

Synthesis of Core Shell Poly(Styrene) Particles by RAFT Polymerization Using Amphiphilic Copolymers as Surf-RAFT Agent

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Abstract: Here we report, the synthesis of narrow dispersed core shell polystyrene nanoparticles through surfactant free emulsion polymerization (SFEP) using amphiphilic block copolymer (Am-BCP) as a surf-RAFT agent i.e. surfactant as well as RAFT agent in aqueous media. Self-assembly of amphiphilic block copolymer (Am-BCP) in aqueous solution resulted spherical micelles comprising of hydrophilic block as the corona and hydrophobic block in the core of micelles. The formation of spherical micelle and core shell polystyrene nanoparticles were confirmed by using field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and dynamic light scattering (DLS) techniques. Furthermore, the excellent emulsion stability of prepared polystyrene latex was observed in zeta potential analysis. The transmission electron microscopy (TEM) analysis revealed that the synthesized polystyrene nanoparticles displayed core shell morphology. DLS analysis revealed the particle size and particle size distribution of polystyrene latex and it is observed that the particles are narrow dispersed.

Keywords: Amphiphilic block copolymer, surfactant free, emulsion polymerization, Surf-RAFT agent, core shell morphology

I. Introduction

Amphiphilic block copolymers (Am-BCPs) form self-assembled structures i.e. spherical micelles in aqueous solution.¹ Recently, polymeric micelles have engrossed significant interest as a nanoreactor, stabilizer and surfactant, in the synthesis of core shell nanoparticles (CSNPs) owing to their better control on molecular weight distribution (MWD) and particle size distribution (PSD).²⁻⁴ The core shell nanoparticles are special class of materials that possess properties of both the core and shell into one single unit.^{2,5-7} This type of material offer some unique characteristics (1) hydrophilic shell that not only imparts surface functionality but also provides good colloidal stability to the particles (2) core of the particles that can encapsulate hydrophobic monomers, drugs, metals etc.^{8,9} CSNPs have found potential applications in catalysis, surface coatings, biomedical applications, sensing and synthesis of hollow nanoparticles.^{5,10-12}

Surfactant free emulsion polymerization (SFEP) has proven a powerful synthetic tool for the syntheses of narrow disperse polystyrene latexes.¹³⁻¹⁵ Furthermore, SFEP opened versatile route to synthesize clean (surfactant free) polymeric nanoparticles.^{16,17} SFEP has numerous potential advantages over conventional emulsion polymerization like good emulsion stability, easy to form micelle in water, narrow particle size distribution and ease of purification (absence of surfactant).¹⁸⁻²⁰ Despite of several advantages, synthesis of monodisperse polystyrene particles (having size around 100 nm) using SFEP is so far challenging.²¹ Several researchers in the field of colloid and interface science have developed effective way to overcome this problem.^{22,23}

Controlled living radical polymerizations (CLRPs) such as atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP) and reversible addition fragmentation polymerization (RAFT) has open a new era of potential applications in the field of polymer science.²²⁻²⁸ Amongst all, RAFT polymerization has grabbed great interest from scientific community and largely employed for the development of advanced nonomaterials.²⁹ RAFT-end group retained Am-BCPs has latent benefits in surfactant free emulsion polymerization (SFEP) which includes tolerance to wide range of monomers, simple reaction condition, better control on molecular weight and morphology of nanoparticles.³⁰

In present work, we report the synthesis of core shell polystyrene nanoparticles in surfactant free emulsion polymerization (SFEP) using amphiphilic block copolymers as a both surfactant and RAFT agent i.e. surf-RAFT agent. The influence of concentration of amphiphilic block copolymers (Am-BCPs) on the emulsion stability and morphology of core shell polystyrene nanoparticles were studied with field-emission electron microscopy (FE-SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS) and zeta potential study. The present approach of SFEP will open the new avenue to produce smart nanomaterials for speciality applications.

II. Experimental

2.1 Materials

Styrene was purchased from Sigma-Aldrich and passed through basic alumina column to remove inhibitor. Potassium persulphate (KPS), N, N-Azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich and recrystallized from methanol before use. Tetrahydrofuran (THF), Diethyl ether, 1, 4-Dioxane and Dichloromethane (DCM) were purchased from Fluka. All spectroscopic aqueous samples were prepared using HPLC grade water received from Fisher Scientific.

2.2 Synthesis

Am-BCP as surf-RAFT for the miniemulsion polymerization of styrene:

The amphiphilic diblock copolymer was employed as surf-RAFT for the polymerization of styrene. Into a 10 mL oven dried ampule, aqueous micellar solution of block copolymer (1mg/ml, 2 mL) and styrene (0.4 mL, 0.016 mmol) was taken. The resultant reaction mixture was then deoxygenated with flushing dry nitrogen for 30 minutes. An aqueous solution of KPS (0.84 mg, 0.003 mmol) was then added in to above reaction mixture, this is followed by ultrasonication for 15 min. Polymerisation reaction was further carried out by placing an ampule, containing miniemulsion, in a preheated oil bath (75°C) for 12 h.

2.3 Characterizations

2.3.1 Sample preparation:

Stock aqueous solutions of amphiphilic block copolymers (P2 and P3) were prepared through self-assembly process. In detail, 20 mg of polymer was dissolved in 2 mL THF and 2 mL HPLC water was added slowly at the rate of 1 μ L/s with rapid stirring to induce the self-assembly of polymer. To quench the polymeric assemblies, 18 mL water was added after 4 hours. Finally, THF was removed by evaporation at room temperature for 2 days.

2.3.2 Gel Permeation Chromatography (GPC):

Molecular weights and polydispersity index (PDI) of all polymers were determined by Gel Permeation Chromatography (GPC) using polystyrene standard and eluted in THF at flow rate of 0.2 mL/min at 25°C on a Water Alliance GPC model (GPC, Waters 515 HPLC) fitted with Waters 2414 refractive index detector and Styragel HR 2 DMF column. All samples were filtered after 24 h of dissolution in THF followed by GPC analysis.

2.3.3 Dynamic Light Scattering (DLS):

The hydrodynamic diameter and particle size distribution of the block copolymer micelles and polystyrene latexes were measured by using a Malvern Zetasizer Nano S90 instrument equipped with a He-Ne laser (633 nm) at a scattering angle of 173°.

2.3.4 Field Emission-Scanning Electron Microscopy (FE-SEM):

The morphology of diblock copolymers and polystyrene latexes were observed with Carl Zeiss Ultra-55 field emission-scanning electron microscopy (FE-SEM) using EHT detector at an accelerating voltage of 5 kV. The samples were prepared by depositing a drop of diluted aqueous solution on glass plate and exposing the glass plate for 12 h for drying at room temperature before the experiment was performed.

2.3.5 Transmission Electron Microscopy (TEM):

The morphology of diblock copolymers and polystyrene latexes were observed with FEI, Technai Model No. 2083 transmission electron microscopy (TEM) at an accelerating voltage of 200 kV. The samples were prepared by depositing a drop of diluted aqueous solution on carbon coated copper (200 mesh) grid and the grid was kept for 12 h for drying at room temperature before the experiment was performed.

III. Result And Discussion

Amphiphilic block copolymers can self-assemble into various morphologies including micelles, cylindrical and vesicles in aqueous media. Spherical micelles formed in aqueous solution were characterized by transmission electron microscopy (TEM), field emission-scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and dynamic light scattering (DLS). Fig. 1 shows the TEM images of Am-BCPs with varying hydrophobic chain length named as P2 (5K) and P3 (10K). TEM images showed the spherical micelles for P2 and P3 having size in the range of 160-190 nm and 280-320 nm respectively. Dynamic light scattering (DLS) results showed that amphiphilic block copolymers formed spherical micelles having average hydrodynamic diameter (D_h) in the range of 190 ± 50 and 300 ± 50 for P2 and P3 respectively (Fig. 2). DLS results have shown well agreement with TEM results.

Table 1: Summary of Polystyrene latexes S1 – S6.

Polymer	M_n^a (g mol ⁻¹)	PDI ^a	Hydrodynamic Size ^b	
			DLS (nm)	TEM (nm)
S1	43295	1.46	208 \pm 50	190–240
S2	31446	1.58	470 \pm 50	410–520
S3	23131	1.81	816 \pm 50	830–950
S4	43653	1.28	334 \pm 50	310–360
S5	48356	1.60	410 \pm 50	390–500
S6	89083	2.16	583 \pm 50	450–600

^a Determined by gel permeation chromatography. ^b Hydrodynamic diameter determined by DLS and TEM at 25°C.

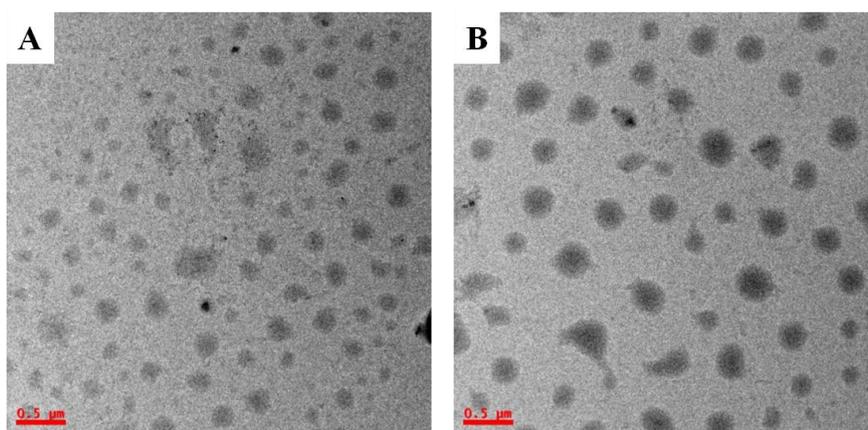


Figure 1: TEM images of copolymer aqueous solutions for P2 (A) and P3 (B).

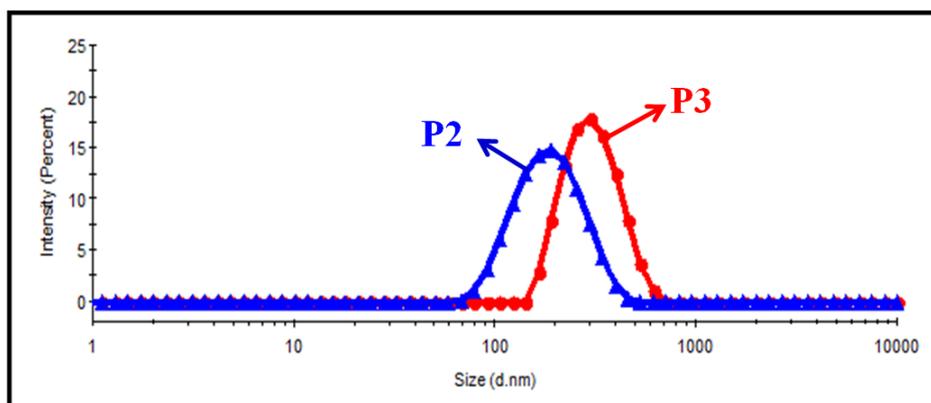


Figure 2: DLS plots of P2 and P3 obtained from the aqueous solution of polymers

Role of Am-BCP as surf-RAFT agent for preparation of miniemulsion polymerization:

It is evident from TEM analysis that the Am-BCPs have formed spherical micelles in aqueous solution. These micelles act as nano reactor for the polymerization of styrene. For this miniemulsion polymerization of styrene three different concentrations (1 mg/mL, 0.5 mg/mL and 0.25 mg/mL) of aqueous micellar solutions of both P2 and P3 were used to understand the effect of concentration of micellar solution on the morphology and stability of polystyrene latex. For 1 mg/mL concentration of micellar solutions of P2 and P3, the monodisperse polystyrene latex was obtained. It is seen from Fig.4 that the resulted narrow dispersed polystyrene nanoparticles displayed core shell morphology having size 190 nm and 310 nm for P2 and P3, respectively. Similarly, for 0.5 mg/ml concentration of aqueous micellar solution we have observed polystyrene nanoparticles having good control on particle size and particle size distribution having sizes 410 nm and 390 nm for P2 and P3, respectively. Furthermore, for 0.25 mg/mL micellar concentration, prepared polystyrene latex showed core shell morphology for P3 having size 450 nm but in case of P2 we did not observe core shell morphology for polystyrene particles having size 830 nm. From these results, it is observed that the higher concentration of aqueous micellar solution of copolymers (P2 and P3) had good control on morphology as well as particle size distribution of synthesized polystyrene latexes.

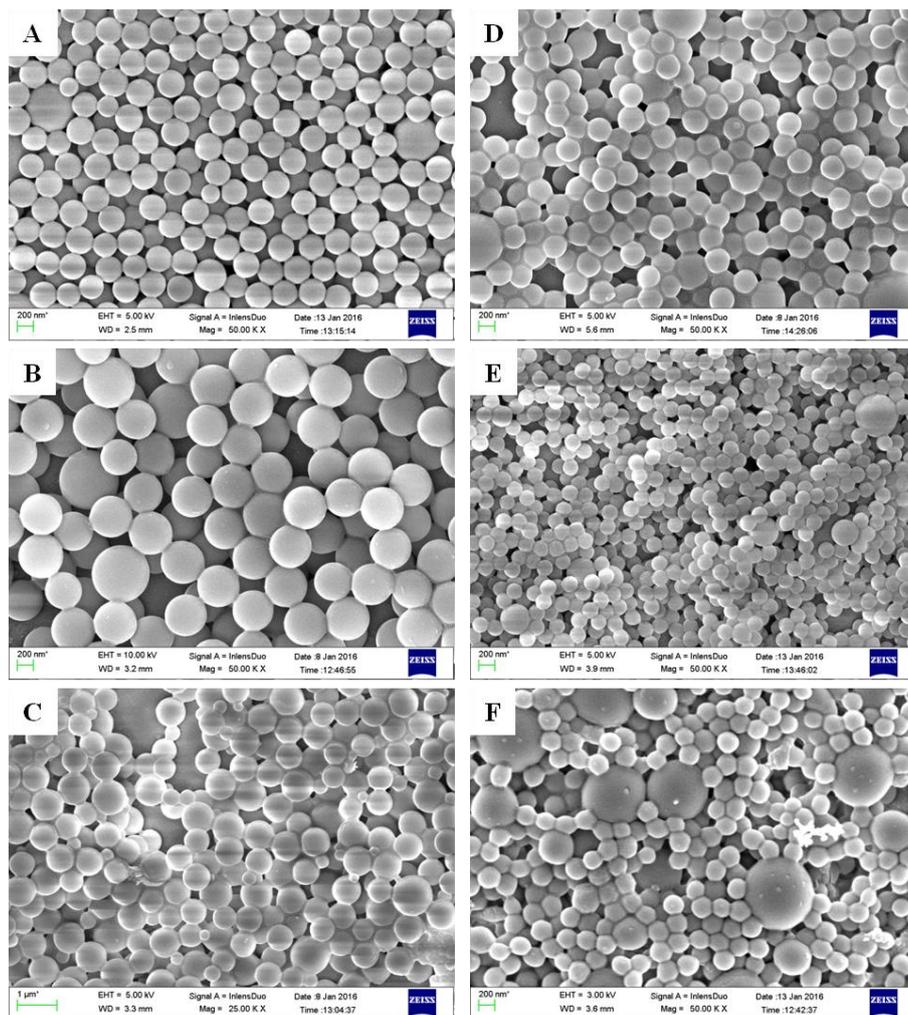


Figure 3: FE-SEM images of polystyrene latex; 1) A & D for 1 mg/mL, 2) B & E for 0.5 mg/mL and 3) C & F for 0.25 mg/mL of aqueous micellar solution of P2 and P3. (A,B,C and D,E,F corresponds to P2 and P3, respectively)

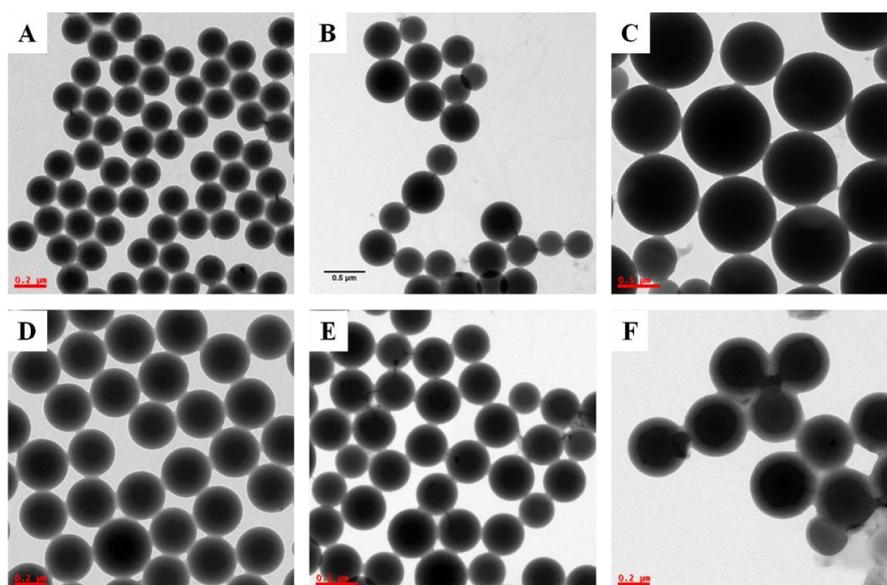


Figure 4: TEM images of polystyrene latex; 1) A & D for 1 mg/mL, 2) B & E for 0.5 mg/mL and 3) C & F for 0.25 mg/mL of aqueous micellar solution of P2 and P3. (A,B,C and D,E,F corresponds to P2 and P3, respectively)

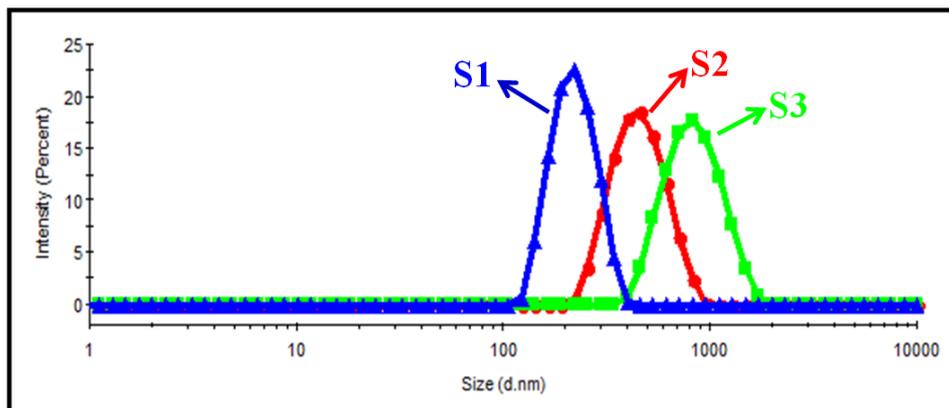


Figure 5: DLS plots of polystyrene latex S1, S2 and S3 obtained from the aqueous solution of copolymer P2.

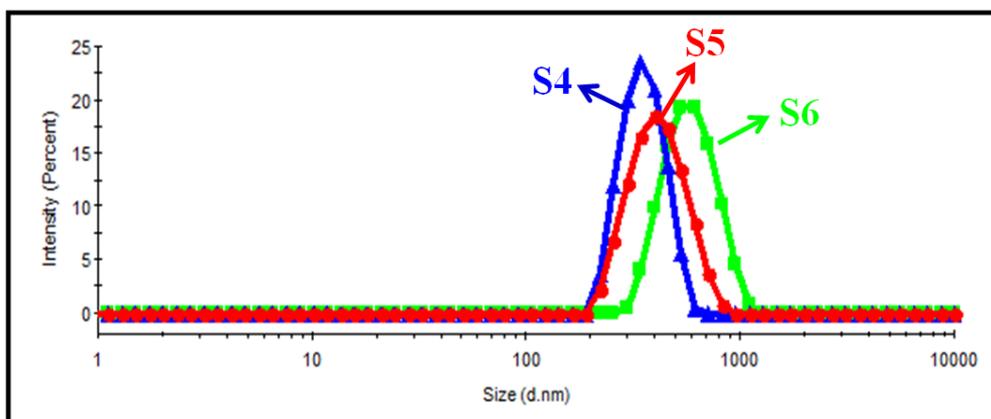


Figure 6: DLS plots of polystyrene latex S4, S5 and S6 obtained from the aqueous solution of copolymer P3.

To determine the emulsion stability of synthesized polystyrene latexes, zeta potential study was carried out. Zeta potential analysis of polystyrene latex has proved that all the polystyrene latexes synthesized here have excellent emulsion stability. For higher concentration of aqueous micellar solution, latex displayed excellent emulsion stability. This proves the role of concentration of aqueous micellar solution in emulsion polymerization. GPC analysis of synthesized polystyrene latexes show narrow polydispersion and better control on molecular weight using surf-RAFT agent which is very clear from Fig.7. These GPC results also prove that presence of RAFT functional group at the end of amphiphilic block copolymers which effectively works as RAFT agent for the preparation polystyrene latexes.

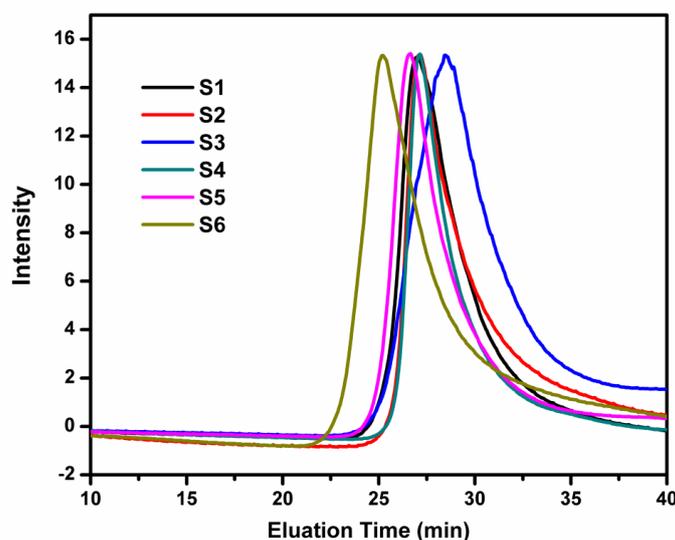


Figure 7: GPC traces of polystyrene latexes (S1-S6) prepared using Am-BCP as surf-RAFT agent.

IV. Conclusion

In this study, we have synthesized narrow dispersed core shell particles through surfactant free miniemulsion polymerization of styrene in water. The microscopic (FE-SEM, AFM and TEM) and scattering (DLS) studies have displayed amphiphilic block copolymer (Am-BCP) formed spherical micelles in aqueous solution. These self-assembled micelles of block copolymers were employed as surfactant as well as RAFT agent i.e. surf-RAFT agent for the miniemulsion polymerization of styrene in aqueous media. The Am-BCPs provided excellent emulsion stability to the polystyrene latexes, observed by zeta potential study. TEM analysis revealed that the polystyrene nanoparticles showed core shell morphology in which polystyrene is the core and Am-BCP as the shell of nanoparticles. It can be concluded that surf-RAFT agent method can lead to the development of advance nanomaterials with specialty applications compared to traditional surfactant and RAFT agent.

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