicity or swelling of PDMAEMA by absorbing water in latex nanoparticle.

1. Introduction

Stimuli-responsive polymers are some of the most important classes of intelligent materials that have different applications such as being used in smart biotechnologies, gene-deliveries, chemosensors, and also biomedicine [1,2]. The core-shell latex nanoparticle is a significant category of

stimuli-responsive polymers that has been extensively investigated in recent years [3]. Many methods have been proposed for the preparation of core-shell latex nanoparticles among which the emulsion polymerization is the most applicable and efficient method [4]. Any changes in polymerization conditions can significantly affect the particle size and

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the morphology of the core-shell latex nanoparticles [5,6]. In the stimuli-responsive latex nanoparticles, the core or shell should be based on responsive polymers that display the variation of physical or chemical properties in response to induced external stimuli.

Many scientific reports focused on the synthesis and applications of temperature-responsive polymers. Most temperature-responsive polymers have LCSTs, and display the phase separation or insolubility by increasing temperature above LCSTs of these polymers [7–11]. Two temperature-responsive polymers include poly(*N*-isopropyl acrylamide) (PNIPM) and PDMAEMA. Until now, various amphiphile core-shell nanoparticles have been synthesized by using PNIPAM as core or shell, as Zhang et al. [12] developed thermo-responsive hollow microgels based on PNIPAM which was prepared by the seeded emulsion polymerization of P(styrene (St)-co-NIPAM) as core and a cross-linked PNIPAM shell. Naseem et al. [13] successfully synthesized temperature and pH responsive PS-P(*N*-isopropylmethacrylamide-acrylic acid) [PS-P(NIPMAM-Aac)] core-shell particles. The responsivity of CSNP was investigated by the variation in particle size. As the pH increased, at the first the particle size increased and then decreased due to the protonation and deprotonation of the carboxylate group respectively. These synthesized core-shell particles were used as adsorbents for the heavy metals removal. Mazloomi-Rezvani et al. [14] fabricated core-shell nanoparticles by the inverse emulsion polymerization in which the gold nanoparticle was used as core and developed stimuli-responsive polymers for a smart drug-delivery system with different shells such as poly(acrylic acid) (PAA), poly(methacrylic

acid) (PMAA), PNIPAM, poly(*N*, *N*'methylenebis(acrylamide)) (PMBA), poly(2-hydroxyethyl methacrylate) (HEMA) and PDMAEMA. They investigated the drug loading and releasing in each of these nanoparticles. Hu et al. [15] reported the preparation of copolymer nanoparticles by using styrene as a commercial monomer and 2(dimethylamino)ethyl methacrylate (DMAEMA) via the emulsion polymerization, and investigated the drug releasing of these nanoparticles with the changes in pH. Fuji et al. [16] fabricated stimuli-responsive particles as foam stabilizers: pH and temperature dual-responsive with using PS particles carrying PDMAEMA hairs (PDMA-PS particles). Hemmatpour et al. [17] synthesized nanotubes, modified and functionalized them by using (3-Aminopropyl)triethoxysilane (APTES), alpha-bromoisobutyryl bromide (BiBB) and PDMAEMA. The sensitivity of prepared nanotubes to pH was investigated by the solution stability and particle size. Those nanotubes were more stable at a low pH due to the repulsion of the protonated tertiary amine groups. Dehghani et al. [4] synthesized cross-linked PMAA nanoparticles as polyelectrolyte seeds by the distillation precipitation polymerization (DPP) and then functionalized with DMAEMA and 2-hydroxyethyl methacrylate (HEMA) via the seeded emulsion polymerization to prepare core-shell nanoparticles with various morphologies. Results showed that the feeding method effected the morphology of the latex nanoparticles and different morphologies were achieved by changing the feeding method to ones such as core-shell and Janus particles.

An advantage of amphiphilic core-shell nanoparticles is their unique properties of

being easily controlled by changing the composition and structure of the core or shell [15,18-20]. In addition, the sequence of monomers especially has an impact on the properties of amphiphile core-shell nanoparticles such as the particle size, particle swelling and particle responsivities, which have been used in many applications. In recent studies, among smart polymers, PNIPAM is one of the most studied materials due to its thermal properties [9-11, 17, 21]. CO₂-responsive polymers gained much attention in addition to temperature-responsive polymers, because CO₂ is a cheap, available, and safe gas [22]. PDMAEMA is one of the polymers which is also responsive to CO₂ in addition to temperature [12, 6, 23-29]. PDMAEMA has an LCST of about 41 °C [1,2], which exhibits a phase separation behavior above this temperature and becomes insoluble in the aqueous medium.

In the present study, stimuli-responsive amphiphile core-shell latex nanoparticles were synthesized by the seeded-emulsion polymerization of PDMAEMA as the responsive hydrophilic core and PS as a hydrophobic shell. In addition, we investigated the influence of temperature and bubbling of CO₂ gas on particle size of smart latex nanoparticles. The conversion of the polymerization reaction and the colloidal stability are two important parameters in the emulsion polymerization, so the influence of the temperature, initiator concentration and feeding approach were investigated on both parameters.

2. Experimental

2.1. Polymer characterization

The dynamic light scattering (DLS) analysis was carried out by a particle size analyser model Vasco3 made by Cordouan company.

The samples were diluted 100 times by DI water. For the SEM analysis, one droplet of dispersion with 1000 dilution and staining with phosphotungstic acid was placed on a small sheet of aluminium and dried at the ambient temperature for 24 h. After drying, the SEM images visualization was conducted on LEO Vp1450 device at a voltage of 20 kV.

The solid content of emulsion and the polymerization conversion were calculated by using equations 1 and 2. In equation 1, m_S , m_M , m_C , m_I and m_W are the weights of the surfactant, monomer, cross-linker, initiator, and water respectively. In equation 2, m_1 , m_2 , m_3 are the weight of the dry polymer, latex polymer, and sample container respectively:

$$\text{Solid content} = (m_S + m_M + m_C + m_I) \text{ (g)} / (m_W) \text{ (g)} \quad (1)$$

$$\text{Conversion} = (m_2 - m_1) / (m_3 - m_1) / (\text{solid content}) \quad (2)$$

2.2. Synthesis of stimuli-responsive latex nanoparticles

PDMAEMA-PS latex nanoparticles were prepared by the seeded emulsion polymerization as shown in Figure 1. All polymerizations were carried out in a 50 ml three-neck glass reactor equipped with a reflux condenser.

The reaction temperature was controlled in the range of 70-75 °C. The polymerization was performed using styrene and DMAEMA as monomers, SDS as the surfactant, EGDMA as the crosslinker and KPS as the initiator. The final conversion and solid content were calculated by equations 1, 2. The emulsion polymerization recipe has been given in Table 1.

For the investigation of the effect of the feeding method, three methods for synthesis of amphiphilic core-shell nanoparticles of PDMAEMA-PS were performed. The amount of ingredients of three methods were constant,

and just the feeding approach (i.e. the time of the initiator injection, surfactant or monomer) was changed. In method 1, the DMAEMA monomer was injected into the system, the initiator was injected for 40 min and the surfactant was slowly injected during the time of synthesis. For method 2, the initiator was added in 40 min and the DMAEMA and surfactant were entered from the beginning of

the polymerization. According to method 3, the DMAEMA monomer and surfactant were entered into the polymerization set-up, and then the initiator was injected into the system in about 20 min. For the investigation of the effect of temperature, the method 3 was implemented at two temperatures of 70 and 75 °C.

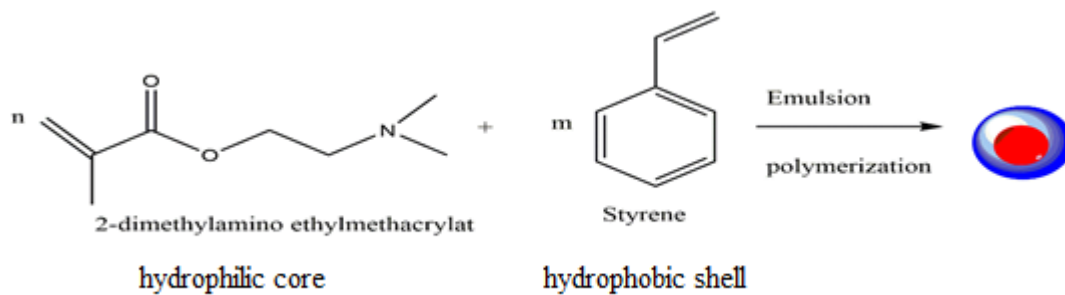


Figure 1. Schematic representation for the synthesis of PDMAEMA-PS CSNPs.

Table 1

Recipe for the amphiphilic core-shell emulsion polymerization of PDMAEMA-PS.

Ingredient		Weight (g)	Comment
First monomer	DMAEMA	0.33	17 wt % based on monomer
Cross linker	EGDMA	0.038	2 wt % based on monomer
Surfactant	SDS	0.11	5 wt % based on monomer
Initiator	KPS	0.02	1 wt % based on monomer
Second monomer	Styrene	1.68	83 wt % based on monomer

3. Results and discussion

Figure 2A indicated the SEM result of the stimuli-responsive latex nanoparticles that confirmed the particle size about 200 nm and spherical morphology. In addition, Figure 2B showed the DLS results of PDMAEMA-PS core-shell nanoparticles which confirmed the result of SEM images. The DLS results were plotted for the CSNPs at two temperatures of 25 °C, below the LCST of PDMAEMA, and 70 °C, above the LCST of PDMAEMA. According to DLS results, the hydrodynamic diameter of CSNPs particles increased from 696 nm to 1066 nm due to changing

temperatures below and above the LCST of PDMAEMA. In fact, swelling and deswelling of CSNPs could be related to water absorption and release respectively. They are soluble in water at the ambient temperature, and display the phase separation or insolubility with increasing the temperature above the LCST. But the particle size increased at 70 °C, above the LCST of the PDMAEMA, which could be the result of the aggregation of the latex nanoparticles [4,30,31]. The DLS analysis was used to investigate the CO₂-responsivity of the PDMAEMA-PS CSNPs (shown in Figure 2B)

and to study the change of particle size. The particle size of the latex nanoparticles was increased from 696 nm to 853 nm because the CO₂ bubbling in latex might led to formation of carbonic acid. The resulting carbonic acid reacts with the tertiary amine functional group of PDMAEMA and could lead to the protonation and quaternization of CSNPs.

Therefore, the CO₂ bubbling led to the increase of the hydrophilicity of the PDMAEMA core, the increase of swelling and particle size of CSNPs. The responsivity of the stimuli-responsive core-shell latex nanoparticles toward CO₂ and temperature was confirmed by DLS analysis.

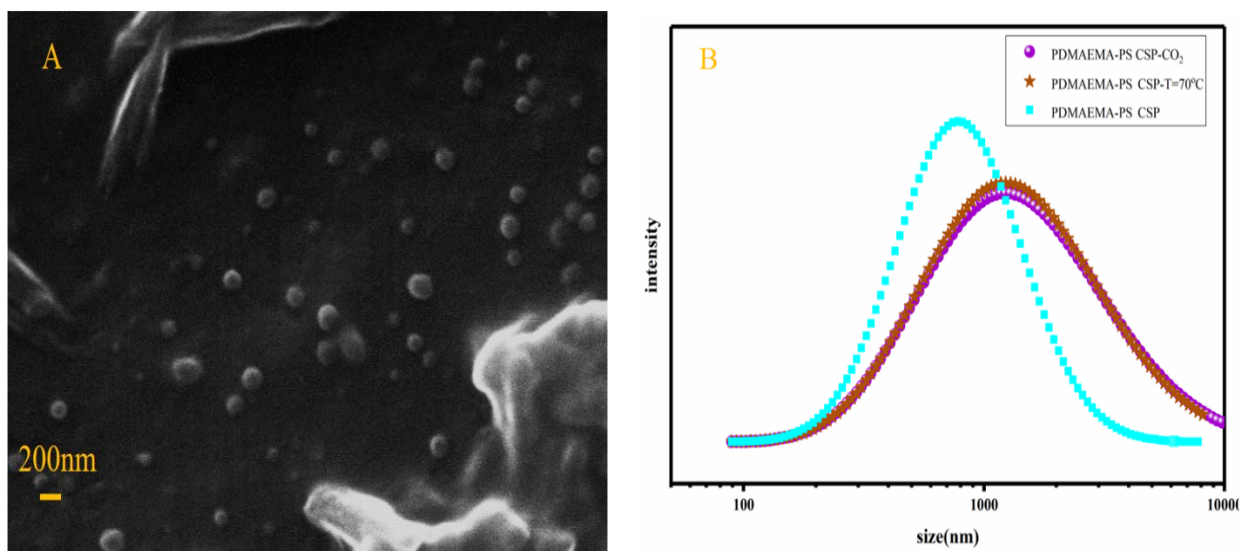


Figure 2. SEM image (A) and DLS analyses (B) of synthesized PDMAEMA-PS amphiphile core-shell nanoparticles in response to CO₂ and temperature.

In Figure 3A, the effect of the feeding method of synthesis was investigated on the obtained solid content and the conversion of the emulsion polymerization. Because of the constant amounts of ingredients used in the synthesis through three aforementioned methods, the obtained solid contents were the same. However, the conversion was changed by altering the feeding method. The polymerization conversion increased when the time of injection of the initiator decreased in the method 3 compared to the method 1. The stability of the synthesized polymers by method 3 was greater than that of the same in methods 1 and 2 (as shown in Figure 3B). Because the initiator was injected for a longer time in method 1, PDMAEMA was formed

and the injection of the surfactant during synthesis led to not having enough surfactant to cover the entire surfaces of the polymer particles [6, 32-35]. In method 2, similar to method 1, the PDMAEMA was formed but the amount of the initiator was low for continuing synthesis and the formation of PS, because the initiator was injected at a longer time and the chains terminated with free radicals, thus polymer samples synthesized by method 2 had less stability because of remaining styrene in the synthesis medium. In method 3, because the surfactant was present from the beginning of the polymerization, there was enough surfactant in the system to cover the entire surface of all particles, resulting in a good stability of latex polymers.

Figure 4A showed the influence of temperature on the solid content and the polymerization conversion as two main studied parameters. According to previous results, the feeding method 3 was selected to synthesize the CSNP at various temperatures. The obtained solid content was unchanged due to the constant amount of ingredients of

synthesis, but the conversion varied with changing of reaction temperature as expected. At a higher polymerization temperature, the conversion would be increased, resulting in lowering the number of remaining monomers in the prepared latex. Similarly, the latex stability could be increased as shown in Figure 4B.

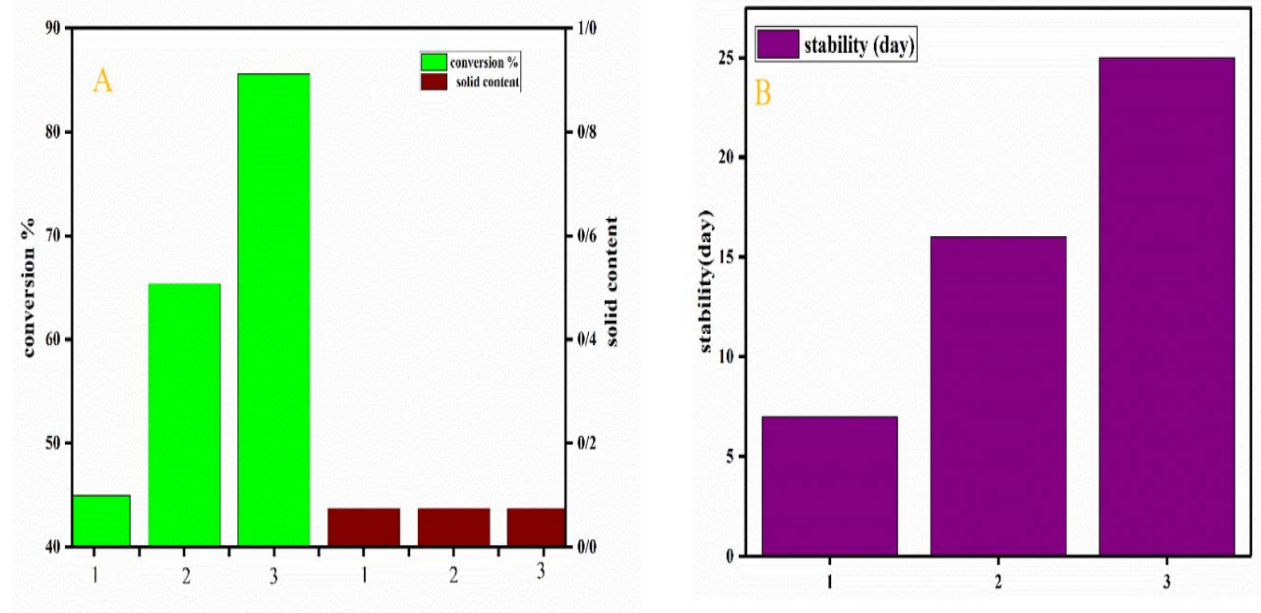


Figure 3. Influence of the feeding method on (A) the polymerization conversion and (B) the latex stability of PDMAEMA-PS CSNPs.

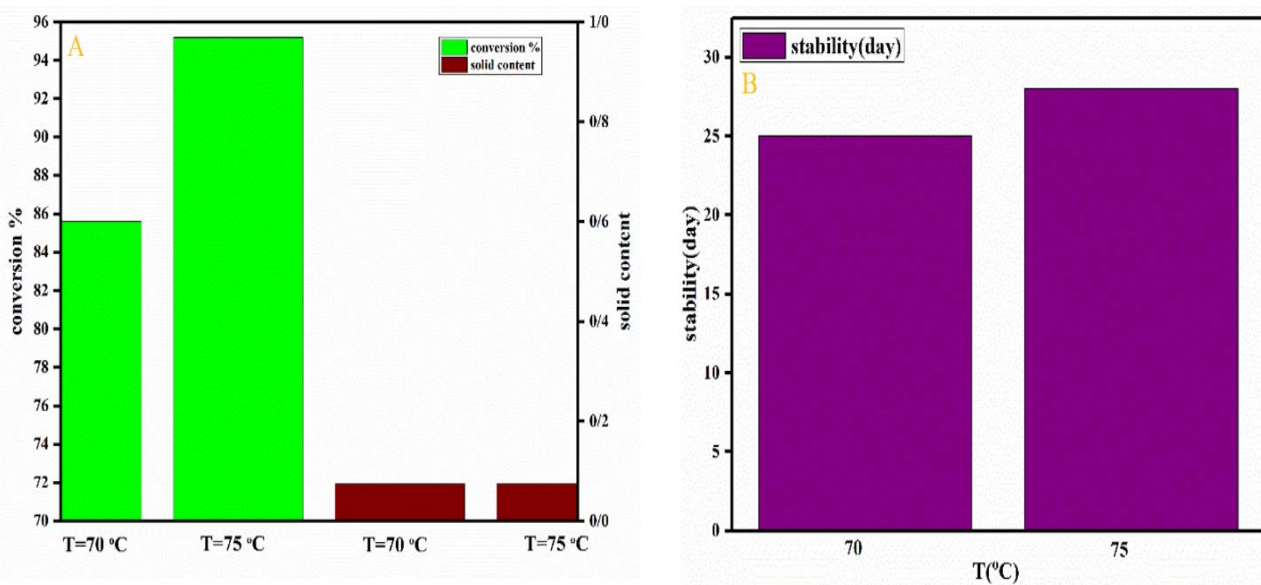


Figure 4. Effect of the reaction temperature on (A) the polymerization conversion and (B) the latex stability of PDMAEMA-PS CSNPs.

In Figure 5, the effect of the initiator concentration (based on weight percent of total monomers) ranging from 2 to 8 wt % was investigated on the polymerization conversion. As the amount of the initiator

increased, consequently the formation of free radicals increased, resulted in an increase of the polymerization rate and the final produced polymer samples, so the reaction conversion was enhanced as expected.

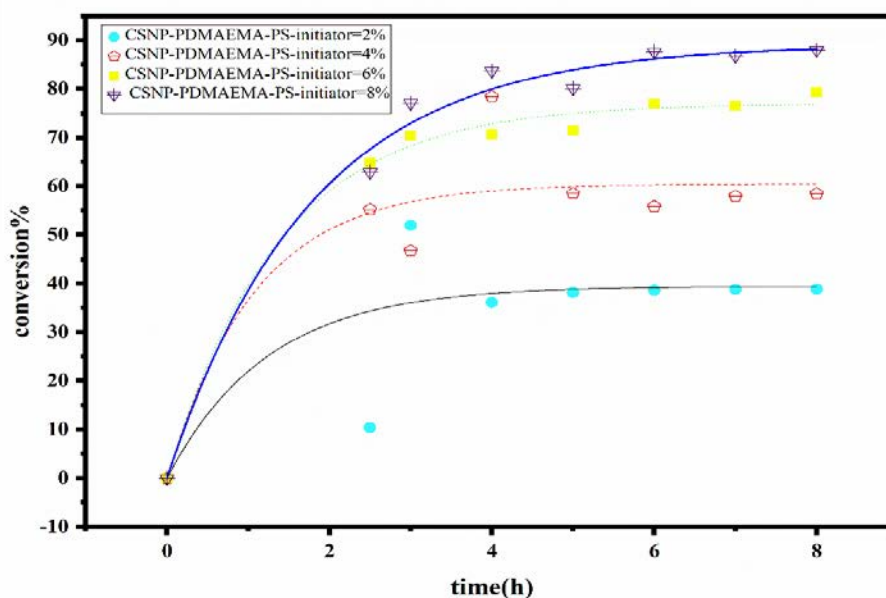


Figure 5. Influence of initiator on the emulsion conversion of the synthesized PDMAEMA-PS CSNPs.

As shown in Figure 6, by increasing of the polymerization conversion, the remaining monomers in the polymerization system were reduced and the prepared latex showed more stability at higher reaction conversions. As the amount of the initiator increased, there

were more free radicals to continue the synthesis and formation of PS, and caused the remaining monomer in the latex to decrease with increasing conversion which led to more stability.

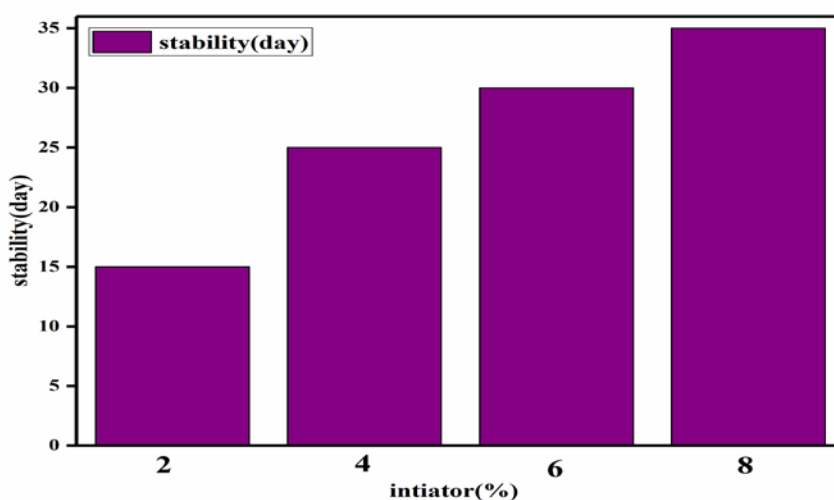


Figure 6. Effect of the initiator weight percent on the latex stability of the synthesized PDMAEMA-PS CSNPs.

4. Conclusions

In this work, the dual-responsive amphiphile core-shell nanoparticles have been synthesized by the seeded emulsion polymerization. The prepared PDMAEMA-PS CSNPs were responsive to temperature and CO₂ stimuli. The influence of the feeding method on the conversion and stability of the colloidal solution was investigated in detail. The DLS and SEM characterizations were used to evaluate the particle size and morphology evaluation of synthesized stimuli-responsive amphiphile core-shell nanoparticles. The particle size of PDMAEMA-PS CSNPs was significantly increased by CO₂ gas bubbling and changing the temperature of the latex solution. At temperatures above the LCST of PDMAEMA core, the aggregation of nanoparticles might have occurred and polymer samples with bigger particle size were observed. Also the CO₂-bubbling perhaps quaternized the tertiary amine functional group of PDMAEMA and increased the hydrophilicity of the PDMAEMA core, so the particle size of latex samples could increase.

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