

Research Article

Styrene-DVB Copolymers: Influence of Cyclohexanol and 1-Butanol on Matrix Structure

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Abstract

In order to induce permanent porosity in the classical matrix, styrene-DVB copolymers were synthesized by suspension copolymerization technique in the presence of a number of inert diluents as pore forming agents. It was found that a mixture of non-solvating diluents such as cyclohexanol and 1-butanol served as the most efficient combination for obtaining macroporous solvent impregnated copolymers of highest porosity. Porous texture and morphology analyses by BET surface area, compressive strength, apparent density as well as % swelling and scanning electron microscopy.

Keywords: Diluents, Copolymerization, Synthesis, Surface area, Swelling

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Introduction

During the past few decades styrene- DVB copolymers have emerged as a potent choice of chemists as well as industries owing to their versatile application. These copolymers serve as excellent starting material for synthesis of cationic ion exchange resin [1-4]. On modifying the nature of functional group attached at the aromatic ring of polystyrene these support exhibit manifold applications [5-9] such as

- reactive polymers,
- gel permeation chromatography column packings,
- polymer supported catalysts, absorbents,
- polymer immobilized extractions,
- precursors for active carbon spheres.

These polymers have been a subject of interest due to their characteristics like remarkable mechanical stability and features of these polymers mainly emerge due to their highly porous structure and swelling properties [10-11].

Macroporous styrene-DVB is mainly prepared by free radical crosslinking copolymerization of styrene and DVB monomers in the presence of an inert diluent. When no diluent is used in the polymerization process, the obtained copolymers are compact gels [12-14]. The porosity of the network appears in the solvent allowing a significant swelling. If the inert diluent is used during copolymerization a phase separation occurs. This phenomenon gives rise to a porous network. The morphology of these copolymers obtained by suspension copolymerization is influenced by the polymerization parameters [15-18] such as

- crosslinking agent (DVB) amount,
- diluent nature (either solvent or non-solvent),
- degree of monomers, porogen agent content, reaction temperature etc.

The main aim of our present study is to show that the structure of copolymers of styrene and DVB prepared from same mixture of reactants while keeping the polymerization conditions identical varied with the kind of diluent used. The copolymerization was studied in presence of various diluents and $Mg(OH)_2$ as suspending agent. Effect of diluents on characteristics of beads like BET surface area, apparent density, swelling and surface morphology has been reported in the present paper.

Experimental

Materials

Chemicals required for the present study i.e. Styrene, Divinyl benzene, Magnesium hydroxide, Sodium chloride, Benzoyl peroxide, Toluene, n-Heptane, 1-Butanol, Trimethyl pentane, 2-Ethyl hexanoic acid, Lauryl alcohol, benzyl alcohol, 2-Methoxy ethanol, cyclohexanol, Cyclohexanone, Cyclohexane, Bis 2- ethyl phosphate, Tris n-butyl phosphate, Methyl ethyl ketone, 2- Ethyl hexanol were procured from trade.

Purification of monomers, initiator and solvents (diluent)

Styrene and DVB were purified by treatment with 5% NaOH solution followed by washings with water, dried over anhydrous sodium sulphate and finally vacuum distilled. Benzoyl peroxide was recrystallized from chloroform. Diluents (solvents) have been used without further purification.

Copolymerization procedure

Suspension copolymerization of styrene and DVB was carried out in a double walled glass reactor fitted with a nitrogen inlet, condenser and mechanical stirrer. The organic phase (monomers, initiator and solvent) was introduced in the reactor containing the aqueous phase (water, Mg(OH)₂ and NaCl) at room temperature. The temperature was raised to 80⁰C and reaction carried out for 6 hrs. The copolymers beads were filtered and washed with water followed by methanol. The beads were vacuum dried at 80-100⁰C for 48 hrs [19-20].

Formulation

Chemical	In Parts
Styrene	80.0
DVB	20.0
Bz ₂ O	1.0
Water	200.0
Mg(OH) ₂	2.0
NaCl	10.0
Diluent	100.0

Characterization

Styrene- DVB copolymers beads are cross linked resins and characterized by the following techniques: FTIR spectra were recorded in the range 400-4000 cm⁻¹ using Nicolet spectrophotometer in KBr pellet. The apparent density of the styrene-DVB copolymer beads was determined using graduated cylinder method as per IS7330-1974.

Swelling (%) in toluene was measured by taking 5g oven dried sample in a stoppered test tube. The sample was soaked with 20 ml toluene for 24 hrs at ambient temperature. Toluene was filtered and beads were padded dried with a filter paper and weighed [20].

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

The surface area of styrene-DVB copolymer beads was measured from conventional N₂ sorption isotherm on autosorb IC-M/s Quanta chrom, USA following the BET method. Mechanical strength of styrene- DVB copolymer beads was recorded on Good- Brand Testometric micro-350 tensile tester (UK) with a cross head speed of 0.5mm/min. Compressive strength was calculated from the force required to crush the bead divided by bead area. 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 JFC-1100 sputter coating unit.

Result and discussion

In the present study we have used a number of mixtures of diluents with the aim to induce maximum porosity in copolymer beads obtained by suspension copolymerization of styrene and DVB. The actual mechanism of pore formation is précised as follows.

When we used a mixture of non-solvent diluent for the suspension copolymerization, during the polymerization process there is a mixture consisting of non-solvating diluent and solvated monomer of polystyrene chain. The ratio between the non-solvating diluent and solvating compound changes during the copolymerization. As the process proceeds, the system becomes richer in non-solvating diluent and thus separation of phase (polymer and diluent phases) occurs. As the network chain form, the growing chain have tendency to entangle inside the virtually unswollen nuclei. The structure which is obtained has large entangled nuclei connected by a number of coiled inter-molecular chains. In this way polymer and diluent phases are segregated. The distribution of diluent between polymer and diluent phases at the end of copolymerization determined the total porosity of resulting copolymer. On removal diluent we get a porous network composed of various agglomerates of basic practical (micro gels) more or less fused together. Spaces left between these agglomerates are the matrix pores. A mixture of the two non-solvating diluent such as cyclohexanol and 1-butanol gave result in present study.

Infra-Red

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

Apparent density

The copolymer beads show maximum porosity when apparent density is low i.e. low value of apparent density is desirable for macroporous polymer. The value of apparent density changes from 0.35 to 0.70 g/cm^3 when mixture of diluent changes as per given in **Table 1**. However when mixture of cyclohexanol and 1-butanol was used it gives higher apparent density value of about 0.7 g/cm^3 . This indicates less porosity. Similarly styrene-DVB copolymer beads having lowest apparent density value were achieved when mixture of non-solvating diluent cyclohexanol and 1-butanol is used; it gives lower apparent density value about 0.35 g/cm^3 . This shows higher porosity in styrene-DVB copolymer beads. All these variation in apparent density values of styrene-DVB copolymer beads were explained on the basis of polymer-solvent interaction or solubility parameter values.

Table 1 Characterization of styrene-DVB copolymers in presence of mixtures of diluents

Sr. No	Mixtures of diluents	Quantity	Swelling (%)	Apparent density (g/cm^3)	Compressive strength (Mpa)	Surface area (m^2/g)
1.	Cyclohexanol/Toluene	50:50	59.1	0.637	11.6	69.84
2.	Cyclohexanol/Benzyl alcohol	50:50	67.7	0.475	7.0	94.32
3.	Cyclohexanol/2-ethyl hexanol	50:50	69.0	0.418	6.2	121
4.	Cyclohexanol/n-butyl alcohol	95:05	68.0	0.550	6.0	102
		90:10	63.0	0.520	6.1	160

Swelling measurement

Highly porous nature of beads governs higher swelling in solvent and vice-versa. Toluene was selected as solvent for determining the swelling of styrene-DVB copolymer beads. The swelling measurement changes from 59.0% to 84.2%. Highest % swelling was achieved in presence of mixture of diluent cyclohexanol and 1-butanol. This further indicates highest porosity in styrene-DVB copolymer beads. The lower % swelling was obtained in presence of mixture of diluent toluene-cyclohexanol.

Compressive strength

Low value of compressive strength is desirable for copolymer beads of high porosity. When styrene-DVB copolymer beads are subjected to compressive strength measurements; results into values in the range 5.6 Mpa to 15.3 Mpa. Lowest compressive strength value was achieved in mixture of diluent i.e. 1-butanol and cyclohexanol, indicates highest porosity of styrene-DVB copolymer beads. Highest compressive strength value was achieved in mixture of cyclohexanol and toluene about 15.3 Mpa, indicates poor porosity.

Surface area

When copolymerization is done in presence of diluent, highly porous structures are formed which becomes evident by increased BET surface area of resulting beads. Highest surface area of $224 \text{ m}^2/\text{g}$ was obtained when mixture of cyclohexanol and 1-butanol were used.

Surface morphology

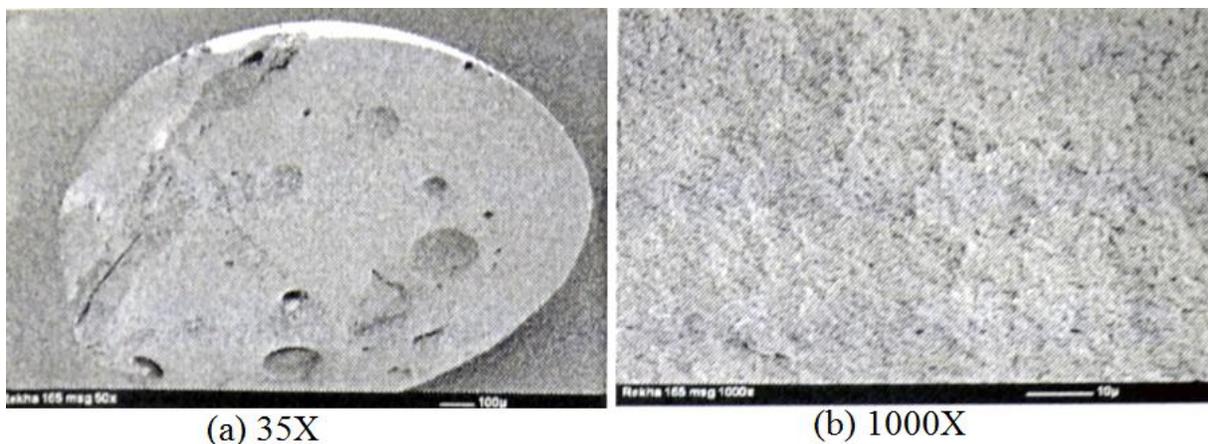


Figure 1 Surface examination of styrene-DVB copolymers cut beads prepared in presence of cyclohexanol diluent

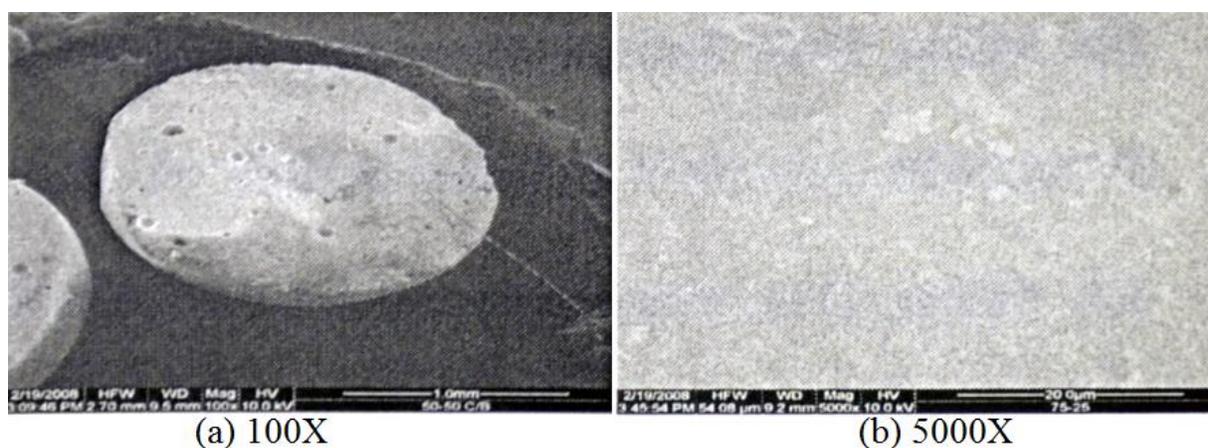


Figure 2 Surface examination of styrene-DVB copolymers cut beads prepared in presence of cyclohexanol-1-butanol mixture in ratio 75-25.

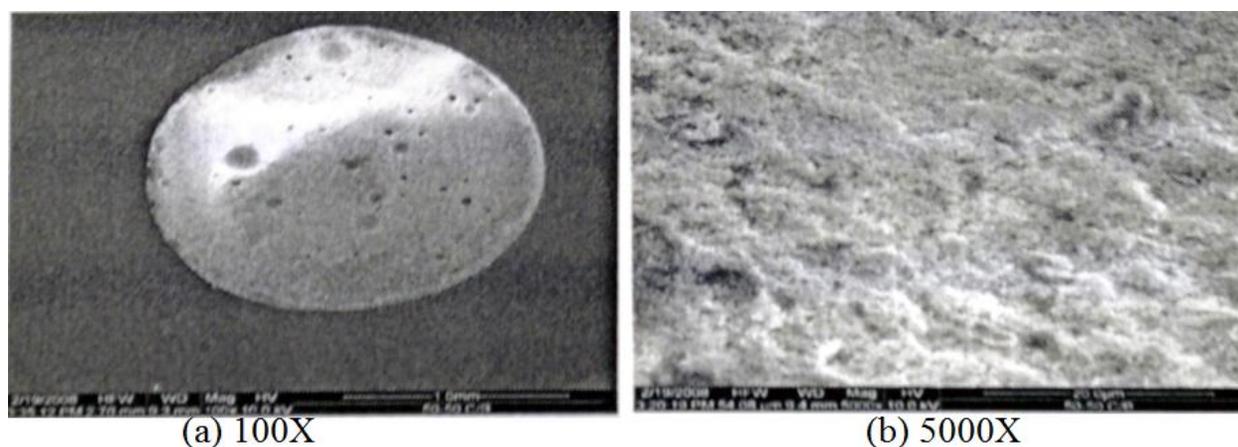


Figure 3 Surface examination of styrene-DVB copolymers cut beads prepared in presence of cyclohexanol-1-butanol mixture in ratio 50-50

Scanning electron microscopy was used to study the surface morphology. When copolymerization is done in absence of diluent, we get a smooth and plane surface with no or few holes, voids or micro defects. On the contrary, when diluent is incorporated heterogeneous surface with increased number of holes, voids and micro defects were obtained. On using mixture of cyclohexanol and 1-butanol as diluent a highly heterogeneous surface was obtained, as shown in **figure 1**, **figure 2** and **figure 3**.

Conclusion

The mixture of cyclohexanol and 1-butanol served as the most efficient combination for obtaining macroporous solvent impregnated copolymers of highest porosity. This is further confirmed by other parameters such as BET surface area, apparent density, and compressive strength as well as % swelling.

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