



# Effect of various synthesis parameters on styrene–divinylbenzene copolymer properties

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## Abstract

Suspension polymerization technique was used to synthesize porous polystyrene polymer cross-linked with divinylbenzene. The effects of various synthesis parameters (amount of initiator, cross-linker and diluent, type of diluent and agitation speed) were evaluated for average particle size, particle size distribution and surface morphology. The results analyzed by SEM, TEM, EDX, FTIR and sieving showed that average particle size decreases with increasing initiator amount. Optimum uniformity was obtained at low initiator amount and high cross-linker amount. The results also showed that type of diluent does not affect average particle size, while particle distribution and surface morphology were affected by agitation speed.

**Keywords** Suspension polymerization · Polystyrene polymer · Initiator · Agitation speed · Cross-linking density

## Abbreviations

ACN	Acrylonitrile
AIBN	Azobis isobutyl nitrile
DVB	Divinyl benzene
PAAm	Polyacrylamide
PMMA	Poly methyl methacrylate
PVA	Polyvinyl acetate
PVC	Polyvinylchloride

## 1 Introduction

PS polymer cross-linked with DVB (PS-co-DVB) with uniform particle size and porous structure has received significant interest due to their versatile applications in the field of biotechnology, colloid sciences, polymer foams, column packing for gel permeation chromatography and as catalyst support [1–10]. Owing to their extensive uses, synthesis of porous PS polymer with narrow size distribution has been the subject of research for many years.

Several heterogeneous polymerization techniques are available for the synthesis of PS polymer, such as suspension, emulsion, dispersion, precipitation and seeded [11–19].

Seeded polymerization technique is expensive and difficult to be carried out, whereas dispersion and precipitation polymerization techniques are relatively easy and effective for synthesis of monodisperse PS polymer with one drawback that organic solvent which is used as a dispersing agent is unfriendly to the environment [20, 21]. Suspension and emulsion polymerization techniques are widely used to obtain porous polymer and these techniques are distinguished based on the size of polymer produced. Emulsion technique produces polymer particles less than 1  $\mu\text{m}$  and suspension comprises particles of size greater than 1  $\mu\text{m}$  [22–25]. The comparative study of all the polymerization techniques is summarized in Table 1.

Polymer properties such as particle size, porosity, pore size, pore volume, rigidity, reactivity and functionality play an important role in the synthesis of polymer particles [26]. Various synthesis parameters like type and amount of initiator and diluent, cross-linker amount, cross-linking density, agitation speed, type of reactor and stirrer, polymerization temperature are key factors which are responsible for the properties of polymer particles. As polymer properties are highly tunable, as a result, can be easily altered by varying the amount and type of different synthesis parameters [20, 27–29].

Particle size is one of the decisive parameters of polymer which influences the polymer reactivity. Particle size and agitation speed both are inversely proportional to one another. High and low agitation speed produce smaller and larger polymer particles, respectively [30–35]. Also, type

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**Table 1** Comparison of various polymerization techniques

Techniques	Suspension	Emulsion	Dispersion	Precipitation	Seeded
Discovery	1920	1920	1970	1990	1980
Particle size ( $\mu\text{m}$ )	5–2000	0.06–0.8	0.1–20	0.1–8	0.5–200
Solubility in medium	Monomer and initiator both are insoluble	Monomer is insoluble and initiator is soluble	Monomer and initiator both are soluble	Monomer and initiator both are soluble	Monomer and initiator both are soluble
Easiness/Cost	Easy and cheap	Easy but can be costly	Easy and cheap	Easy but can be costly	Cheap but can be time-consuming
Particle size dispersion	Polydisperse	Polydisperse	Monodisperse	Monodisperse	Monodisperse
Applications	Porous polymer	Porous polymer	Nonporous and noncross-linked polymer	Highly porous and highly cross-linked polymer	Uniform porous polymer particles
Examples	PS, PVC, PVA, PAAm, etc.	PS, PMMA, PAAm, etc.	PS, PMMA, etc.	TFE, ACN, etc.	PS, PMMA, etc.

and amount of diluent affect the particle size and surface morphology. Diluents are of two type by affinity towards the aqueous phase (non-reactive phase); solvating and non-solvating diluents. Solvating diluents have less affinity towards aqueous phase that increases interfacial tension between two phases and hence resulting in smaller particles and vice versa for non-solvating diluents. Thus, we can conclude that particle size is mainly affected by agitation speed and type of diluent [2, 11, 27, 36–40].

Many researchers, including Rodrigo et al., reviewed the morphological characteristics of poly (Sty-co-DVB) micro-particles synthesized by suspension method [41]. Lu et al. studied the effects of porogen mixture and DVB content on the surface performance of the styrene-DVB porous microspheres. Particles with spherical shapes and pore size were obtained when the ratio of toluene/cyclohexanol is 1:2 and DVB concentration in the range of 40–60% [42]. Hulubei et al. investigated the effect of various physical and chemical factors affecting the morphology of polyimide-based porous cross-linked beads by suspension polymerization [43].

From all the techniques, suspension polymerization is the best method which is simple to use and easy to perform and also have a low level of impurities. Although suspension polymerization has been extensively investigated, their practical applicability is limited due to their lower productivity and thermal stability and it provides polymers with a particle size in the range 5–2000  $\mu\text{m}$  with polydispersity and non-uniformity in size [22, 44–48]. Therefore, there is a need to produce monodisperse polymer particles with reduced particle size via suspension polymerization technique. In the present study, porous PS polymer with narrow size distribution and cross-linked with DVB was synthesized by suspension polymerization technique. Effects of various parameters i.e. initiator, cross-linker and diluent amount, diluent type, agitation speed on polymer average particle size, particle size distribution and surface morphology were investigated.

## 2 Experimental

### 2.1 Materials

AIBN (98% purity, Avra synthesis); DVB (50% purity, Tokyo Chemical Industry); Styrene (98% purity, Avra synthesis); Toluene (99.5% purity, S. D. Fine Chemical); n-Hexane (98.5% purity, Merck Specialities); Calcium carbonate (99% purity, S. D. Fine Chemical); Gelatin (99% purity, Sisco Research Laboratories); Sodium sulfate (99% purity, S. D. Fine Chemical); were used as obtained. Other chemicals and solvents were of analytical grade.

### 2.2 Synthesis of the PS-co-DVB polymer by suspension polymerization

PS-co-DVB copolymer was prepared by using the following scheme. For organic phase; styrene (monomer), AIBN (initiator), DVB (cross-linker) and toluene (diluent) were added according to Table 2. The aqueous phase was prepared by adding gelatin, calcium carbonate (stabilizer) and

**Table 2** Synthesis reaction conditions for PS-co-DVB copolymerization

Constituents	Amount <sup>a</sup>
Organic phase	
AIBN	0.5 wt%
DVB	30.0 wt%
Toluene	100 wt%
Aqueous phase	
Distilled water	100 wt%
Organic phase/aqueous phase	1/3

<sup>a</sup>For all constituents: amount is in relation to monomer phase

sodium sulfate (surfactant) into distilled water (polymerization medium). The aqueous phase was poured into the organic phase in a 1L batch reactor at room temperature and then placed in a water bath. After mixing, the temperature was raised to 60 °C for 4 h, followed by 90 °C for 2 h, at constant stirring speed of 550 rpm. After completion of the reaction, resulting polymer particles were filtered off and washed carefully with distilled water. Finally, the particles were dried in an oven at 70 °C. The particles obtained as spherical beads were separated by sieving. The effect of different parameters (initiator, cross-linker and diluent amount, diluent type, agitation speed) were studied by varying the polymerization conditions. Table 3 shows the standard recipes of PS-co-DVB copolymerization and synthesis reaction conditions.

### 3 Characterization

#### 3.1 Surface area (BET)

The Brunauer–Emmett–Teller (BET) surface area and porosity of the given samples were analyzed using surface area and porosity analyzer (ASAP 2020, Micrometrics). The degassing temperature was 100 °C for these samples.

#### 3.2 Surface morphology (SEM)

Scanning electron microscopy (SEM) was used to describe the surface morphology of polymer particles and their average particle size, using SEM: EVO 18-20-45 system. The dried polymer particles were covered with a thin gold layer in a vacuum system for analysis.

#### 3.3 Particle size and distribution

Particle size and their distribution were estimated by sieving using ASTM (E 11-04) method. The size of mesh was varied from 0.150 mm to 0.205, 0.250, 0.280, 0.350, 0.470 and 0.780 mm, respectively. Initially all the polymer particles were filled at the uppermost stack. The smaller polymer

particles were separated from the larger ones by passing through the upper stack to the lower stack where larger particles were retained on the uppermost stack. Particle size distribution was evaluated using each percentage weight fraction of the sieved particles and then average particle size was calculated [40].

#### 3.4 Transmission electron microscopy (TEM)

Porous structure formation and pores arrangement were confirmed by transmission electron microscopy (TEM) and images were recorded using TECNAI 20G system. Also, transmission electron micrograph was used to observe particle size distribution and the arrangement of pores present in a porous polymer support.

#### 3.5 Fourier transform infra-red spectroscopy (FTIR)

In order to predict the functional groups attached during the polymer synthesis, a NICOLET-5700 (Thermo Electron Corporation) Fourier Transform Infra-Red (FTIR) spectrometer unit operating at a resolution of 6 and 32 scans and between the wave number range of 500–3500 was used.

#### 3.6 Cross-linking density

For characterizing the polymer network, often used is polymer crosslinking density. Cross-linking density determines the swelling behavior of a polymer and it was calculated from the Flory-Rehner theory [49, 50].

#### 3.7 Monomer conversion

During the copolymerization of PS-co-DVB polymer, monomer conversion was determined gravimetrically after taking the appropriate amount of sample at different time intervals. These samples were placed in an aluminum capsule and weighed immediately. After that toluene and *p*-benzoquinone were added into it to stop the propagation followed by vacuum drying until constant weight was obtained [11].

**Table 3** Polymerization recipes and reaction conditions for various experiments

Elements	No of Experiments <sup>a</sup>													
	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12	E13	E14
AIBN (wt%)	0.1	0.5	1.0	1.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DVB (wt%)	30.0	30.0	30.0	30.0	5.0	10.0	20.0	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Toluene/n-Hexane (%)	100/0	100/0	100/0	100/0	100/0	100/0	100/0	50/50	0/100	100/0	100/0	100/0	100/0	100/0
Monomer: Diluent	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:2	1:2.5	1:3	1:2	1:2
Agitation (rpm)	550	550	550	550	550	550	550	550	550	550	550	550	400	700

<sup>a</sup>For all experiments, Temperature = 60–90 °C, Polymerization time = 6 h, Organic/aqueous phase = 1/3

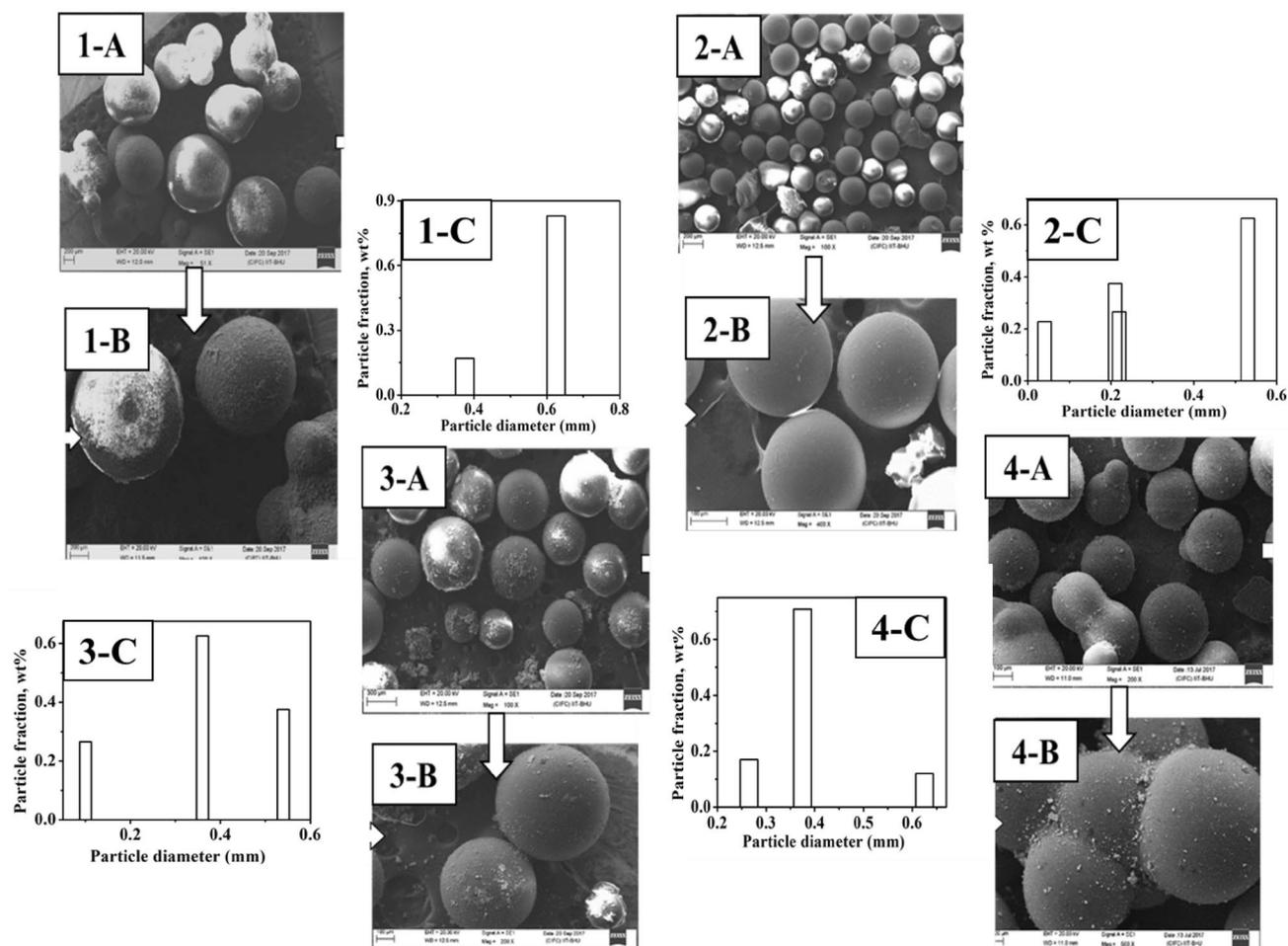
## 4 Results and discussion

### 4.1 Effect of initiator amount

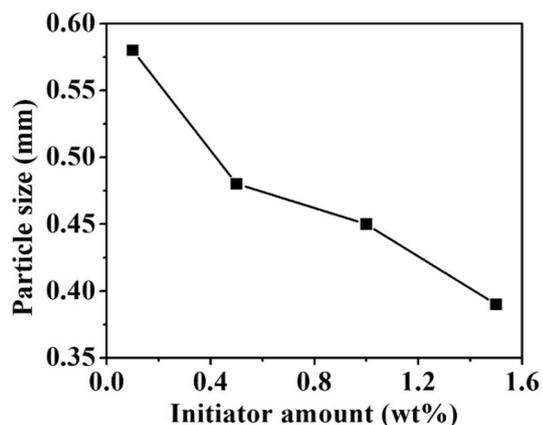
Using the standard recipe and reaction conditions (Table 3), the effect of initiator amount of 0.1, 0.5, 1.0 and 1.5 wt% AIBN based on monomer phase was studied. Four experiments (E1, E2, E3, and E4) were carried out and results were analyzed by SEM and sieving (Fig. 1). Figure 1 shows the particle distribution and surface morphology of polymer particles, affected by initiator concentration. At low initiator amount (0.1 wt. %, E1), clusters of polymer particles were formed [Fig. 1 (1.a)]. In Fig. 1 (1.b) it is clearly shown that polymer particles surface is fused which may be due to low polymerization rate at an insufficient amount of initiator. As initiator amount increased to 0.5 wt% (E2), more spherical and monodisperse particles were produced without fusion [Fig. 1 (2.a)].

The polymer particle surface was also observed as smooth and was also confirmed by Fig. 1 (2.b). When initiator amount was further increased (1.0 and 1.5 wt%; E3, E4), again particles cluster formation takes place and polydisperse particles were formed [Fig. 2 (3.a, 4.a)]. Also, at higher initiator amount of 1.5 wt% (E4), polymer particles started to diffuse and accumulate [Fig. 1 (4.b)].

This type of morphology at higher initiator amount may be due to the deficient amount of cross-linker agent and stabilizer, due to which polymer particles were unstable and several holes were formed on the particles surface. Also, at higher initiator content and higher polymerization rate, the collision chances of large polymer particles increases and at that time, if stabilizer amount is not sufficient, those large polymer particles form clusters due to which surface diffuse. The reason for non-uniformity in particle size is the polymerization rate, which becomes too fast at highest initiator content (1.0–1.5 wt%). The particle size distribution was



**Fig. 1** SEM micrographs and histograms of polymers prepared at different initiator amount: (1) E1, 0.1 wt%; (2) E2, 0.5 wt%; (3) E3, 1.0 wt%; (4) E4, 1.5 wt%; **a** polymer particle distribution ( $\times 100$ ); **b** particle surface morphology ( $\times 400$ ); **c** histogram of particle size



**Fig. 2** Effect of initiator amount on polymer particle size

calculated by using each percentage weight fraction after sieving analysis and is shown in Fig. 1 (1.c, 2.c, 3.c, 4.c).

It is well known that an initiator has a significant effect on average particle size (Fig. 2). Table 4 shows the effect of initiator content on particle appearance, size uniformity, size distribution and average particle size. From these four experiments (E1, E2, E3 and E4), it was concluded that 0.5 wt% of initiator amount is appropriate for producing smooth, monodisperse polymer particles without coalescence and fusion.

## 4.2 Effect of cross-linker amount

Using the standard recipe and reaction conditions (Table 3), effect of different cross-linker amount (5.0, 10.0, 20.0 and 30.0 wt% DVB based on monomer phase) was studied. Four experiments (E5, E6, E7 and E2) were carried out at 0.5 wt% initiator amount and analysis was done by SEM and sieving (Fig. 3).

At low DVB concentration (5.0 wt%, E5), fused and polydisperse particles were produced [Fig. 3 (1.b)]. This may be due to the low concentration of DVB, which is

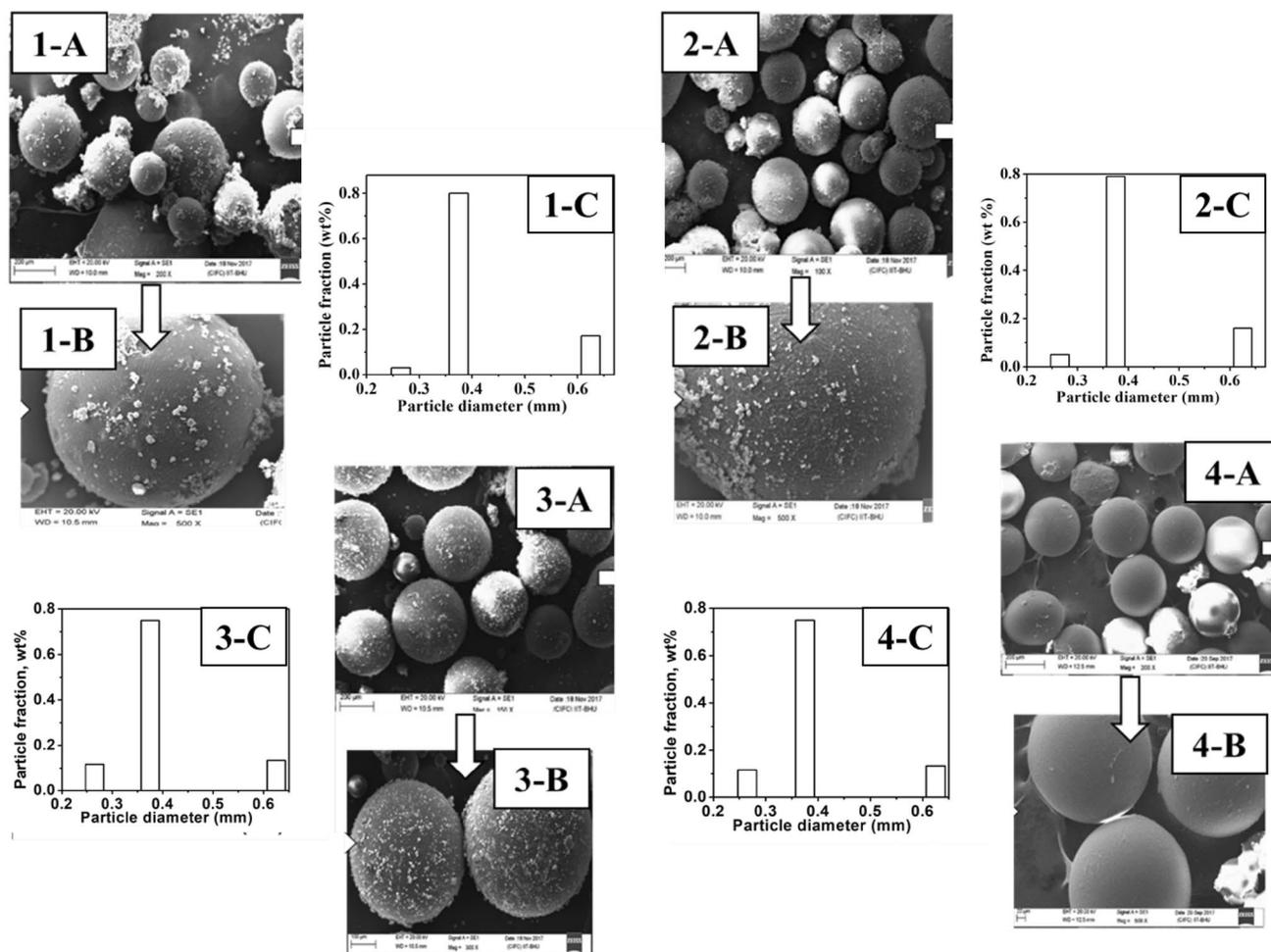
very less to produce enough crosslinking sites to maintain polymer particle sphericity. Figure 3 shows the particle distribution and surface morphology of polymer particles, affected by DVB concentration. When DVB amount was increased (from 5.0 to 30.0 wt% (E5-E7 and E2)) particles with harder and shrunk surface were obtained. At 10 wt% of DVB, polymer particles had a rough surface and dented tracks on it, however as DVB amount was increased from 20.0 to 30.0 wt%, the polymer particles surface become smoother because of enough availability of DVB for producing sufficient cross-linking sites [Fig. 3 (3.b, 4.b)].

The particle size distribution is shown in Fig. 3 (1.c, 2.c, 3.c, 4.c). Polymer particle shape was unchanged as DVB amount increased from 5.0 to 30.0 wt% and average particle size decreased slightly because of the shrunk surface. Usually, cross-linking density increases as DVB amount increases. This nature of cross-linking density and average particle size is summarized in Table 5. Cross-linking density plays a pivotal role in cross-linked polymers as it not only affects the chemical composition but also influences the physical properties of the resulting polymer, such as strength, rigidity, particle size, swelling, etc. The increase in the amount of DVB forms a denser network and reduces the  $M_c$ , the average molecular weight of cross-linked chains. The swelling behavior is also affected by DVB and it decreases as cross-linking density increases because dense copolymers swelled very less. The result shows that particles size decreases due to surface shrinkage and particle density increases because of denser polymer network as chain entanglement occurs at higher DVB, during polymerization (Fig. 4).

Table 5 summarizes the effect of cross-linker content on particle appearance, size uniformity, size distribution and average particle size. From these four experiments (E5, E6, E7 and E2), it is concluded that 30 wt% of cross-linker amount is suitable for producing monodisperse polymer particles without coalescence and fusion and with a smooth surface.

**Table 4** Effect of initiator amount on polymer properties

Experiment (initiator, wt%)	Particle appearance	Particle size uniformity	Particle size distribution (wt%)					Average particle size (mm)
			< 0.205 (mm)	0.205–0.25 mm	0.25–0.28 (mm)	0.28–0.47 (mm)	0.47–0.78 (mm)	
E1 (0.1)	Fusion, coalescence	Non-uniform	–	–	–	0.17	0.83	0.58
E2 (0.5)	No coalescence	Uniform	–	0.04	0.21	0.22	0.53	0.48
E3 (1.0)	Coalescence (less)	Non-uniform	–	–	0.10	0.54	0.36	0.45
E4 (1.5)	Coalescence (more)	Non-uniform	–	–	0.17	0.71	0.12	0.39



**Fig. 3** SEM micrographs and histograms of the polymers prepared at different cross-linker amount: (1) E5, 5.0 wt%; (2) E6, 10.0 wt%; (3) E7, 20.0 wt%; (4) E2, 30.0 wt%; **a** polymer particle distribution ( $\times 100$ ); **b** particle surface morphology ( $\times 500$ ); **c** histogram of particle size

**Table 5** Effect of the cross-linker amount on polymer properties

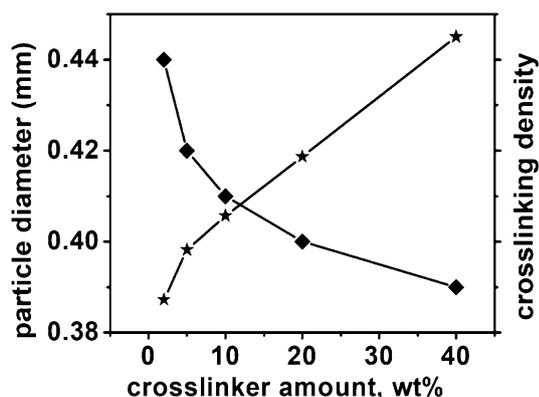
Experiment (cross-linker, Wt%)	Particle appearance	Particle uniformity	Particle size distribution (wt%)				Average particle size (mm)	Cross linking density
			< 0.25 (mm)	0.25–0.28 (mm)	0.28–0.47 (mm)	0.47–0.78 (mm)		
E5 (5.0)	Fusion, no Coalescence	Non-uniform	–	0.03	0.80	0.17	0.42	12.21
E6 (10.0)	Fusion, no Coalescence	Non-uniform	–	0.05	0.79	0.16	0.41	13.12
E7 (20.0)	No Coalescence	Non-uniform	–	0.12	0.75	0.13	0.41	14.70
E2 (30)	No Coalescence	Uniform	–	0.22	0.53	0.25	0.41	16.30

### 4.3 Effect of diluent type

The heterogeneity of the porous polymer network is controlled by the most crucial factor i.e. type and amount of diluent. Thermodynamic affinity of the diluent with the

polymer is estimated by the solubility parameter which controls the formation of pores. [2, 27].

Using the standard recipe and reaction conditions (Table 3), effect of the diluent amount (100/0, 50/50 and 0/100 toluene/n-hexane in relation to monomer phase)



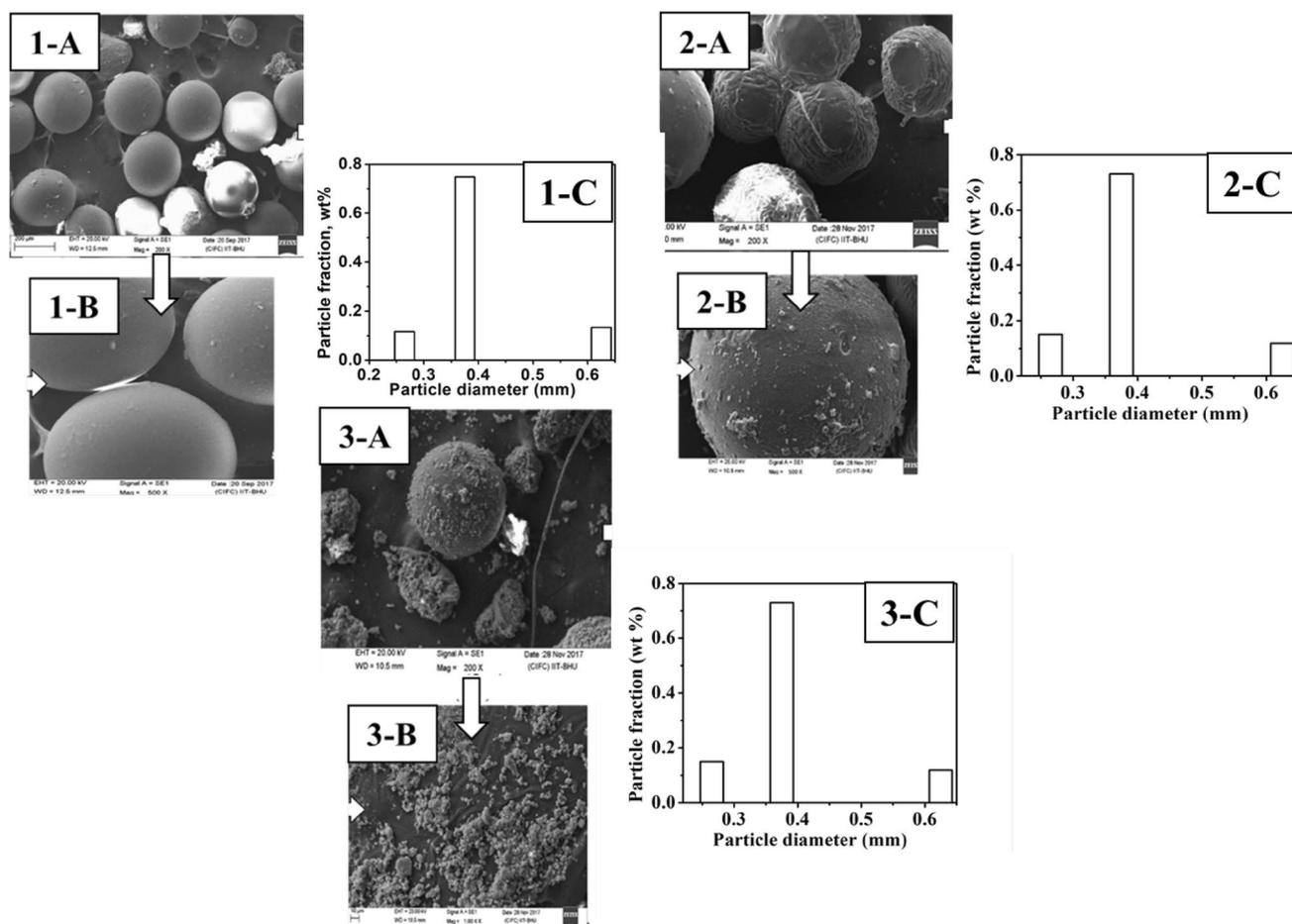
**Fig. 4** Effect of cross-linker amount on polymer particle size and crosslinking density

was studied. Three experiments (E2, E8 and E9) were carried out at 0.5 wt% initiator amount, and 30.0 wt% crosslinker amount and results were analyzed by SEM as well as

sieving. Figure 5 shows the particle distribution and surface morphology of polymer particles, affected by diluent composition. When pure toluene was used as a diluent (E2), particles of uniform size without fusion and cluster formation were produced. Figure 5 (1.b) shows smooth surfaces were obtained for pure toluene.

When 50/50 toluene/n-hexane was used as a diluent (E8), cluster formation of polymer particles was produced, also there was fusion and dimples on the surfaces. In Fig. 5 (2.b) surface morphology clearly shows that surface is very rough and has dented tracks over it. When pure n-hexane was used (E9), the sphericity of polymer particles was destroyed and also, there was some elongation in polymer particles formation as confirmed by Fig. 5 (3.b).

The reason for this kind of surface morphology at higher n-hexane content may be due to the characteristic differences of good and bad diluents as they have different solvency and hence different degree of phase separation which influences the polymer properties. Interestingly, changes in the amount and type of diluent do not affect the average particle size of



**Fig. 5** SEM micrographs and histograms of polymers prepared at toluene/n-hexane ratio: (1) E2, pure toluene; (2) E8, toluene/n-hexane = 50:50; (3) E9, pure n-hexane; **a** polymer particle distribution ( $\times 200$ ); **b** particle surface morphology ( $\times 500$ ); **c** histogram of particle size

polymer particles. Table 6 presented the effect of diluent type and amount on the particle appearance, size uniformity, size distribution and average particle size. From these three experiments (E2, E8 and E9), it was observed that pure toluene should be used for producing monodisperse polymer particles with a smooth surface without coalescence and fusion of particles.

#### 4.4 Effect of diluent amount

Diluent amount is also one of the most remarkable influences which affect the polymer properties together with the diluent type. In case of PS-co-DVB copolymer, toluene and THF as good solvent; while n-hexane, n-heptane and water as bad solvents. From literature, it was analyzed that toluene gives the best result in the case of suspension copolymerization of PS-co-DVB. Hence in recent research works, pure toluene was taken as a diluent for studying the effect of diluent amount on polymer properties [40].

The diluent amount is with respect to monomer (monomer/diluent; v/v) which may be 1:1, 1:2, 1:3, 1:4 or even more. This extent of diluent amount depends on the type and amount of a monomer, crosslinker, type of diluent and stirring speed. previous studies have shown that diluent gives polymer of very low mechanical strength. Therefore there is a limit to increasing the ratio of monomer to diluent. In this research work, different monomer/diluent ratio of 1:1, 1:2, 1:2.5 and 1:3 was taken for studying the particle size distribution, surface morphology and average particle size.

The effect of the diluent amount was studied using the standard synthesis conditions shown in Table 3. Four experiments (E2, E10, E11 and E12) were carried out at different ratios (1:1, 1:2, 1:2.5 and 1:3). Figure 6 shows the scanning electron micrographs and histograms of the PS-co-DVB particle size at the different diluent amount. Figure 6 [1(a), 2(a), 3(a), 4(a)] shows the particle size distribution as monomer to diluent ratio varies from 1:1 to 1:3. The results showed that in case of 1:1 and 1:2 particle size distribution was uniform, while non-uniform particle distribution was achieved with 1:2.5 and 1:3. This type of performance may be due to

the formation of emulsions at the higher amount of diluent, which does not allow the formation of polymer particles. Due to the emulsion, there was coalescence, fusion, and non-uniformity in size distribution.

Figure 6 [1(c), 2(c), 3(c), 4(c)] shows the particle size distribution and average particle size. As the ratio increased from 1:1 to 1:2, more uniformity in particle distribution was observed and particle size also reduced. However as the ratio goes to a higher value, particle size increases and non-uniformity came into the picture due to fusion and elongation in particles, which is not desirable. Hence the optimized value of monomer to the diluent ratio of 1:2 was used for further studies. Table 7 shows the effect of the diluent amount on average particle size, particle size distribution (Fig. 7).

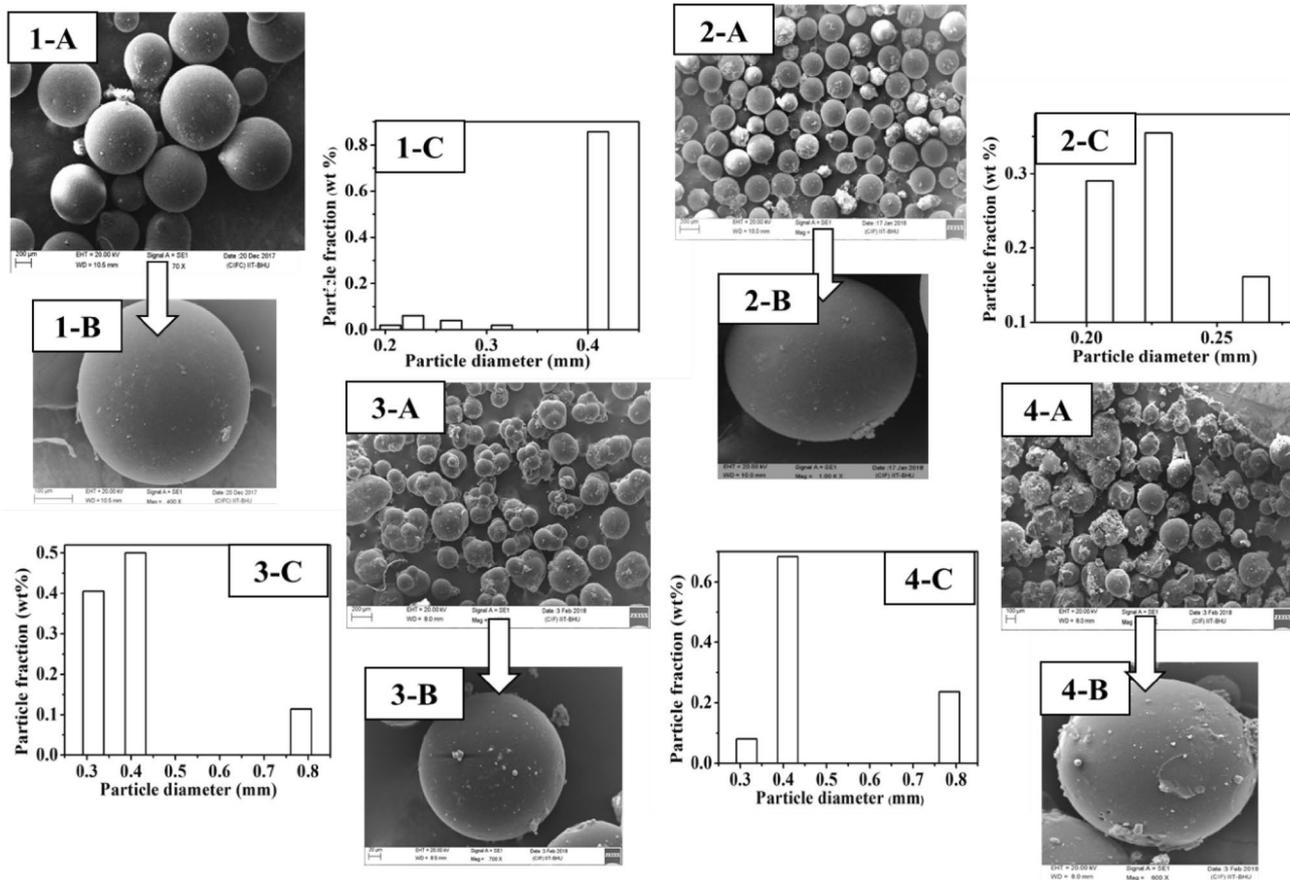
#### 4.5 Effect of agitation speed

The effect of agitation speed was studied using the standard synthesis conditions (Table 3). Three experiments (E13, E10 and E14) were carried out using three different agitation speeds (400, 550 and 700 rpm). Agitation speed is one of the most important factors affecting a heterogeneous system, mainly in controlling the particle size. It is well known in the literature that the final particle size and size distribution are affected by initial drop size distribution.

Figure 8 shows the scanning electron micrographs and histograms of the PS-co-DVB particles at different stirring speed. Figure 8 [1(a), 2(a), 3(a)] shows the particle size distribution as agitation speed vary from 400 to 700 rpm. In all the cases there is no accumulation and fusion in the particle size distribution. From Fig. 8 [1(b), 2(b), 3(b)] it was confirmed that particle spherical surface morphology was also maintained; as there were no dented tracks over the particle surface. The reason for this type of particle morphology may be due to the selection of the appropriate value of stirring speed. As it is well established in the literature that agitation speed should be 200–800 rpm; near and beyond this range, there will be severe conditions with rough particle surface and non-uniform distribution [42].

**Table 6** Effect of toluene/n-hexane composition on polymer properties

Experiment (Tol/n-hex, wt%)	Particle appearance	Particle size uniformity	Particle size distribution (wt%)				Average particle size (mm)
			< 0.25 (mm)	0.25–0.28 (mm)	0.28–0.47 (mm)	0.47–0.78 (mm)	
E2 (100/0)	No fusion, no coalescence	Uniform	–	0.117	0.749	0.134	0.41
E8 (50/50)	No fusion, coalescence	Non-uniform	–	0.160	0.730	0.110	0.39
E9 (0/100)	No fusion, coalescence, distorted surface	Non-uniform	–	0.150	0.731	0.119	0.39



**Fig. 6** SEM micrographs and histograms of polymers prepared at different diluent amount: (1) E2, monomer: diluent=1:1; (2) E10, monomer: diluent=1:2; (3) E11, monomer: diluent=1:2.5; (4) E12,

monomer: diluent=1:3; **a** polymer particle distribution ( $\times 70$ ); **b** particle surface morphology ( $\times 400$ ); **c** histogram of particle size

**Table 7** Effect of diluent amount on polymer properties

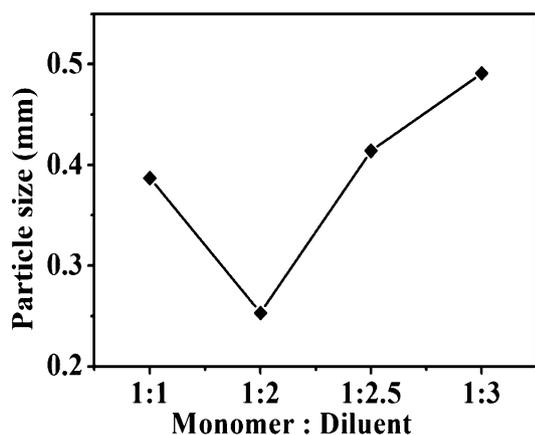
Experiment	Monomer: diluent	Particle size distribution	Surface morphology	Average particle size (mm)
E9	1: 1	Uniform	Smooth	0.387
E10	1: 2	Uniform	Smooth	0.253
E11	1: 2.5	Non-uniform	Smooth	0.414
E12	1: 3	Non-uniform	Rough	0.491

Figure 8 [1(c), 2(c), 3(c)] shows the particle size distribution and average particle size. At 400 rpm, particle size was 0.479 mm, while it was 0.398 and 0.253 mm at 550 and 700 rpm, respectively. The results confirmed that high stirring speed allows a decrease in particle size and vice versa. Also, high stirring speed improves the contact of two phases and resulted in the uniformity of the particle size. Thus the optimized value of agitation speed was 700 rpm, and it was used for further analysis in the current research work. Table 8 shows the effect of agitation speed on particle size distribution, particle surface smoothness and average

particle size. As expected, the average particle size decreases with increasing agitation speed (Fig. 9).

#### 4.6 Synthesis of PS-co-DVB copolymer at optimized synthesis condition

At optimized value of synthesis parameters; initiator (0.5 wt%), cross-linker (30.0 wt%), diluent (pure toluene), agitation speed (700 rpm) and diluent amount (1:2; monomer: diluent); a PS-co-DVB copolymer was synthesized by suspension polymerization technique and various

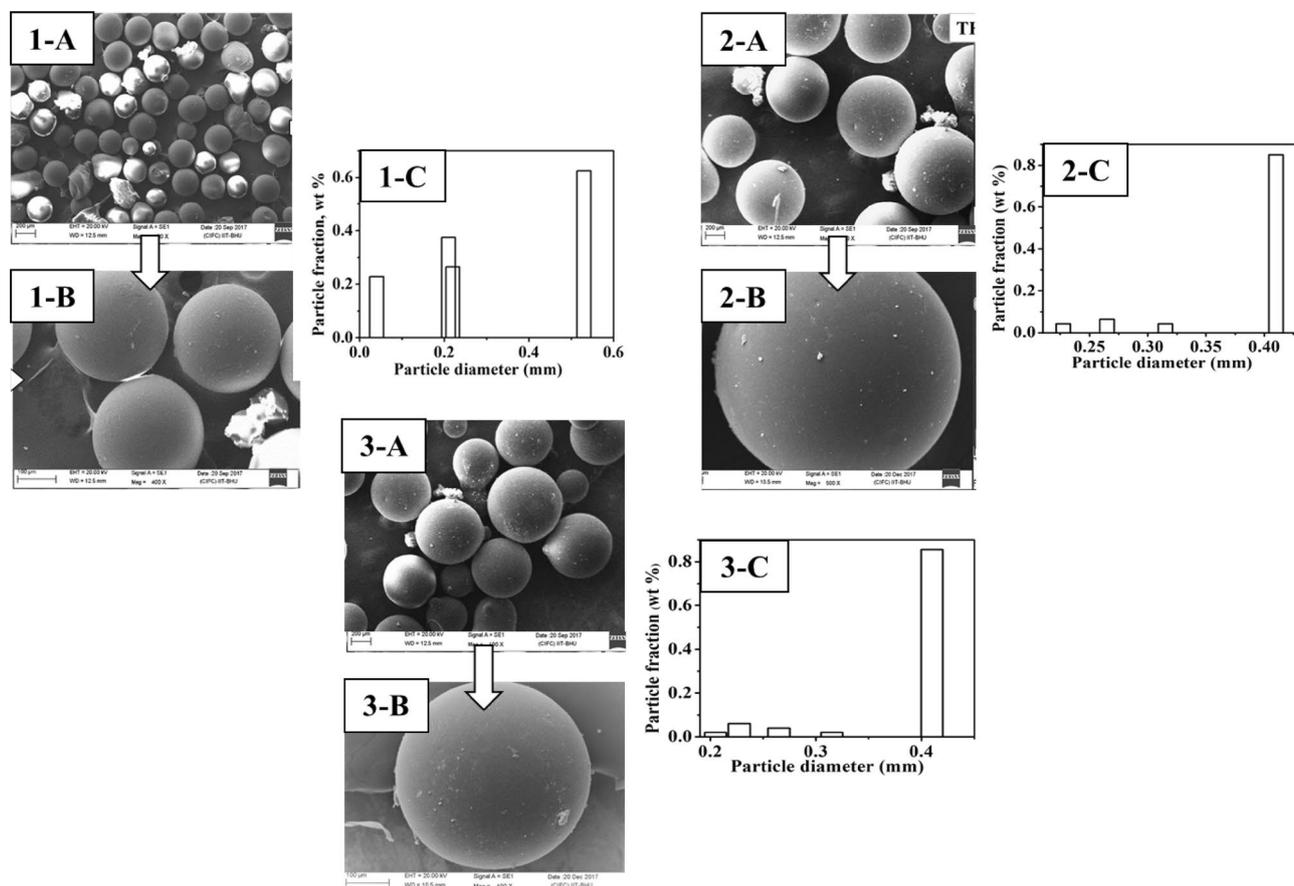


**Fig. 7** Effect of monomer to diluent ratio on polymer particle size

characterizations including; scanning electron microscopy (SEM), transmission electron microscopy (TEM), elemental analysis using energy dispersive X-ray (EDX), average particle size (using sieving) and fourier transform infra-red spectroscopy (FTIR) were done. Figure 10 show the SEM,

TEM, EDX, FTIR analysis and particle size histogram of the polymer at optimized conditions. SEM shows the particle size distribution (uniform); EDX shows elemental analysis; TEM also shows particle size distribution as well as particle overlapping. Figure 10a represents the polymer particle distribution which is uniform and particles could be produced without fusion, coalescence and with a smooth surface at these synthesis conditions. But there is some non-uniformity in the particle size distribution (Fig. 10b) as particle surface boundaries coinciding with the surrounding particle. However, TEM image also shows the distribution of polymer particles. Fringes at the surface boundaries and the alignment of pores inside the material are observed. This confirms that pores (pore size = 44.21 nm) were generated in the polymer.

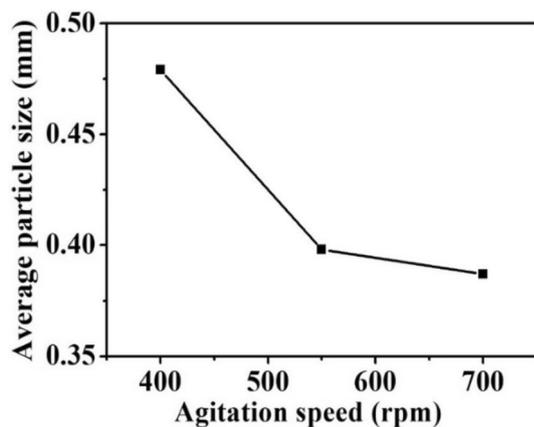
Figure 10d shows the histogram of PS-co-DVB copolymer particles (particle size = 0.253 mm) produced at the optimized reaction condition. FTIR (Fig. 10e) confirms the formation of  $-C=H$ ,  $-C=CH_2$  and benzene groups. Figure 10e represents two FTIR spectra; (1) for polymer particles synthesized at monomer to diluent ratio of 1:1 and (2) for 1:2 ratio of monomer to diluent. Both samples contain same functional groups attached to the benzene ring; thus



**Fig. 8** SEM micrographs and histograms of polymers prepared at different stirring speed: (1) E13, 400 rpm; (2) E10, 550 rpm; (3) E14, 700 rpm; **a** polymer particle distribution ( $\times 70$ ); **b** particle surface morphology ( $\times 400$ ); **c** histogram of particle size

**Table 8** Effect of agitation speed on polymer properties

Experiment	Agitation speed (rpm)	Particle size distribution	Surface morphology	Average particle size (mm)
E13	400	Uniform	Smooth	0.479
E10	550	Uniform	Smooth	0.398
E14	700	Uniform	Smooth	0.253

**Fig. 9** Effect of agitation speed on polymer particle size

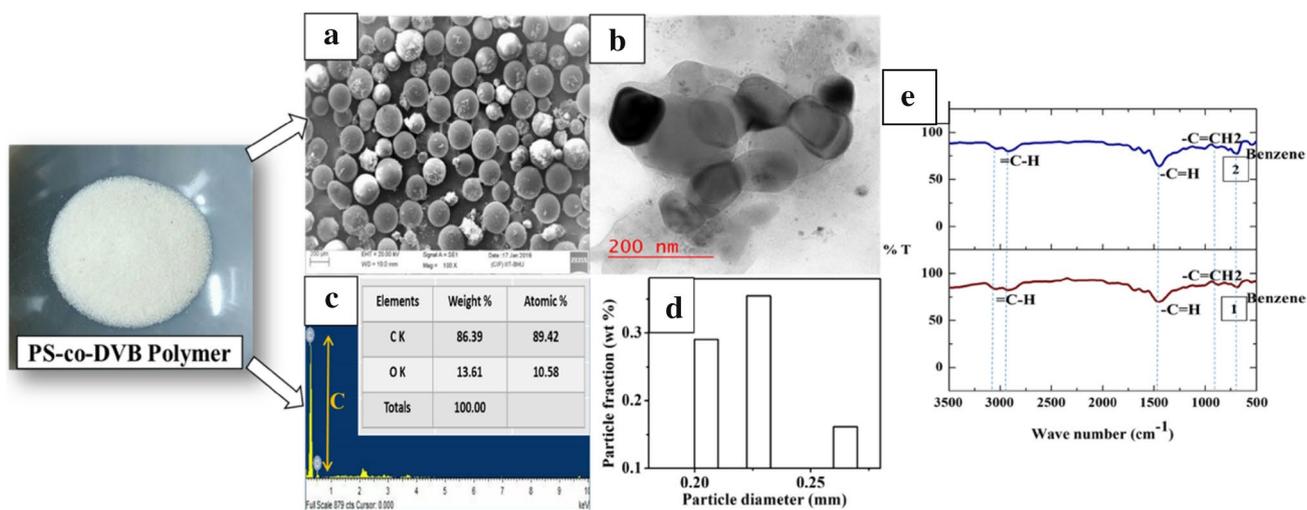
confirms that there is no difference of diluent amount on FTIR spectra. Table 9 shows the characteristics of PS-co-DVB copolymer particles in optimized reaction conditions. Thus, we may conclude that at these reaction conditions, a small size mesoporous copolymer with uniform smooth particles without fusion and coalescence were produced by

conventional suspension polymerization technique. Also, at the optimized synthesis conditions, 35% monomer conversion was achieved after 7 h of copolymerization reaction. Figure 11 shows the variation of monomer conversion with reaction time.

## 5 Conclusions and general remarks

PS-co-DVB copolymers with different particle size were produced through suspension polymerization technique. Effect of initiator and cross-linker amount were evaluated for average particle size and size distribution. Further, the effect of toluene/n-hexane composition was studied on particle size distribution and surface morphology. The following conclusions were drawn by varying the various synthesis parameters:

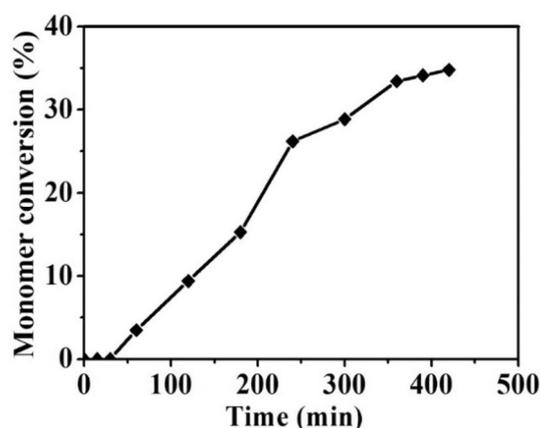
- Initiator concentration of 0.1–1.5 wt% and cross-linker amount in the range of 5.0–30.0 wt% was used for the synthesis of spherical polymer particles. The optimized value of cross-linker was 30.0 wt% at 0.5 wt% of the initiator
- A combination of the good and bad diluent of toluene and n-hexane was benefited to control the phase separation and results showed that type of diluent has no effect on average particle size, while particle distribution and surface morphology were affected
- Further, the effect of diluent amount and agitation speed were estimated for average particle size and size distribution
- At these optimized synthesis conditions (Table 9), a monomer conversion of 35.0% was achieved

**Fig. 10** **a** Scanning electron micrograph (SEM); **b** transmission electron micrograph (TEM); **c** EDX and Elemental analysis; **d** particle size histogram; **e** FTIR analysis of polymer particles (1) at monomer

to diluent ratio of 1:1 and (2) at monomer to diluent ratio of 1:2; synthesized at optimized reaction condition

**Table 9** PS-co-DVB copolymer properties at optimized synthesis conditions

Polymer	PS-co-DVB
Optimized synthesis conditions	Initiator = 0.5 wt% Cross linker = 30.0 wt% Diluent = pure toluene Monomer: diluent = 1:2 Agitation speed = 700 rpm
Particle size (mm)	0.253
Pore size (nm)	44.21
Surface area (m <sup>2</sup> g <sup>-1</sup> )	< 5
Crosslinking density	12.21
Monomer conversion (%)	35.0
Particle appearance	Uniform particle size distribution without fusion and coalescence

**Fig. 11** Monomer conversion at optimized synthesis conditions

Thus, the experimental results showed that initiator, cross-linker and diluent are the most convenient variables to adjust the particle size distribution of porous polymers. These porous polymers are widely used for academic as well as industrial purposes. Among all the polymers available, PS-co-DVB is one of the most suitable polymers used as a catalyst support in various reactions such as oxidation, hydrogenation, epoxidation, etc. [42, 45, 51–58]. The novelty of this experimental work is the synthesis of uniform as well as small size polymer particles via suspension method.

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