

# Suspension Copolymerization of Styrene and Divinylbenzene: Formation of Beads

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**ABSTRACT:** Suspension copolymerization of styrene and divinylbenzene (DVB) was carried out using benzoyl peroxide as initiator and magnesium hydroxide as suspending agent in water at 80°C under nitrogen atmosphere to produce styrene–DVB copolymer beads. These beads were characterized by infrared spectroscopy, thermal gravimetric analysis, and scanning electron microscopy. Porosity generated in styrene–DVB copolymer beads by incorporation of

solvents in the polymerization system was confirmed by SEM micrograph, apparent density, swelling measurements, and Brunauer, Emmett, Teller surface area. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3559–3563, 2006

**Key words:** suspension copolymerization; suspending agents; resins; beads and porous structure

## INTRODUCTION

The development of styrene–divinylbenzene (DVB) copolymers with well-defined porous structures has gained significant importance. These copolymers are widely used as ion-exchange resins, gel permeation chromatography column packings, polymer supported catalysts, precursors for carbon spheres and absorbents. The success of styrene–DVB copolymer resins in these speciality areas depends heavily on the availability of the type of porous structure. Such polymers have therefore been the subjects of a large number of studies. Styrene–DVB copolymers were mainly prepared by copolymerization of styrene and DVB in water at temperatures 60–80°C under nitrogen atmosphere, using free radical initiators and in presence of suspending agents.<sup>1</sup> Hydrophilic organic substances such as gelatin, starch, hydroxyl ethyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, poly(diallyl dimethyl ammonium chloride), styrene–maleic anhydride copolymer, etc., were used as suspending agents in these copolymerization. Metal salts of inorganic nature, i.e., carbonates, silicates, oxides, sulfates, and phosphates of calcium, barium, aluminum, magnesium etc., have been reported as suspending agents. Recently magnesium hydroxide ( $Mg(OH)_2$ ) has also been reported as suspending agent in patent literature.<sup>2</sup> It was claimed that styrene–DVB copolymer beads or spheres of uniform size were achieved. However, copolymerization of styrene and DVB has not

been studied in presence of  $Mg(OH)_2$  to achieve styrene–DVB copolymer spheres. Further inert diluents (solvents, non solvents, or polymers) were incorporated during polymerization to produce porous and heterogeneous structures in styrene–DVB copolymers.<sup>3,4</sup>

Therefore, copolymerization of styrene and DVB was carried out in presence of  $Mg(OH)_2$ , and formation of beads is reported in the present communication. Effect of diluents such as toluene, heptane, and mixture of toluene–heptane on pore formation in styrene–DVB copolymer also has been reported in the present communication.

## EXPERIMENTAL

### Materials

Styrene monomer (Acros), divinylbenzene (DVB), and benzoylperoxide (Aldrich), magnesium hydroxide ( $Mg(OH)_2$ , centra drug House, M'bay), sodium chloride (NaCl), toluene, and heptane (M/S S.d. fine, M' bay) were procured from trade. These chemicals were used without purification.

### Purification of monomers and initiator

1. Styrene and DVB were treated with 5% NaOH solution to remove inhibitor followed by several washings with water. The monomers were dried with anhydrous sodium sulfate and finally vacuum distilled
2. Benzoyl peroxide ( $Bz_2O_2$ ) was recrystallized using chloroform as a solvent.

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**TABLE I**  
Effect of Temperature on Copolymerization of Styrene-DVB<sup>a</sup>

Time (min)	% Conversion		
	60°C	70°C	80°C
90	0.3	6.0	25.0
120	5.0	8.0	28.0
180	55	30.0	30.2
240	8.8	42.0	58.0
300	9.2	50.0	65.0
360	10.2	71.0	77.0

Styrene, 80; DVB, 20; Mg(OH)<sub>2</sub>, 2; NaCl, 10; water, 200; Bz<sub>2</sub>O<sub>2</sub>, 1 (in parts).

<sup>a</sup> Time vs. conversion data at 80°C.

### Copolymerization procedure

Suspension copolymerization of styrene and DVB was carried out in a round-bottom flask fitted with a nitrogen inlet, condenser, and mechanical stirrer.

The solution containing the monomers (styrene/DVB) and Bz<sub>2</sub>O<sub>2</sub> was introduced in the flask containing the aqueous phase (water, Mg(OH)<sub>2</sub>, and NaCl) at room temperature. The temperature was then raised to 60–80°C using 0.5–1.5% Bz<sub>2</sub>O<sub>2</sub> as initiator and the reaction was carried out for 90–360 min time intervals. The copolymer beads were then filtered and washed with water followed by methanol. The beads were finally sieved, washed with water and methanol, and vacuum dried at 50°C for 24 h. The overall conversion of the monomers to solid copolymer was determined gravimetrically.

### Characterization

Styrene-DVB copolymer beads are crosslinked resins and characterized by the following technique:

#### Infrared spectroscopy (IR)

FTIR spectra were recorded in the range 400–4000 cm<sup>-1</sup> using Nicolet spectrophotometer in KBr pellet.

#### Apparent density

The apparent density of the styrene-DVB copolymer beads was determined using graduated cylinder method as per IS7330–1974

#### Swelling measurements

Five grams of oven-dried (50°C for 10 h) sample was taken in a stoppered test tube. The sample was soaked with 20 mL toluene for 24 h at ambient temperature. Toluene was filtered and beads were padded dried

with a filter paper and finally dried at 50°C for 10 h and weighed.<sup>5</sup>

$$\% \text{ Swelling} = \frac{\text{Increase in wt of beads}}{\text{Original wt of beads}} \times 100$$

### Thermal gravimetric analysis (TGA)

Thermal degradation was studied using TGA 2950 thermogravimetric analyzer in air from room temperature to 700°C at a heating rate of 10°C/min.

### Surface morphology

JEOL JSM-840 scanning electron microscope was used to study surface morphology of styrene-DVB copolymers at 5 kV after coating the specimens with a thin layer of gold in a JFC-1100 sputter coating unit.

## RESULTS AND DISCUSSION

Copolymerization of styrene and divinylbenzene (DVB) was carried out under nitrogen atmosphere using Mg(OH)<sub>2</sub> as suspending agent. Time of polymerization was varied from 90 to 360 min. The conditions for copolymerization are shown in Table I and II. In each polymerization batch, % conversion was recorded gravimetrically. Following polymerization parameters were studied:

### Effect of temperature

The effect of temperature on styrene-DVB copolymer conversion was studied using 1% Bz<sub>2</sub>O<sub>2</sub> as initiator and polymerization temperature of 60, 70, 80°C, respectively (Table I). Conversion was 0.3% in 90 min and increases to 10.2% at the end of 360 min. When temperature was raised to 70 and 80°C, percent conversion also increases to 71.0 and 77.8%, respectively, in 360 min. Thus, it can be safely concluded that at constant initiator concentration (1% Bz<sub>2</sub>O<sub>2</sub>), percent

**TABLE II**  
Effect of Initiator Conc. on Copolymerization of Styrene-DVB<sup>a</sup>

Time (min)	% Conversion at Bz <sub>2</sub> O <sub>2</sub> concentration (%)		
	0.5	1.0	1.5
90	10.0	25.0	70.8
180	–	50.2	72.0
240	24.0	58.0	76.6
360	57.5	77.8	85.5

Styrene, 80; DVB, 20; Mg(OH)<sub>2</sub>:NaCl:water = 2:10:200 (in parts).

<sup>a</sup> Time vs. conversion data at 80°C.

TABLE III  
Optimized Parameters for Polymerization

Mg(OH) <sub>2</sub>	2 (in parts)
NaCl	10 (in parts)
Water	200 (in parts)
DVB	5, 10, 15, 20, 25, 30, 35, 40, 50 (in parts)
Styrene	95, 90, 85, 80, 75, 70, 65, 60, 50 (in parts)
Bz <sub>2</sub> O <sub>2</sub>	1 (in parts)
Temperature	80°C
Time of polymerization	90, 120, 180, 240, 300, 360 min

conversion increases with increase of time and temperature. Increase in percent conversion at high temperature may be explained as that at higher temperature, the half-life of the initiator is reduced, which may produce more radicals, resulting in more polymeric chain to propagate as well as crosslink and form more network copolymers.<sup>6</sup> Therefore, 80°C was selected as temperature for copolymerization of styrene and DVB.

#### Effect of initiator concentration

The effect of initiator concentration of 0.5, 1.0, and 1.5% Bz<sub>2</sub>O<sub>2</sub> based on the monomer phase on copolymerization were studied at 80°C (Table II). Styrene-DVB copolymer conversion was 10.5% at 0.5% Bz<sub>2</sub>O<sub>2</sub> in 90 min at 80°C. This conversion further increases to 60.0% in 360 min at 0.5% Bz<sub>2</sub>O<sub>2</sub> and 80°C. When concentration of Bz<sub>2</sub>O<sub>2</sub> was increased to 1%, the copolymer conversion was increased to 25.0 and 77.8% in 90 and 360 min, respectively, at 80°C. Similarly copolymer conversion increased to 70.8 and 85.5% in 90 and 360 min, respectively, at 1.5% (Bz<sub>2</sub>O<sub>2</sub>) and 80°C. The result reveals that the conversion increases with the increase in initiator concentration as a result of more radicals formed in the initiation step.<sup>6</sup>

Table II also indicates that copolymerization is very fast (70–80% conversion in 90 min) at 1.5% Bz<sub>2</sub>O<sub>2</sub> and 80°C. However, copolymerization is controlled and progressive when 1.0% Bz<sub>2</sub>O<sub>2</sub> was used as initiator. Therefore, condition for copolymerization using 1.0% Bz<sub>2</sub>O<sub>2</sub> at 80°C was taken as optimized condition. Under these conditions styrene was copolymerized at 80°C with 5–50% DVB to get styrene-DVB copolymers of varying DVB content (Table III).

#### Characterization

Styrene-DVB copolymers containing 5–50% DVB were characterized by various techniques as follows:

#### IR

Characteristic absorption bands of styrene and DVB were observed in the FTIR spectra of styrene-DVB copolymers. IR spectra show strong absorption at 699

cm<sup>-1</sup> due to phenyl ring and at 3020 cm<sup>-1</sup> due to aromatic C—H stretching. Further, IR peaks at 2919 and 2852 cm<sup>-1</sup> might be due to aliphatic C—H stretching, and small but broad peak at 3447 cm<sup>-1</sup> due to —OH indicate the presence of moisture in the IR spectra of styrene-DVB copolymers. Sharp peak at 1489 cm<sup>-1</sup> of aromatic C—H may be due to presence of phenyl ring. Presence of aromatic V C—H, aliphatic C—H, and C=C peaks in FTIR spectra of styrene-DVB copolymer is in conformity with the reported literature.<sup>7</sup>

#### Thermal degradation

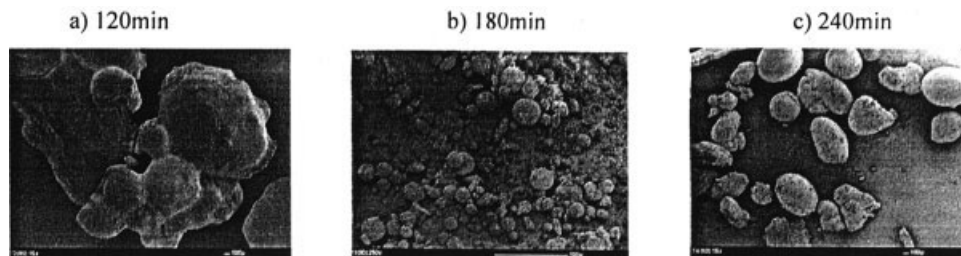
Styrene-DVB copolymers were subjected to thermal degradation in air. Initial decomposition temperature (IDT) and temperature corresponding to 50% degradation taken from the thermograms data indicate that styrene-DVB copolymer containing 5% DVB has IDT of 190°C and *T*<sub>50</sub> of 402°C (Table IV). When DVB content was increased to 10% in styrene-DVB copolymer, IDT increased to 195°C. Further, with the increase of DVB content to 20%, both IDT and *T*<sub>50</sub> increased to 210 and 425°C, respectively, and 50% DVB and content were 290 and 456°C, indicating that with increase of DVB content both IDT and *T*<sub>50</sub> increase. These data indicate that increased incorporation of DVB led to increased crosslinking of styrene-DVB copolymers, resulting into increased IDT and *T*<sub>50</sub> and hence thermal stability of these copolymers.<sup>8</sup>

#### Surface morphology

Copolymerization of styrene and DVB was carried out at 80°C and reaction was terminated after various time

TABLE IV  
Thermal Degradation of Styrene-DVB Copolymers

No.	DVB (%)	IDT (°C)	Temp (°C) at 1% wt loss			
			10%	30%	50%	70%
1	5	190	345	390	402	425
2	10	195	350	397	405	432
3	20	210	360	417	425	447
4	30	240	375	410	430	450
5	40	250	405	431	444	458
6	50	290	425	444	456	466



**Figure 1** Formation of beads at various polymerization time intervals scanning electron micrographs: (a) 120 min ( $\times 15$ ), (b) 180 min ( $\times 250$ ), and (c) 240 min ( $\times 15$ )

intervals like 90, 120, 180, 240, and 360 min, respectively. Reaction started immediately with the milky color followed by mass formation (90 min), which converts to gel in 120 min. Further polymerization for 180, 240, and 300 min leads to beads formation. Surface morphology of these copolymers was examined by scanning electron microscopy (SEM). These micrographs indicate that beads were formed after 180 min and remained in the fused state (Fig. 1). Further increase of copolymerization time results into bead separation as well as increase of particle size, with some amount of distortion in shape of the beads. This transformation of beads (spherical) through loose, amorphous gel and other stages of polymerizations was also observed by Kun and Kunin.<sup>9</sup> According to them bead formation accomplished in three stages. In the first stage, monomers are converted into copolymer, polymer chain become less and less swollen, and then become entangled by further progress of the polymerization. At the end of this stage, the nuclei are formed. In the second stage, sphere beads formation of entanglements between the polymer chain increase and nuclei then aggregate into microspheres. In the third stage, microspheres aggregate forming particle more or less separated by large holes.<sup>9</sup>

#### Porosity generation in styrene–DVB copolymer beads

Suspension copolymerization in the presence of solvents referred to as diluents is a well-known technique for the preparation of heterogeneous structures with good properties. Thermodynamically good solvents

produce structures with small pores while bad solvents produce structures with large pores.<sup>4,10,11</sup> In our present study, toluene, heptane, and their mixtures were employed as diluents and their effect on porosity of styrene–DVB copolymer beads was examined. Beads formed in presence of toluene, heptane, and their mixture were examined by scanning electron micrographs. These micrographs (Fig. 2) indicate the generation of porosity in styrene–DVB copolymer beads, indicating the pore formation when polymerization was carried out in presence of toluene, heptane, and toluene–heptane mixture. Further decrease in apparent density and consequent increase in swelling measurements and BET surface area indicate the formation of pores in styrene–DVB copolymer beads (Table V). Apparent density of styrene–DVB copolymers was found to be 0.9890 g/mL. However, apparent density decreases to 0.9166 and 0.6660 g/mL, when 25 and 100% toluene was added as diluents in the system. Similarly, apparent density 0.7333 g/mL was achieved at 50% heptane as diluents. Intermediate values were achieved when toluene–heptane were employed as diluents in the system (Table V). Surface area of the resultant beads increased from 54.5 to 92.3 m<sup>2</sup>/g in presence of toluene–heptane mixture (75:25). Also 31% swelling in toluene for styrene–DVB copolymers was observed when no diluents were added. Swelling (%) of these beads increased to 125.0 and 51.0, respectively, at a diluents level of 100 parts of toluene and heptane, respectively. However, swelling further changed to 48% in presence of toluene–heptane mixture (50:50). Increased swelling in



**Figure 2** Porosity generation in styrene copolymer beads (by SEM) in presence of (a) Toluene ( $\times 2000$ ), (b) Heptane ( $\times 500$ ), and (c) Toluene–heptane mixture ( $\times 250$ ).

TABLE V  
Characteristics of Styrene–DVB Copolymer Beads

No.	Dilution degree (%)		Apparent density (g/mL)	Swelling (%)	Surface area (m <sup>2</sup> /g)
	Toluene	Heptane			
1	—	—	0.9890	31.0	54.5
2	25	—	0.9166	—	—
3	50	—	0.7500	74.0	59.0
4	100	—	0.6660	125.0	79.4
5	—	100	0.5960	51.0	74.1
6	25	75	0.5880	36.0	90.0
7	75	25	0.5830	45.0	92.3
8	50	50	0.5430	48.0	90.6

styrene–DVB copolymers may be due to varied porous structure formation in presence of toluene and heptane as diluents. Thus, porosity is generated in the styrene–DVB copolymer beads due to addition of inert diluents (toluene, heptane, or mixture), resulting in decrease in density and increase in swelling and surface area values. These findings are in agreement with those reported in the literature.<sup>10–12</sup>

### CONCLUSIONS

Suspension copolymerization of styrene and DVB was carried out in water using Bz<sub>2</sub>O<sub>2</sub> as initiator and Mg(OH)<sub>2</sub> at 80°C under N<sub>2</sub> atmosphere. Effects of temperature and initiator concentration on copolymer conversion for different time intervals were studied. Formation of beads was monitored by SEM. These beads were characterized by IR, TGA, and SEM. Thermal stability of these beads increases with the increased incorporation of DVB in styrene–DVB copolymer. Further porosity generated in beads by incorporation of solvents (toluene and heptane) was confirmed by SEM micrographs, apparent density, % swelling, and BET surface area.

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