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1, 6-Hexanediol Diacrylate Cross-linked Polystyrene-A novel catalyst support system-Its synthesis, swelling capacity studies and surface morphological analysis

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Abstract

Cross-linked polymers with specific properties are widely used as catalyst support as they are inert, non toxic and non volatile and offer advantageous features of heterogeneous catalysis such as thermal stability selectivity and recyclability to homogeneous system. The ease of separation from the reaction products lead to operational flexibility. Here we report the synthesis, characterisation and comparative study of swelling capacity and surface morphology of different mol % of styrene –HDODA copolymer. Suspension polymerisation is used for the preparation of Styrene - 1, 6-hexanediol diacrylate (HDODA) copolymer beads with different mole percent of HDODA content. They can be used as catalyst support, as the base for the preparation of cation exchangers and anion exchangers. The characterizations of the polymers were done by FTIR spectroscopy and SEM analysis.

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Keywords: Cross-linked polymers, polystyrene, HDODA, swelling;

1. Introduction

Cross linked polymers are used in a wide variety of scientific and technological applications with high value added materials such as ion exchangers, medical and chemical application as absorbents and as supported catalysts [1-3]. The various forms of polymer supports for the preparations of heterogeneous catalyst are in the form of colloids, flakes, gel beads, etc [4].

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In solid phase synthesis cross linked polystyrene resins are generally used as solid supports [5].There are a large number of reasons for using cross-linked polystyrene as catalyst support [6-14].They are experimentally more useful because of their ease of filtration [15-19]. An important characteristic of polystyrene beads is their ability to absorb certain organic solvents (swelling) [20]. These swelling causes a phase change of the bead from a solid to solvent swollen gel, and therefore the reactive site are accessed by diffusion of reactant through a solvent swollen gel network. The degree of cross-linking determines the solubility, extent of swelling, pore size and mechanical stability of the polymer. The degree of swelling directs the effective pore size and molecular weight exclusion limit for penetration of the reagent. Lightly cross linked polystyrene has been most commonly used because of its common availability and low cost and shows considerable swelling in various solvents [20].
But resins based on divinyl benzene cross-linked polystyrene (PS-DVB) supports show low metal ion uptake. This may be due to low flexibility and hydrophobic character of the polymer backbone. This limits its demand in catalytic applications. Here a new cross-linker 1, 6-hexanediol diacrylate (HDODA) which is flexible and possess optimum hydrophobic hydrophilic balance [21] is inspected for its suitability in catalysis. We report the swelling capacity and surface morphology of different mole percentage of HDODA cross-linked polystyrene (PS-HDODA) for the establishment of its suitability in catalysis.

2. Experimental

2.1. Materials and methods

Styrene and HDODA were purchased form Sigma Aldrich. Acetone, methanol, toluene, DMF, DCM, benzoyl peroxide and PVA were obtained from Merck chemical company. The FTIR spectra were recorded on a Bruker IFS-55 spectrometer using KBr pellets. The scanning electron micrographs were taken using a Hitachi S-2400 instrument. Swelling studies were conducted under room temperature.

2.2. Synthesis of 2, 4, 6 & 8 mol% HDODA cross-linked polystyrene [22]

Free radical suspension polymerisation is used for the synthesis of cross-linked polystyrene. For the synthesis of 2% HDODA cross-linked polystyrene a mixture of styrene (98mmol), HDODA (2mmol), Toluene (8ml) and benzoyl peroxide (1g) was prepared. It is then suspended into a 1% solution of PVA. The above mixture is mechanically stirred at 80 ^{0} C. Polymerisation reaction (Fig 1.) was completed after 6 hrs. The beaded product was collected by filtration. It is then washed with hot water, acetone, and methanol. The product resin was extracted using acetone to remove linear polymers and low molecular weight impurities and dried at 80 ^{0} C. Beads were sieved into different size using standard sieves. Polymers of 4, 6 & 8% HDODA cross-linking were prepared by adjusting the relative amounts of the monomer (Table 1).

Table 1. Preparation of HDODA cross-linked polystyrene.

HDODA (mol %)	Amount of monomers		Yield (g)
	Styrene (ml)	HDODA (ml)	
2	11.20	0.40	9.24
4	11.00	0.90	8.23
6	10.77	1.34	8.68
8	10.54	1.79	9.17

2.3. Swelling studies

1-2 g of the resin was placed in sintered crucible and kept in a beaker containing the solvent. After 24 hours the solvent was carefully sucked out from the crucible. The swollen and dry weights were measured. The experiment was repeated with other solvents. The swelling data were expressed in mL/g of the resin. (Table 2)

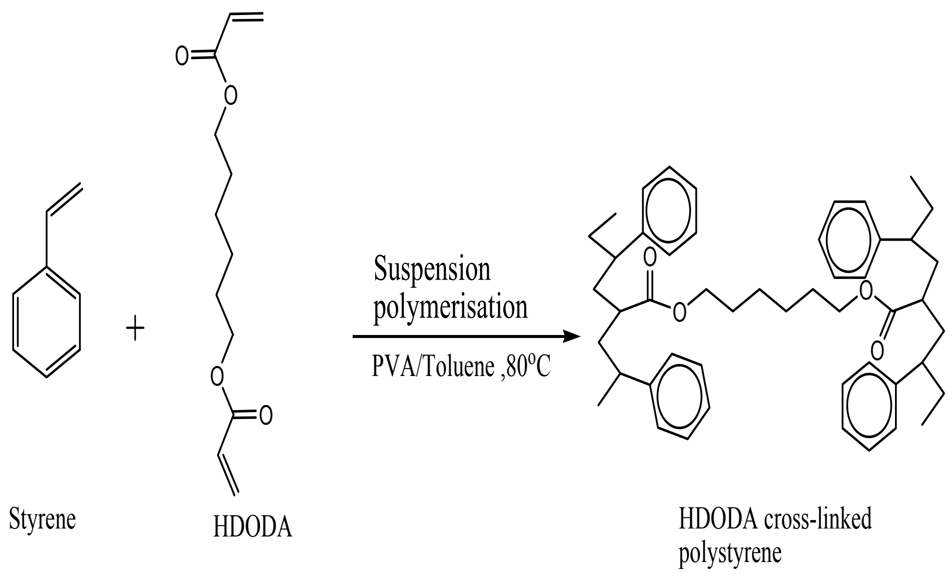


Fig 1. Polymerisation reaction of styrene with HDODA [23]

3. Results and discussion

Polystyrene with 2-8 mol% HDODA cross-links were obtained by free radical suspension copolymerisation of the monomers at 80 ^{0}C. Benzoyl peroxide was used as the radical initiator and toluene as the inert solvent. Polymers with varying extent of the cross-links were prepared by adjusting the mol % of the monomers in the feed. Swelling capacity measurements of the cross-linked polymers were carried out in DCM, DMF, and NMP (Table 2). The graphical representation of swelling capacities was given in figure 2. The swelling range of the polymers in DCM was 10.01-6.44mL/g. In DMF the swelling range was 7.51-5.68 mL/g. But in NMP it was 9.26-6.38 mL/g. 2% cross-linked polymer showed greater swelling with all solvents.

With increasing cross-linking percentage, swelling capacity gets decreased. This reduction arises from contraction of polymeric chains with increased cross-linking resulting in decreased intake of solvent. We have obtained greater swelling was in the solvent DCM, which was 10.01-6.44 mL/g. The FTIR spectra of different mol % copolymers are shown below (Fig 3), where A2, A4, A6 and A8 represents 2, 4, 6, and 8 mol% HDODA cross-linked polystyrene respectively.

Table 2. Swelling studies

Solvent	Cross-linking Percentage of the polymer	Swelling capacity mL/g of resin
DCM	2	10.01
	4	8.61
	6	7.94
	8	6.44
NMP	2	9.26
	4	8.02
	6	7.35
	8	6.38
DMF	2	7.51
	4	6.95
	6	6.23
	8	5.68

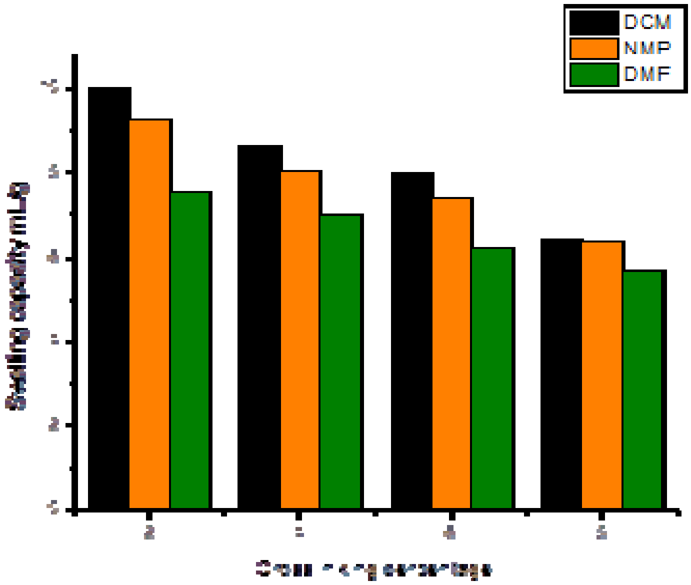


Fig 2. Graphical representation of swelling capacity measurement

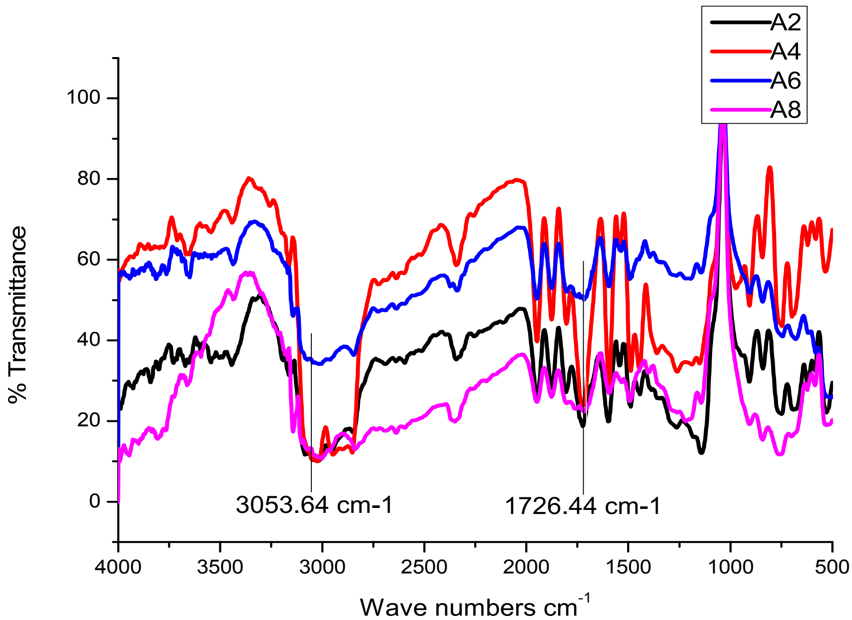
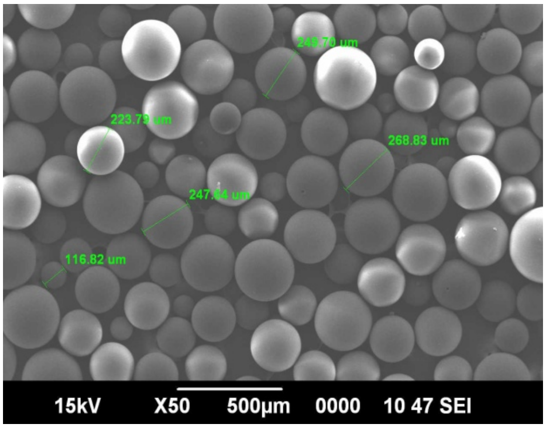
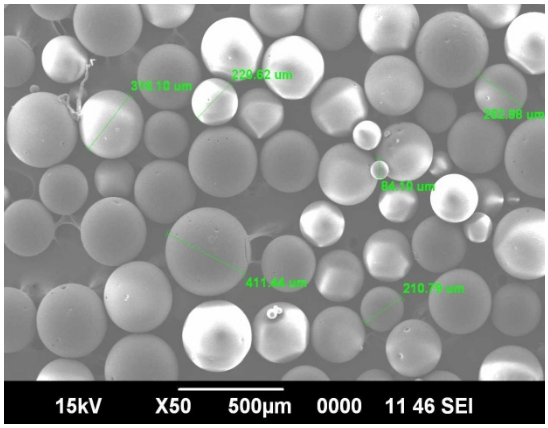
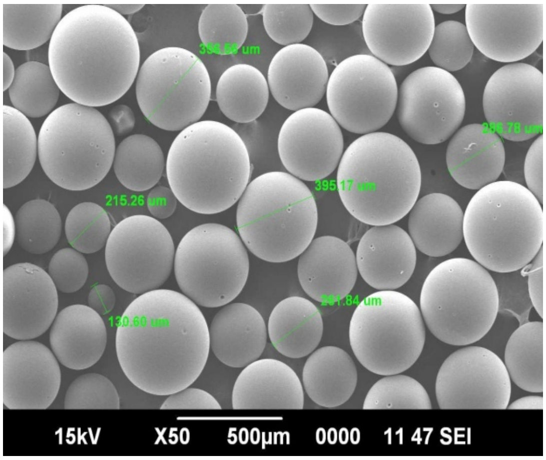


Fig 3. FTIR spectra of HDODA cross linked polystyrene





(a) (b)



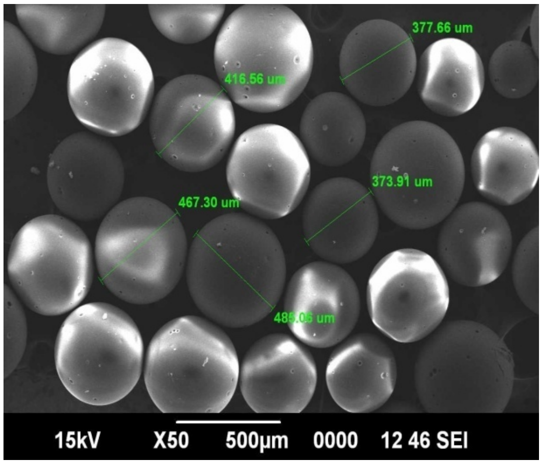


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Fig 4. SEM image of (a) 2% HDODA cross-linked polystyrene, (b) 4% HDODA cross-linked polystyrene, (c) 6% HDODA cross-linked polystyrene, (d) 8% HDODA cross-linked polystyrene .

Scanning electron microscopy is used to study the shape, size, morphology and porosity of the polymers. The change in surface morphology of the polymers on increased cross-linking was investigated using this technique. In the present study SEM was used to probe the change in morphological features of HDODA cross-linked polystyrene. A comparison of SEM patterns of the different mol% HDODA cross-linked systems (Fig 4) indicated that the surface of the 8% HDODA cross-linked system is more roughen than the other three. This is due to the contraction of the polymer matrix by increased cross-linking. With greater cross-linking the rigidity of the polymer bead also increased and hence the swelling in different solvents varied

4. Conclusion

Cross-linked polymers can be used as catalyst support. They are experimentally more useful because of their ease of filtration and recyclability. The degree of cross-linking determines the solubility, extent of swelling and mechanical stability of the polymer. The extent of swelling is inversely proportional to the degree of cross-linking. PS-DVB systems showed hydrophobic and rigid nature. PS-HDODA posses optimum hydrophobic hydrophilic balance due to the presence of two acrylate linkages and is flexible due to the presence of six carbon chain. In the present work a systematic investigation of swelling capacity and change in surface morphology of different mol%

HDODA cross-linked polystyrene has been presented. From the swelling capacity studies, we have obtained the highest value for 2% PS-HDODA system and hence higher the degree of penetration of the reagent, helps in ease of the reaction. The SEM image of the polymeric system shows the 2% PS-HDODA system has the most smoothen surface than the others. As the cross-linking density increases the surface become more roughen. 8% HDODA cross-linked system has most roughen surface. 2% PS-HDODA cross-linked polystyrene system is flexible, shows hydrophobic hydrophilic balance and shows better swelling in some common solvents, hence it is more useful as catalyst support among the four.

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