



## **Preparation of Temperature-Responsive Core-Shell Polymer Nanoparticles for Enhanced Oil Recovery Application**

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### **Abstract**

A particular core-shell polymer nanoparticle of poly(N-isopropylacrylamide)/polystyrene (PNIPAM-PS) was synthesized for EOR applications in tight carbonate reservoirs. The CSP of PNIPAM-PS was synthesized by two-stage emulsion polymerization at 70 °C using KPS initiator, and SDS surfactant and ethylene glycol dimethacrylate (EGDMA) as stabilizer. The obtained polymers were characterized by dynamic light scattering (DLS) particle size analysis, scanning electron microscope (SEM) and differential scanning calorimetry (DSC) thermal analysis. Experimental results showed that CS nanoparticle sizes are in the range 50-130 nm. The CS nanoparticles with porous and spherical morphology were observed by SEM pictures. Furthermore, the ability of polymer particles to be effective in the reservoir's temperature was investigated.

**Keywords:** Core-shell polymer, PNIPAM-PS, Polymer flooding, Enhanced oil recovery, mobility ratio

### **Introduction**

Polymer injection is one of the known chemical methods for enhanced oil recovery (EOR), which involves the injection of a displacing fluid (polymer solution) into an oil reservoir to mobilize the crude oil trapped, due to the fingering effect or heterogeneity, in the reservoir porous rocks [1]. In such applications, the displacing phase should have a mobility lower than the mobility of the reservoir oil phase [2]. There are a wide range of polymer and co-polymer types applied for EOR all around the world. The most common EOR polymers are polyacrylamides (HPAM) [3], biopolymers (Xanthan Gum) [4], superabsorbent polymer composites (SAPc) [5], and hydroxy ethyl cellulose (HEC).

Most of the Iranian carbonate reservoir rocks has a very low injectivity due low matrix permeability and small pore size distributions. Hence, a new smart nanoparticle polymer which permeates the reservoir with an appropriate injectivity may be a remedy for this drawback. Beside this important parameter, other specific properties such as polymer efficiency in presence of the reservoir brine, mechanical degradation residence, thermal stability at reservoir temperature, low retention (e.g., adsorption) in porous rock, efficiency in presence of oil or gas and sensitivity to O<sub>2</sub>, H<sub>2</sub>S and pH need to be considered for synthesizing and evaluating of a new developed polymer [6]. The goal of this research is synthesis of a special core-shell polymer particles for EOR applications in Iranian tight carbonate reservoirs.

For this purpose, the core-shell polymer nanoparticles based on poly-N-isopropylacrylamide (PNIPAM) as hydrophil core, and also poly-styrene (PS) as hydrophobe shell was prepared by seed-emulsion polymerization method. This polymer has a lower critical solution temperature



(LCST) point, above that the polymer exhibits phase separation behavior and becomes insoluble in the medium. This feature has made it possible to polymerize the acrylamide monomers at temperatures above their LCST by emulsion polymerization and to prepare the desired polymer nanoparticles. Two important points were considered here. First, because of the high solubility of polyacrylamides in water, they were crosslinked by ethylene glycol dimethacrylate (EGDMA). So, after completion of the reaction, the porous spherical morphology of the particle, which was created at a temperature above its LCST, was preserved. Second, the time of addition of crosslinker was critical, because it had a great influence on the size of the final polymer particles [7].

### **Materials and Methods**

The used materials are N-isopropylacrylamid (NAIPAM; 99%, stabilized with 500 ppm MEHQ (monomethyl ether of Hydroquinone), EXIR wein Austria), 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 as stabilizer 1,2-ethanediol dimethacrylate ethylene dimethacrylate, EXIR wein Austria) and Deionized (DI) water.

Synthesis and preparation of PNIPAM-PS CSP nanoparticles was carried out according to the recipe of McPhee et al. [8], with some modifications in using different materials and amounts, shown in table 1. To prepare styrene, alumina column was used to remove the inhibitor and also to further purification. The reactor was stabilized at 70°C in a thermostated water bath by means of a magnetic heater (IKA C-MAG) as shown in Figure 1. In order to prepare PNIPAM seed particles, a mixture of PNIPAM with SDS and deionized water was stirred at 300 rpm for 20 minutes. Afterward, KPS dissolved in deionized water was added to the reactor. Then, EDGMA (crosslinker) was injected slowly by syringe whithin 20 min. The styrene monomer and a solution of SDS (according to Table 1) were added simultaneously to PNIPAM seed mixture by dropping funnel for 2 h. The whole process of polymerization took almost 5.5 h and when the milky latex was observed, the polymerization was completed.

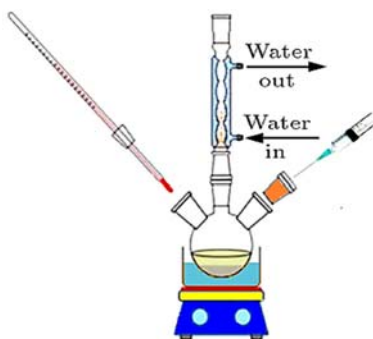


Figure 1. Scheme of the polymerization setup.

Dynamic light scattering (DLS) tests was conducted by Particle Size Analyzer model Vasco3 made by Cordouan company.



Scanning electron microscopy (SEM) tests were done to evaluate the samples. For the SEM test, we placed a drop of sample (10 times diluted by DI water) on the surface of a small aluminum sheet. 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.

Also differential scanning calorimetry (DSC) was carried out in the range of 25-200 °C to measure the glass transition temperature ( $T_g$ ) of the sample in order to investigate the homogeneity of the core-shell nanoparticles.

**Table 1. The recipe used for the multistage polymerization with styrene**

Ingredient		Weight (g)	Comments
Monomer	NIPAM	0.7	1.4 % solids content
Cross Linker	EGDMA	0.07	10 wt % based on monomer
Surfactant	SDS	0.01	-
Initiator	KPS	0.029	-
Medium	DI Water	100	-
Second monomer	Styrene	2.275	-
Second surfactant	SDS	0.272	Dissolved in 10 g DI water
Feed rate ( $\mu\text{L}/\text{min}$ )		30 (start feeding at 20 min of reaction)	
Reaction time		5.5 h	

### Results and discussion

Figure 2 shows the DLS results of PNIPAM-PS nanoparticles. The average diameter of core-shell particles is in the range of 50 to 130 nm. The test was performed at two different temperatures of 25 °C and 45 °C (below and above LCST of PNIPAM, which is 30-33 °C). As shown in Figure 2, there are one-peak distributions for particle sizes at both temperatures, which indicates that the core-shell structure was successfully synthesized. Particle size was decreased by increasing temperature, which can be attributed to the temperature-responsivity of the PNIPAM and reduction of the core size at temperatures above LCST.

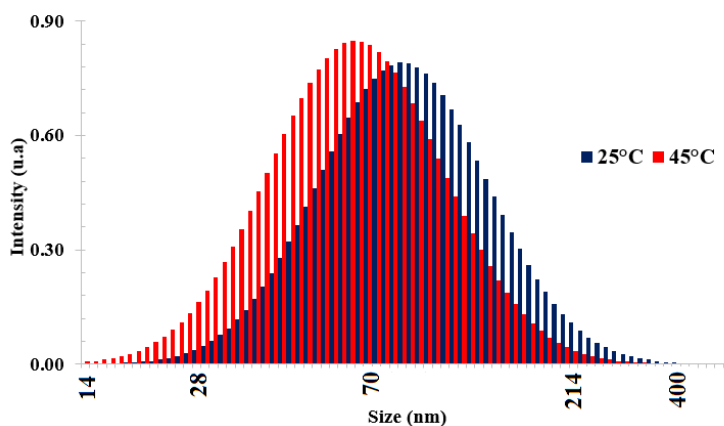


Figure 2. Size distribution of the synthesized core-shell nanoparticles.



obtained by DLS at 25 °C and 45 °C

Figure 3 shows SEM results of the synthesized polymer at two magnifications. It confirms that the particle sizes are between 50 to 300 nm. Also, it can be seen (Figure 3a) that the surface of the formed particles have porous morphology that results in special characteristic for the synthesized polymer. This porous morphology would increase the elution of the hydrophobic shell (PS) in reservoir oil to trap out the hydrophilic core (PNIPAM). Beside this feature, it is expected that flow properties and transport performance of polymer would be improved [9]. It has been reported that the porosity of the polymer increases with decreasing monomer concentration [10].

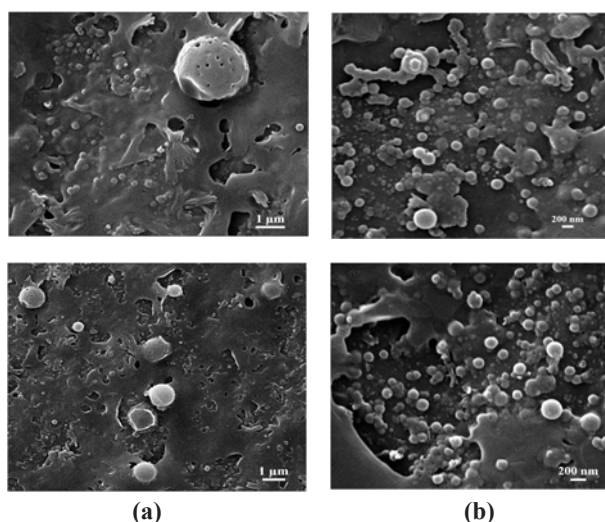


Figure 3. SEM micrographs of synthesized PNIPAM-PS CSP at two different magnifications of a) 1μm and b) 200μm.

DSC analysis was used to measure the glass transition temperature ( $T_g$ ) of the sample in order to investigate the homogeneity of the core-shell nanoparticles. As expected, Figure 4 shows a single transition in DSC thermo gram in the range of 100-150 °C, because of the core-shell morphology of the nanoparticles. According to Figure 4, the observed  $T_g$  is in the range of 140-150 °C which is above the  $T_g$ s of the PS (100 °C) and the PNIPAM (130 °C). The positive shift of the  $T_g$  is attributed to slight crosslinking of the PNIPAM core which can lead to reduction of the chain mobility and also increasing  $T_g$ . It should be pointed out that the observation of single transition in DSC curve is a significant factor which confirms the homogeneity of the two polymer matrices in the core-shell nanoparticles and also efficient grafting of hydrophobic PS on hydrophilic PNIPAM core.

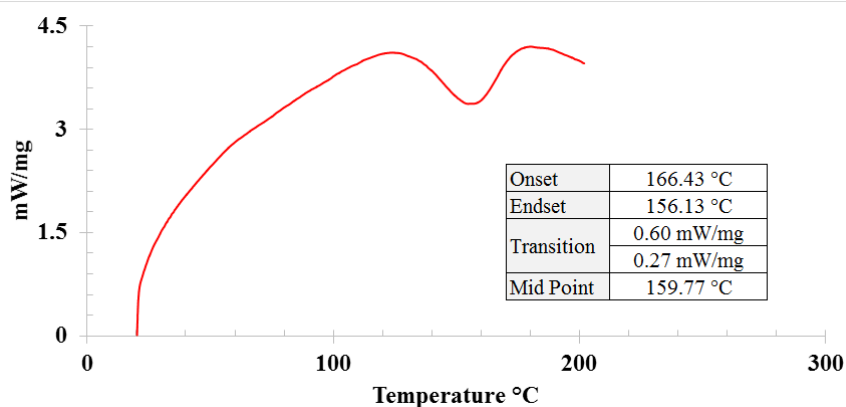


Figure 4. DCS of presented CSP of PNIPAM-PS nananoparticles.

### Conclusion

In this research, nanoparticles of polyacrylamide-polystyrene were successfully synthesized, as core-shell multicomponent nanostructures for EOR applications in tight carbonate reservoirs. It was done through simultaneous emulsion processes of N-isopropylacrylamide dilute solution and styrene. The results revealed that the particle sizes are in the range of 50-130 nm. The SEM results cleared the size of the particles, confirmed the distribution of the sizes and special characteristic porous morphology of the particles. DSC tests confirmed the presence of polystyrene shell and polyacrylamide core.

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