

Effects of Crosslinking Agents and Inert Diluents on the Characteristics of Crosslinked Polystyrene Copolymers

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ABSTRACT: The suspension copolymerization of styrene with various vinyl crosslinking monomers, that is, dimethacrylates and divinylbenzene, was carried out with poly(vinyl alcohol) as the suspending agent. The effect of the crosslinking monomers on the characteristics of the styrene copolymers was also studied, and the styrene–divinylbenzene copolymers were found to be the most thermally stable. Inert diluents were added during styrene and divinylbenzene copolymerization to achieve porous, crosslinked polystyrene. Furthermore, the influence of the diluents on the formation of porous styrene–divinylbenzene copolymers was investigated by surface area, pore volume, pore

diameter, apparent density, swelling percentage, and compressive strength measurements and the surface morphology. It was observed that among the inert diluents studied, cyclohexanol was the most effective diluent, leading to the styrene–divinylbenzene copolymer beads with maximum porosity. A surface morphology study of the polystyrene copolymer beads supported the porosity in these copolymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1531–1537, 2008

Key words: copolymerization; crosslinking; macroporous polymers

INTRODUCTION

Macroporous polymers are prepared by the suspension copolymerization of styrene (St) with vinyl crosslinking monomers in the presence of a diluent.^{1–3} This diluent may be extracted after polymerization, leaving holes or pores in the copolymer structures. Polymeric solvents, nonsolvents, or mixtures of them may be used as diluents, leading to different kinds of pore size distributions. Detailed studies concerning the suspension copolymerization of St with divinylbenzene (DVB) were first reported by Kun and Kunin.⁴ The porous structure formation was attributed to phase separation of the copolymer that formed during the polymerization process. Consequently, the selection of a diluent as a precipitant is important in determining the porous structure of polymer beads. Almost all porous polymers are characterized by a relatively broad pore size distribution. Typically, they contain micropores smaller than 2 nm in diameter, mesopores with sizes varying from 2 to 50 nm, and macropores with diameters larger than 50 nm. The pores are irregular voids between clusters of globules (mesopores) or voids inside a globule (micropores). Several works have dealt with the synthesis of porous St–DVB matrices with various diluents.^{5–10} However, the reported

results cannot be compared because of differences in the polymerization conditions. Crosslinked copolymers of St and methyl methacrylate with dimethacrylates have also been reported in the literature but not evaluated as porous materials for specific applications.¹¹ It is therefore felt that the effects of the crosslinking agent and diluent should be studied, with the polymerization conditions and suspending agent kept identical. We have already reported the suspension copolymerization of St and DVB in the presence of magnesium hydroxide and poly(vinyl alcohol) (PVA) as suspending agents.^{12,13} The effects of crosslinking agents and diluents on the characteristics of crosslinked polystyrene are reported in this communication.

EXPERIMENTAL

Materials

The chemicals required for this study, that is, St (Acros, Belgium), DVB (a 50% mixture of isomers; Fluka, Steinheim, Germany), PVA (87–89% hydrolyzed, weight-average molecular weight = 124,000–186,000; Aldrich, Steinheim, Germany), benzoyl peroxide (Aldrich), toluene, 1-butanol, 2,2,4-trimethyl pentane, 2-ethyl-1-hexanoic acid, benzyl alcohol, 2-methoxy ethanol, cyclohexanol, cyclohexanone, cyclohexane, bis-2-ethyl phosphate, tris-*n*-butyl phosphate, methyl ethyl ketone, and 2-ethyl-1-hexanol, were procured from trade. Dimethacrylates such as bisphenol A dimethacrylate (BADMA; Acros) and

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neopentyl glycol dimethacrylate (NGDMA) and ethylene glycol dimethacrylate (EGDMA; Aldrich) were also procured from trade.

Purification of the monomers, initiator, and solvents (diluent)

The purification of St, DVB, and Bz_2O_2 has already been reported in our earlier communication.¹² Dimethacrylates were also purified in a manner similar to that used for St. Diluents (solvents) were used without further purification.

Copolymerization procedure

The suspension copolymerization of St with each of the crosslinking monomers (DVB or dimethacrylates) was carried out in a double-walled glass reactor, as reported in our earlier publication.^{12,13}

St copolymer beads were isolated and characterized by techniques and measurements such as IR, apparent density, swelling percentage, surface area, porosity (pore volume and pore width), compressive strength, thermal stability, and surface morphology.¹⁴

Characterization

St-divinyl crosslinked copolymer beads were characterized with the following technique: Fourier transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm^{-1} with a Nicolet Impact 410, FT-IR spectrometer, M/s Thermo Fisher Scientific (Madison, WI) in KBr pellets.

The apparent density of the St-DVB copolymer beads was determined per IS7330-1974.

Swelling (%) in toluene was measured with a 5-g oven-dried sample in a stoppered test tube. The sample was soaked with 20 mL of toluene for 24 h at the ambient temperature. Toluene was filtered, and the beads were padded dry with filter paper and weighed:

$$\text{Swelling (\%)} = \left[\frac{(\text{Increase in the weight of the beads})}{(\text{Original weight of the beads})} \right] \times 100$$

The surface area, pore volume, and pore width of the St-DVB copolymer beads were measured from a conventional N_2 sorption isotherm on an Autosorb IC-M/S Quanta Chrom (USA) following the Brunauer-Emmett-Teller (BET) method, Barnett-Joyner-Halenda (BJH) method (mesopore volume), and Dubinin-Radushkevich (DR) method (micropore volume and micropore width),¹⁵ respectively.

The mechanical strength of the St-DVB copolymer beads was recorded on a Good-Brand Testometric Micro-350 tensile tester machine (United Kingdom) with a crosshead speed of 0.5 mm/min. The com-

pressive strength was calculated from the force required to crush the bead divided by the bead area.

A JEOL JSM-840, scanning electron microscope (Tokyo, Japan) was used to study the surface morphology of the St-DVB copolymers at 5 kV after the specimens were coated with a thin layer of gold in a JFC-1100 sputter-coating unit (Tokyo, Japan).

Thermogravimetric analysis was studied with a TGA 2950 thermogravimetric analyzer (TA Instruments, New Castle, DE) in air from room temperature to 700°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The suspension copolymerization of St with each of the crosslinking monomers (DVB or dimethacrylates) was carried out in water under an N_2 atmosphere at 80°C with Bz_2O_2 and PVA as the initiator and suspending agent, respectively. Crosslinking comonomers that were selected for this study included BADMA, EGDMA, NGDMA, butanediol dimethacrylate (BDDMA), hexamethylene glycol dimethacrylate (HMGDMA), and DVB. The following formulation was used in this copolymerization: 80.0 parts St, 20.0 parts crosslinking monomer, 1.0 part Bz_2O_2 , 0.5 parts PVA, 700.0 parts water, 100 parts diluent, a temperature of 80°C, and a copolymerization time of 360 min.

The copolymerization of St with crosslinking monomers resulted in copolymer beads, which were filtered, washed, and dried as reported previously.

FTIR

Characteristic absorption bands of St and dimethacrylates were observed in the FTIR spectra of St-dimethacrylate copolymers. IR spectra showed absorption at 699 cm^{-1} due to a phenyl ring and at 2928 cm^{-1} along with a small peak at 3025 cm^{-1} due to aliphatic C—H stretching. Furthermore, IR peaks at 1747 and 1169 cm^{-1} , characteristics of C=O and C—O—C (esters), respectively, confirmed the incorporation of dimethacrylates into polystyrene chains. Sharp peaks at 1575, 1501, and 760 cm^{-1} of aromatic C—H may have been due to the presence of a phenyl ring. The presence of C—H (aliphatic and aromatic), C=O, and C—O—C peaks in the FTIR spectra of St-dimethacrylate copolymers was in agreement with the reported literature.¹¹ FTIR spectra of St-DVB copolymers have already been reported.¹²

Effect of the crosslinking comonomers on the characteristics of the St copolymers

The crosslinking of polymers is frequently presumed to enhance the thermal stability of polymer systems. Therefore, research on the correlation between the crosslinking and thermal stability of St polymers has been studied with various crosslinking monomers

TABLE I
Thermal Degradation of the Polystyrene Copolymer with Various Crosslinking Monomers

Sample	St:crosslinker	Crosslinker	Compressive strength (MPa)	Swelling (%)	IDT (°C)	Temperature (°C)			IPDT (°C)
						10% weight loss	40% weight loss	60% weight loss	
1	80 : 20	EGDMA	44	44	210	324	365	408	407
2	80 : 20	BDDMA	17	40	180	281	362	387	388
3	80 : 20	NGDMA	43	48	170	277	345	365	405
4	80 : 20	HMGDMA	40	45	150	284	328	353	377
5	80 : 20	BADMA	20	54	225	317	370	395	419
6	80 : 20	DVB	>50	37	235	291	389	425	471

such as DVB and dimethacrylates (EGDMA, NGDMA, BADMA, etc.).

St–dimethacrylate and St–DVB copolymers were subjected to thermal degradation in air, and the results are summarized in Table I. These thermal degradation data were compared to determine the effect of the crosslinking monomer on the thermal stability of the St copolymers (Table I). A perusal of the thermal stability data indicates that St–dimethacrylate copolymers degrade faster than St–DVB copolymers. Among the St copolymers studied, the St–DVB copolymers were found to be most thermally stable, as determined by the high initial decomposition temperature (IDT), temperatures at different weight losses, and high integral procedural decomposition temperature (IPDT) values (relative measure of thermal stability). These data further suggest that the thermal stabilities are in the following order:



However, St–dimethacrylate copolymers had higher swelling (40–54%) and lower compressive strength (17–43 MPa) than the values of 37% and >50 MPa for St–DVB copolymers. The variation in these properties, that is, increased swelling and poor compressive strength in St–dimethacrylate copolymers, may be due to the increased chain length in the dimethacrylate comonomers. Furthermore, these data are in agreement with the reported results.¹⁶

These thermal stability data led us to the conclusion that DVB as a crosslinking monomer results in crosslinked polystyrene of higher thermal stability with high compressive strength and adequate swelling.

Selection of the crosslinking monomer

The characteristics of the polystyrene copolymers, particularly the thermal stability, swelling percentage, and compressive strength, led us to the conclusion that the St–DVB copolymer was better than the

St–dimethacrylate copolymers. Therefore, DVB was selected as a crosslinking monomer for further studies.

Effect of diluents on the characteristics of St–DVB copolymers

The St–DVB copolymer was selected as a system for studying the influence of diluents on achieving porous, crosslinked polystyrene. It has already been reported in the literature^{5–10} that porous beads or networks are obtained when St and DVB are copolymerized in the presence of inert, nonpolymerizable compounds. Therefore, a number of inert diluents were tried to achieve porous beads. These diluents are characterized by differences in the polarity, chemical structure, functional behaviors, and solvent–polymer interaction values¹⁷ that will lead to networks with a large variety of porous structures. Some of the solvents, such as toluene and cyclohexanol, are very good solvents for polystyrene. The influence of these compounds will be reflected in the porous network structure. The diluents' solubility¹⁸ in the water phase is also given in Table II. The solvents used in this study have varied solubility in water. Some of them give an azeotrope with water, but it should be emphasized that the diluents were used together with large volumes of St and DVB, which were not miscible with water. In this case, the distribution coefficients of the diluents between the water and monomer phase are altered, and almost the entire quantity of the diluents is dissolved in the monomer phase. During polymerization in the presence of a good solvent, the chains are at all times fully solvated and less entangled. However, in the presence of precipitating diluents, the system becomes richer in the precipitating diluents, and separation phases occur. As network chains form, they are no longer extended because of high solvent–polymer interaction. The removal of diluents results in the collapse of the expanded network, which results in the formation of porous beads.^{5–10} The resultant beads were analyzed for the swelling percentage, apparent density, compressive strength, and BET surface area and porosity measurements.

TABLE II
Physical Properties of the Diluents

Sample	Solvent	Boiling point (°C)	Solubility parameter [(MPa) ^{1/2}]	Diluent miscibility in water (w/w)
1	Toluene	110	18.1	19.6% (azeotrope)
2	<i>n</i> -Heptane	99	15.1	0.455%
3	Cyclohexanol	161	23.3	6% (azeotrope)
4	2,2,4-Trimethyl pentane	99	—	2%
5	2-Ethyl hexanoic acid	117	—	—
6	Methyl ethyl ketone	80	19.0	27.5%
7	Tri- <i>n</i> -butyl phosphate	—	—	%
8	Benzyl alcohol	205	24.8	1 g/25 mL
9	<i>n</i> -Butyl alcohol	118	23.3	9.1 mL/100 mL
10	2-Ethyl-1-hexanol	185	21.5	720 parts
11	2-Methoxy ethanol	125	—	3.1%
12	Cyclohexane	81	16.8	8.4
13	Cyclohexanone	156	20.3	5
14	Polystyrene	—	20.3	—
15	Poly(vinyl benzene)	—	18	—

Apparent density

St-DVB copolymer beads produced in the presence of toluene as a diluent had an apparent density of 0.538 g/cm³, as given in Table III. These values changed to 0.730, 0.610, and 0.646 g/cm³ when the diluents were changed to cyclohexane, 2,2,4-trimethyl pentane, and cyclohexanone, respectively. When nonsolvating diluents such as cyclohexanol, 1-butanol, and 2-ethyl-1-hexanol were used, the apparent density was further reduced to 0.230–0.426 g/cm³. Although 2-methoxyethanol and benzyl alcohol are nonsolvating-type diluents, still beads of higher apparent density values (0.683 and 0.750 g/cm³) were achieved. Solvents such as methyl ethyl ketone, chlorobenzene, and alkyl phosphates gave beads having apparent density values of 0.440–0.471 g/cm³.

These density values indicate that solvating-type diluents (toluene and cyclohexanone), result in beads having high apparent density values (0.538–0.646 g/cm³). Similarly, St-DVB copolymer beads having the lowest apparent density values were achieved when nonsolvating-type diluents (cyclohexanol) were used in these experiments. The variation in the apparent density values in the polystyrene-divinyl benzene [P(St-DVB)] copolymer beads may be explained on the basis of polymer-solvent interaction or solubility parameter values (Table II). Because of the difference in the solubility parameter values of the nonsolvating diluent and P(St-DVB), collapse of the expanded network structure results in the formation of porous beads.^{6–10} Apparent density values also indicate the porous nature of the St-DVB copolymer beads.

TABLE III
Characteristics of the St-DVB Copolymer Beads in the Presence of the Diluents

Sample	Solvent	Swelling (%)	Apparent density (g/cm ³)	Compressive strength (MPa)	Surface area (m ² /g)
1	No solvent	31	0.989	32.0	55
2	2,2,4-Trimethyl pentane	61	0.330	5.61	153
3	Cyclohexane	12	0.730	nd	109
4	Tri- <i>n</i> -butyl phosphate	29	0.442	8.10	83
5	2-Methoxy ethanol	53	0.683	15.0	73
6	Toluene	34	0.538	9.81	91
7	Bis(ethyl)hexyl phosphate	38	0.456	12.4	69
8	Ethyl methyl ketone	37	0.471	11.4	88
9	Chlorobenzene	74	0.446	5.6	75
10	2-Ethyl-1-hexanol	128	0.426	4.2	217
11	Cyclohexanone	72	0.646	17.7	108
12	<i>n</i> -Butyl alcohol	46	0.283	nd	62
13	Cyclohexanol	89	0.230	3.87	270
14	Benzyl alcohol	11.0	0.750	nd	90
15	Standard	20.0	0.657	9.0	120

nd = not determined.

TABLE IV
Effect of the Cyclohexanol Concentration on the Characteristics of the St–DVB Copolymer Beads

Sample	St : DVB	Cyclohexanol (%)	Compressive strength (MPa)	S_{BET} (N_2 , BET; m^2/g)	V_{micro} (N_2 , DR; cc/g)	V_{meso} (N_2 , BJH; cc/g)	Micropore width (N_2 , DR; Å)
1	80 : 20	25	30	76	0.016	0.0070	33.09
2	80 : 20	50	20	129	0.061	0.2925	32.97
3	80 : 20	75	10.5	181	0.069	0.2975	31.43
4	80 : 20	100	3.8	270	0.107	0.3879	31.40
5	80 : 20	—	34	57.08	—	—	—

S_{BET} = BET surface area; V_{meso} = mesopore volume; V_{micro} = micropore volume.

Swelling measurements

Toluene was selected as the solvent for determining the swelling percentage of the St–DVB copolymer beads. A higher swelling percentage was achieved in copolymers synthesized with cyclohexanol (89%) and 2-ethyl-1-hexanol (128%) as diluents (Table III). Furthermore, toluene as a diluent resulted in copolymers having minimum swelling (34%). These values further indicate the generation of more porous copolymer beads prepared with nonsolvating diluents. Therefore, P(St–DVB) beads prepared in the presence of cyclohexanol as a diluent showed a higher amount of swelling. Solvating-type diluents (toluene) resulted in beads of poor porosity, as indicated by lower swelling percentage values. However, slightly higher values of the swelling percentage in the copolymer beads synthesized with cyclohexane as a diluent cannot be explained. These results further suggest that the porous nature of the beads is responsible for their higher swelling in solvents.^{5–10}

Compressive strength

As mentioned earlier, the incorporation of inert diluents resulted in porous St–DVB copolymer beads. When these beads were subjected to compressive strength measurements, values in the range of 5.6–17.7 MPa (Table III) were obtained. The lowest compressive strength value (3.9 MPa) was achieved when cyclohexanol was used as a diluent, and this indicated the highly porous nature of the St–DVB copolymer beads. Higher compressive strength values for the St–DVB copolymer beads were achieved with 1-butanol, 2-methoxy ethanol, and cyclohexanone (14.2, 15.0, and 17.7 MPa, respectively) as diluents, and this indicated their poor porosity.

Surface area and porosity

The incorporation of a diluent during the copolymerization of St and DVB results in the production of porous structures, as indicated by the increased BET surface area and porosity. The presence of diluents such as toluene, *n*-heptane, cyclohexane, cyclohexanone, and 1-butanol results in P(St–DVB) beads having surface areas in the range of 62–107 m^2/g

(Table III). The highest surface area of 270 m^2/g was achieved when cyclohexanol was employed as the diluent. This was due to the difference in the solubility parameters and CED values of P(St–DVB) and cyclohexanol. CED is the energy of vaporization per cm^3 and square root of CED is known as solubility parameter. It describes the attractive strength between molecules of styrene-divinyl benzene copolymer beads and diluent. Furthermore, cyclohexanol proved to be a strong precipitant diluent in comparison with other diluents. Thus, the highest porosity was achieved in St–DVB copolymer beads with cyclohexanol as the diluent. These results are in agreement with the reported literature.^{6–8} Furthermore, the surface area of the St–DVB copolymers was reduced to 181 and 76 m^2/g , respectively, as the amount of cyclohexanol was reduced from 100 parts to 75 and 25 parts in the polymerization formulation. St–DVB copolymer beads synthesized in the presence of cyclohexanol were also investigated for the micropore volume, mesopore volume, and micropore width, and the results are described in Table IV. For the measurement of these properties, the amount of cyclohexanol was varied from 25 to 100% (with respect to the monomer). As the amount of cyclohexanol increased, the micropore volume and mesopore volume increased linearly. When the amount of cyclohexanol was 25%, the mesopore volume and micropore volume were 0.016 and 0.0070 cc/g, respectively, whereas with 100% cyclohexanol, they increased to 0.107 and 0.3879 cc/g, respectively. Similarly, variation in the micropore width values was also observed with an increased concentration of cyclohexanol.

Surface morphology

St–DVB copolymer beads were subjected to surface morphology study using a scanning electron microscope. Copolymers prepared in the presence or absence of a diluent were cut by a sharp blade at the temperature of liquid nitrogen. A scanning electron micrograph of an St–DVB copolymer synthesized in the absence of any diluent shows a smooth surface with no or few holes, voids, or microdefects [Fig. 1(a,b)]. The presence of a few microdefects in the

surface suggests some limited porosity in St–DVB copolymers prepared without any diluent. However, when a diluent was incorporated during copolymerization, the copolymer surface was found to be heterogeneous (Fig. 2). The presence of cyclohexanol as a diluent during the copolymer formation resulted in phase separation, producing rougher surfaces with an increasing number of holes, voids, and microdefects; this suggested the increased porous nature of the resultant copolymer beads [Fig. 2(a,b)]. The increased porosity of St–DVB copolymers in the presence of cyclohexanol may be due to the formation of more rigid, entangled nuclei resulting in agglomerates with large holes. Furthermore, cyclohexanol is a nonsolvating-type diluent for polystyrene, as indicated by its solubility parameter value (Table I), and leads to better porosity, as reported in the literature.^{4–10} These surface morphology findings are in agreement with the reported literature.

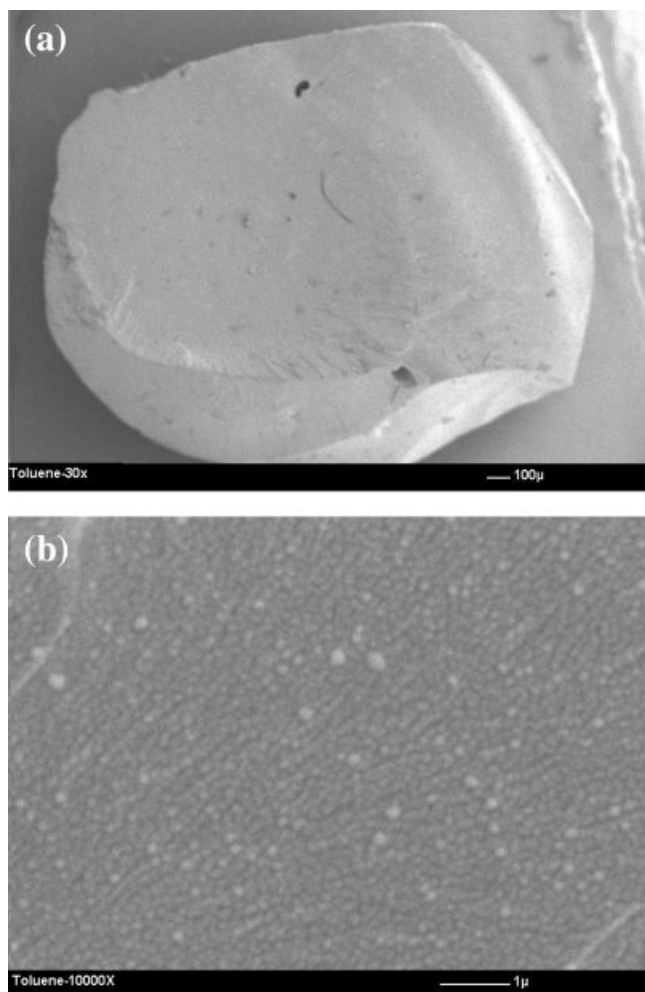


Figure 1 Surface examination of St–DVB copolymer cut beads prepared in the presence of no diluent: (a) 30 and (b) 10,000 \times .

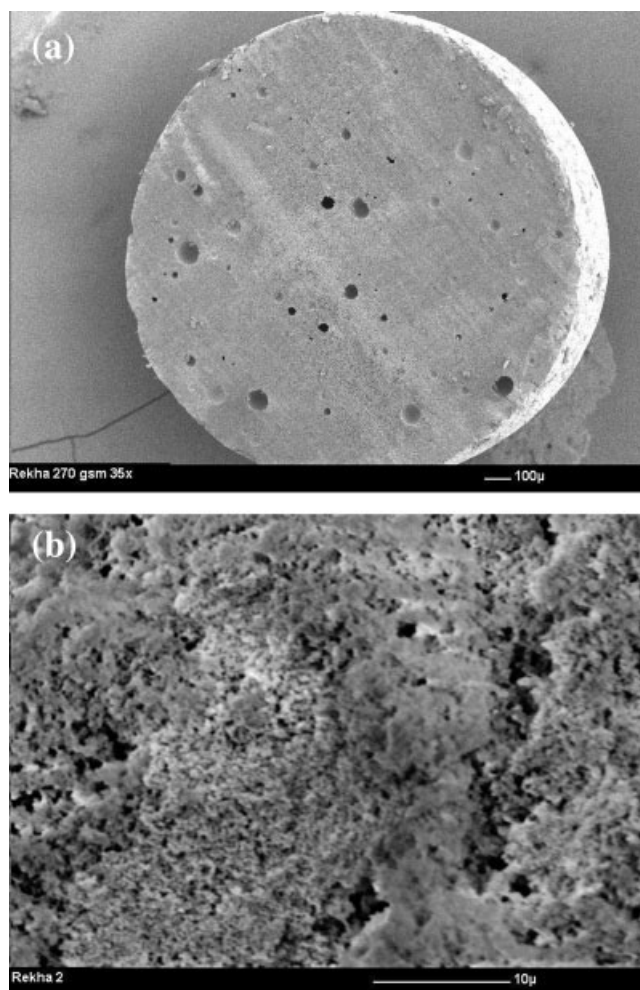


Figure 2 Surface examination of St–DVB copolymer cut beads prepared in the presence of cyclohexanol: (a) 35 and (b) 2000 \times .

CONCLUSIONS

Crosslinked St copolymers were synthesized by the suspension copolymerization of St with vinyl cross-linking monomers (dimethacrylates and DVB) with PVA as the suspending agent, and St–DVB copolymers were found to be the most thermally stable. Furthermore, inert diluents were incorporated during the copolymerization of St and DVB to produce porous, crosslinked St copolymer beads. Among the diluents employed, cyclohexanol resulted in porous St–DVB copolymer beads of the highest porosity, as indicated by the highest BET surface area value. The highest porosity was further confirmed by the swelling percentage, apparent density, and compressive strength values and surface morphology studies of P(St–DVB) beads.

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