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Preparation of Temperature-Responsive PDMAEMA-PS Core-Shell Polymer Nanoparticles

Zeinab Sadat Hosseini[a,d] , **Ali Dashti**[b,d*] , **Amin Abdollahi**[c]

[a] MSc student, Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran.

[b] Associate professor, Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran.

[c] Ph.D Student, Department of Polymer Engineering, Sahand University of Technology, Tabriz, Iran.

[d] Research Laboratory of Polymer Testing (RPT Lab.), Research Institute of Oil & Gas, Ferdowsi University of Mashhad, Mashhad, Iran.

[*]Corresponding author, E-mail: dashti@um.ac.ir.

Abstract

Stimuli-responsive polymer nanoparticles are a significant class of smart materials were investigated extensively in recent years because of potential applications in different fields such as drug-delivery and gen-delivery systems. In this research, a temperature-responsive core-shell polymer nanoparticles (CSPs) by emulsion polymerization of styrene (hydrophobic shell) and dimethylaminoethyl methacrylate (hydrophilic core) was synthesized, which core crosslinked and shell grafted on its surface. Dynamic light scattering (DLS) was used to investigation of particle size and its distribution, and scanning electron microscopy (SEM) used for study of the morphology of core-shell nanoparticles. Obtained results showed that the CSPs have a size about 100 nm. The particle size of CSP was decreased by increasing of temperature above lower critical solution temperature (LCST) of the PDMAEMA. It is due to swelling of core with water below LSCT, and deswelling from water above LCST of the PDMAEMA.

Keywords: Core-shell, temperature-responsive, emulsion polymerization, nanoparticles.

1-Introdction

Core shell particles (CSPs) is included at least two different components, one at the center as a core and coating layer surrounding as a shell. Because of desirable characteristics this class of polymers, They can used different application such as drug delivery, enhanced oil recovery, coating and composites [1-5]. One of this aspect and properties that has gained much attention in last year, is core or shell with stimuli responsive properties. Senff et al. [6] prepared core–shell poly(styrene/ poly(N-isopropylmethacrylamide)) (PSt/PNIPAM) latex with temperature sensitive shell that particle size of PSt core is 42 nm. Studies showed that the latex was stable against flocculation at high temperatures. Chi et al. synthesized thermo responsive core–shell that poly(ethylene glycol) ethyl ether methacrylate (PEGEEMA) as a core and poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) and poly(acrylic acid) as a shell .The core–shell particles have a very narrow size distribution and have biocompatibility.

Zeiser et al. [8] reported a novel design strategy of linearly thermo responsive core-shell microgels, with a shell of poly(N-n-propylacrylamide) (PNNPAM) and a core of poly(N-isopropylmethacrylamide) (PNIPMAM). This material might be advantageous for responsive coatings. Ramli et al. [7] synthesized poly(styrene-co-methyl methacrylate) (P(St-co-MMA)) core and poly(acrylamide-coacrylic acid) (P(AAm-co-AAc)) shell microgels. Due to the interplay of thermodynamics, the resulting CSP cannot simply be described as a core–shell type but can use for drug releasing coatings. Zhang et al. [9] synthesized pH-sensitive core-shell microsphere of sodium acrylate as shell on crosslinked polyacrylamide particle as core by surface-initiated atom transfer radical polymerization (SI-ATRP) that microspheres of this type used for enhance oil recovery. Tamsilian et al. [10] carried out nano inverse emulsion polymerization to prepare core shell PNIPAM nanoparticles as core with hydrophobic coating layer PSt as shell that used for polymer flooding process. Mazloomi-Rezvani et al. [11] fabricated different core-shell nanoparticles with Au as core and stimuli-responsive polymers such as poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), poly(N-isopropylacrylamide) (PNIPAAm), poly(N,N'-methylenebis(acrylamide)) (PMBA), poly(2-hydroxyethyl methacrylate) (PHEMA) and poly((2-dimethylamino)ethyl methacrylate) (PDMAEMA) as shells were via inverse emulsion polymerization that Synthesized core shell nanoparticles were utilized as nanocarriers of DOX as anti-cancer drug and drug release. Hu et al. [12]. synthesized monodispersed poly(styrene-co-N,N′-dimethylaminoethyl methacrylate) nanoparticles (P(St-co-DMAEMA) NPs) by emulsion polymerization that targeted drug delivery to tumors. Fujii et al. [13] fabricated a particulate foam stabilizer sensitive to two stimuli: pH and temperature with using PS particles carrying poly[2(dimethylamino)ethyl methacrylate] (PDMA) hairs (PDMA-PS particles).

The same previously mentioned studies of core-shell particle, in the present work prepared core shell with using PDMAEMA as core and St as shell, This polymer has a lower critical solution temperature (LCST) point, above that the polymer exhibits phase separation behavior and becomes insoluble in the medium that monomers can polymerize at temperatures above their LCST by emulsion polymerization and prepare the polymer nanoparticles. In addition, we investigated the influence of altering temperature and time on nano particle size due to special significance in different applications.

2- Experimental

2-1- materialS and methods

2-dimethyleamino ethyle methacrylate(DMAEMA), Potassium persulfat (KPS; Kian shimi), Styrene (St; above 99%, DAEJUNG Reagent chemical), Sodium dodecyle sulfate (SDS; Purity > 99%, Pars tous), Ethylene glycol dimethacrylate (EGDMA; 98%, 90 to 110 ppm MEHQ)

2-2- Synthesis

PDMAEMA/PSt core shell nano spheres were synthesized via emulsion polymerization with the following procedure: the designated amount of DMAEMA monomer, SDS as surfactant and 30ml distilled water were added into a three necked 50ml flask equipped with a reflux condenser and a mechanical strire for15 min at 70°C. Afterward KPS as initiator and EGDMA as cross linker agent were added drop wise respectively for 20 min at 70°C then styrene were added the solution drop wise for 2.5 h at 70°C. PSt/PDMAEMA core shell nano spheres were prepared from recipe as shown in table1.

Table 1. Recipe for core-shell emulsion polymerization

Ingredient		Weight (g)	Comments
Monomer	DMAEMA	0.33	1.4 % solids content
Cross Linker	EGDMA	0.038	10 wt % based on monomer
Surfactant	SDS	0.11	
Initiator	KPS	0.02	
Second monomer	St	1.68	

2.3. Polymer characterizations

Dynamic light scattering (DLS) tests was conducted by Particle Size Analyzer model Vasco3 made by Cordouan company. For SEM test a drop of dispersion was placed on a small piece of a small aluminum sheet and drying at room temperature for 24 h. After drying, sample was coated with gold by SC 7620 spin coater for 120 seconds and for the next step the SEM images were performed by using of LEO450 Vp device with a resolution of 2.5 nm. The SEM images were photographed under a voltage of 20 kV in different magnifications

3. Results and Discussion

In the attempt to synthesize p (DMAEMA/St) core shell, various experimental parameters were affected on morphology of core shell and particle size. Some factors were time of polymerization, concentration of monomer and temperature [6,8,14,15,16]
The results of two parameters are summarized in Table 2.

Table2. Core-shell samples for DLS analysis

Sample ID	Temperature of DLS test (^{0}C)	Time of polymerization (h)	DLS	
			PDI	Z ave(nm)
CSP8	25	3	0.23	120.3
CSP9	25	4	0.28	359.3
CSP10	25	6	0.145	670.8
CSP8-T	70	3	0.19	57.9

Figure 1 showed the SEM result of core shell nanosphere that confirmed the particle size 100-600 nm.

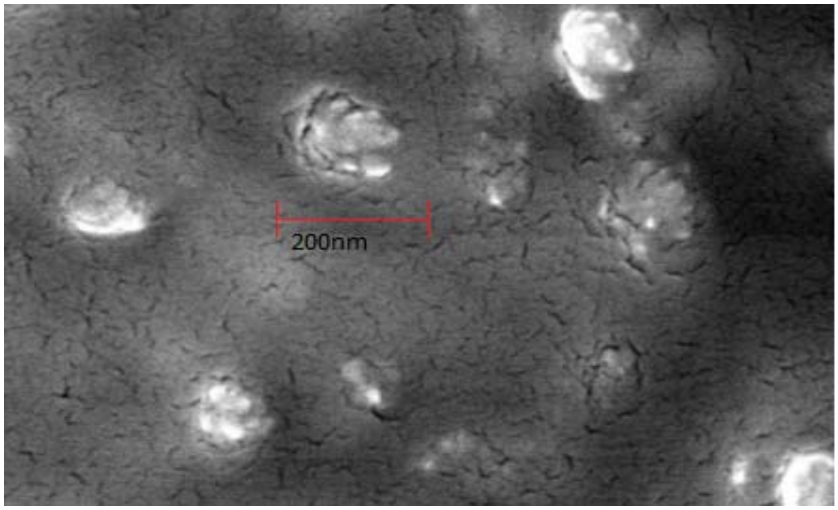

Figure 1. SEM image of PS/PDEAEMA core-shell nanosphere

Figure 2 and 3 showed the Dynamic Light Scattering (DLS) results of poly dimethyleamino ethyle methacrylate – polystyrene nanoparticles. Figure 2 showed the effect of temperature on particle size of core shell. The test was performed at two different temperatures of 25℃ and 70 ℃ (below and above LCST of PDMAEMA). As shown in Figure 2, because there are one-peak distributions for particle sizes at both temperatures, the core-shell structure was successfully synthesized. Particle size was decreased by increasing temperature above LCST of the PDMAEMA. It is due to swelling of core with water below, and its deswelling from water above LCST of the PDMAEMA. Figure 3 showed the effect of time on particle size of core shell. The average diameter of core-shell particles is in the range of 120 And 670 nm. it can be seen that particle size and volume swelling ratio increased with increasing time of polymerization, the results can be explained by free radical mechanism of polymerization, when time increased, there would be more probability for a large number of monomer's free radicals in the system to combine with each other to form macromolecules with long chain and particle size increased [17].

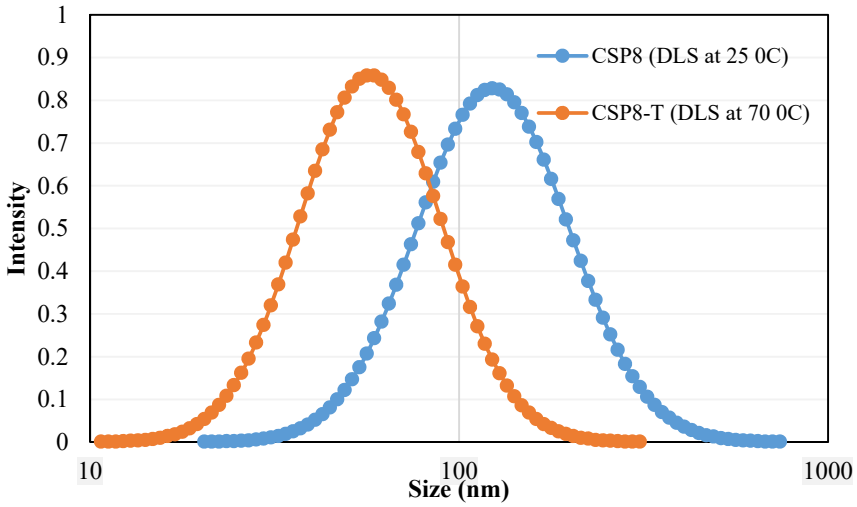

Fig2. Size distribution of the synthesized core-shell nanoparticles by DLS at 25 ℃ and 70 ℃

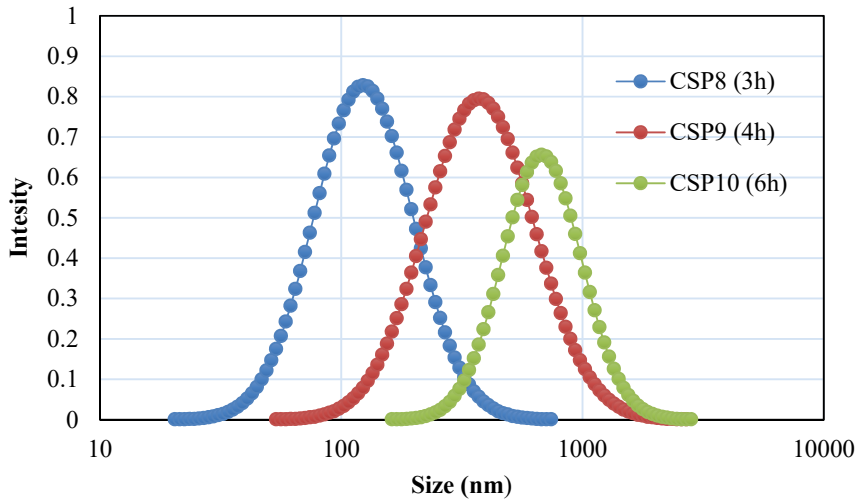

Figure 3. Size distribution of the core-shell nanoparticles at various times of polymerization.

4- Conclusions

In this work was fabricated thermo responsive core-shell sphere based on a PDEAEMA cross linked network and St, due to responsive nature of this nanosphere and particle size can use in different applications such as EOR. DLS and SEM characterization were used to disclose the formulation process and the morphologic evolution from uniform sphericity of the core-shell structure. The particle size of CSPs are significantly decreased with changing the temperature and time of polymerization.

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