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A Comparative Study of Swelling Capacity and Surface Morphology of Different Mol % 1, 6-Hexanediol Diacrylate Crosslinked Polystyrene for Catalytic Applications

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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. They 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. Suspension polymerisation was used for the preparation of polystyrene crosslinked with 1, 6-hexanediol diacrylate resin (PS-HDODA) 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 in heterogenous catalysis. Here we report the synthesis, characterisation and comparative study of swelling capacity and surface morphology of different mol % PS–HDODA copolymer which could be efficiently used in polymer supported catalysis.

Keywords: polystyrene, HDODA, swelling**,** morphology

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 polymer supported catalysts [1-3]. The various forms of polymers as support for the preparations of heterogeneous catalyst included colloids, flakes, gel beads and fibers [4]. In solid phase synthesis crosslinked polystyrene resins are generally used as solid supports [5].There are a large number of reasons for using crosslinked polystyrene as catalyst support [6-14]. They are experimentally more useful because of their ease of filtration and recyclability [15-19]. An important characteristic of polystyrene beads is their ability for swelling and solvation in organic solvents [20]. This property causes a phase change of the bead from a solid to solvent swollen gel, and therefore the reactive sites could be smoothly accessed by diffusion of reactant through the solvent swollen gel network. The degree of crosslinking determines the extent of swelling, pore size and mechanical stability of the polymer and the rate of swelling determines 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 [21]. But resins based on polystyrene exhibit varying metal ion uptake for catalytic applications [22]. Even though the insoluble support is inert it does have significant dynamic influence on the bound substrates. This may be due to hydrophobic character of the polymer backbone. An efficient polymer support for catalytic applications should have an optimum hydrophobic- hydrophilic balance compatible with the reactions being carried out on it. In the present study polystyrene crosslinked with 1, 6-hexanediol diacrylate (PS-HDODA) support is optimised for polymer supported catalytic applications [23]. Here PS-HDODA supports of varying crosslink densities were synthesised, characterized and their swelling capacities and surface morphologies were compared to develop a suitable polymer support for catalytic applications.

EXPERIMENTAL

Materials and methods

Styrene and HDODA were purchased form Sigma Aldrich. Acetone, methanol, toluene, DMF, DCM, benzyl 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.

Synthesis of 2, 4, 6 & 8 mol% HDODA cross linked polystyrene

Free radical suspension polymerisation is used for the synthesis of cross linked polystyrene. For the synthesis of 2% HDODA crosslinked polystyrene a mixture of styrene (11.2ml), HDODA (0.44ml), Toluene as inert diluents (8ml) and benzoyl peroxide (1g) was prepared. It is added to a 1% polyvinyl alcohol (PVA) solution and is mechanically stirred at 80 ^{0} C. Polymerisation reaction (Scheme 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 mesh sizes using standard sieves. Polymers of 4, 6 & 8% HDODA crosslinking were prepared by adjusting the relative amounts of the monomer (Table 1).

Scheme 1: Preparation of PS-HDODA resin by suspension polymerisation [24]

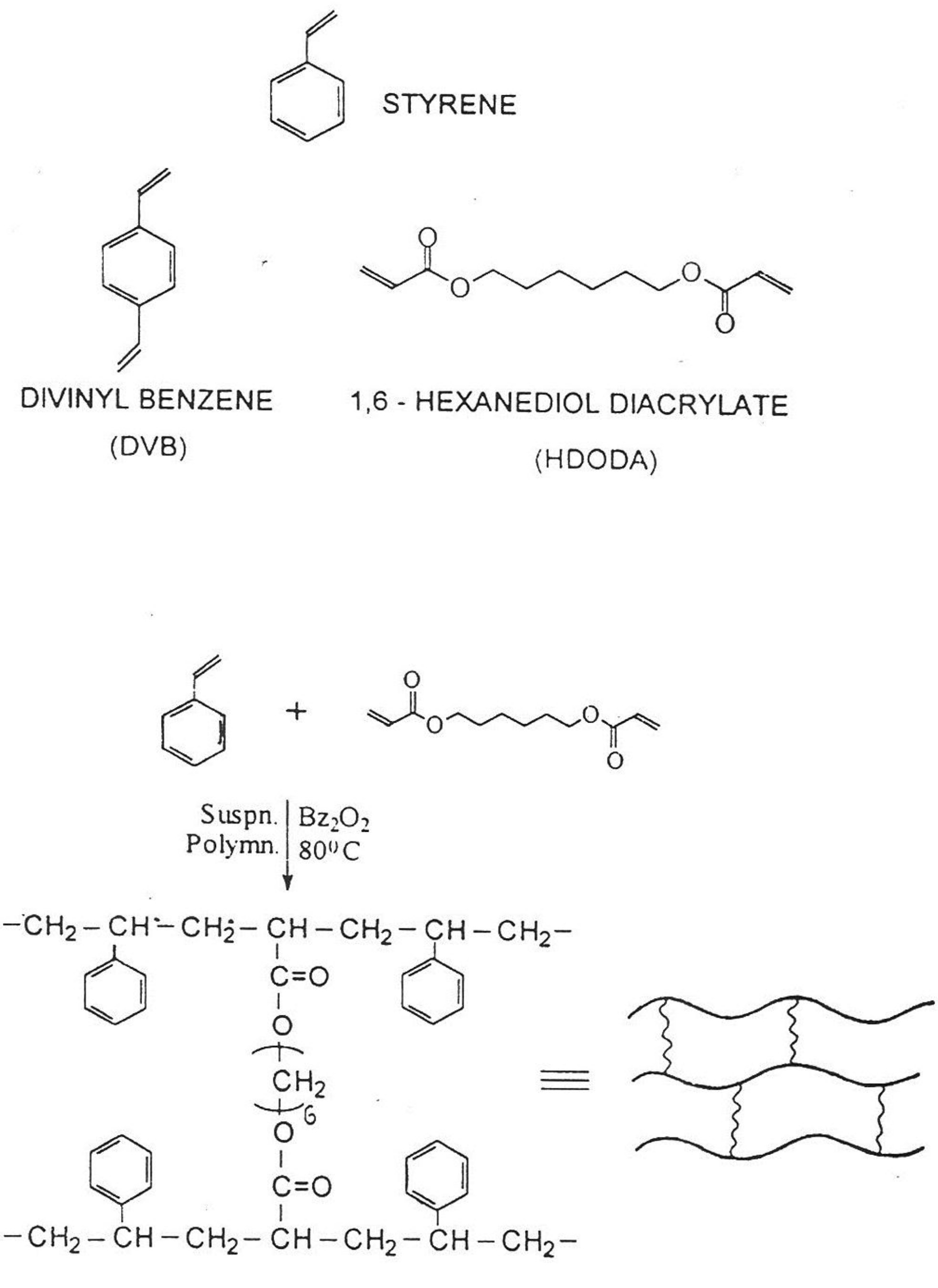


Table 1: Preparation of various mole % HDODA crosslinked polystyrene.

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

Swelling studies

A suitable amount of the resin was weighed and placed in sintered crucible. Solvent was added and kept in a beaker containing the same solvent. After 24 hours the solvent was carefully sucked out from the crucible. The swollen weight was determined. The dry weight also noted. The experiment was repeated with other solvents. The swelling capacities were expressed in mL/g of the resin.

Table 2: Swelling capacity of PS-HDODA resins in organic solvents

Solvent	Crosslinking 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

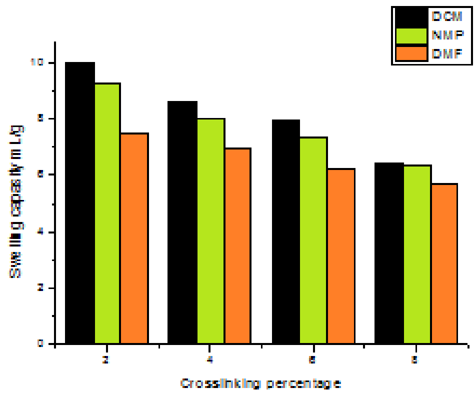


Figure 1: Graphical representation of swelling capacity studies

RESULTS AND DISCUSSION

Polystyrene with 2-8 mol% HDODA crosslinks were obtained by free radical suspension copolymerisation of the monomers at 80 ^{0}C. Benzoyl peroxide was used as the radical initiator and toluene was the inert solvent. Polymers with varying extent of the crosslinks were prepared by adjusting the mol % of the monomers in the feed. The FTIR spectra of different mol % copolymers are shown below (Figure 2), where A2, A4, A6 and A8 represents 2, 4, 6, and 8 mol% HDODA crosslinked polystyrene respectively.

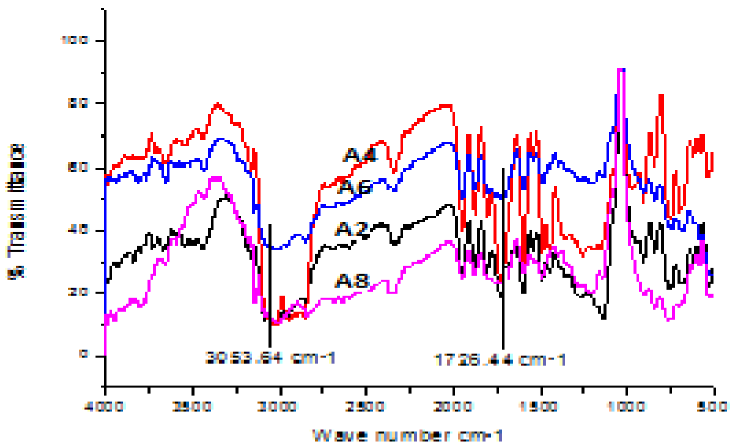
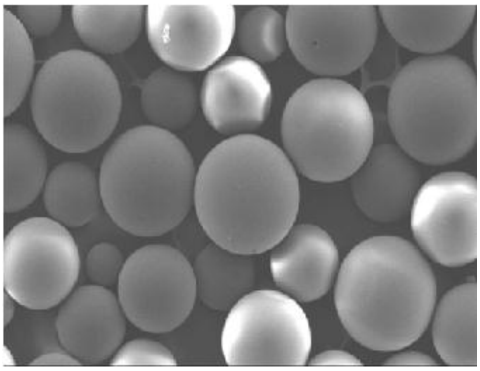
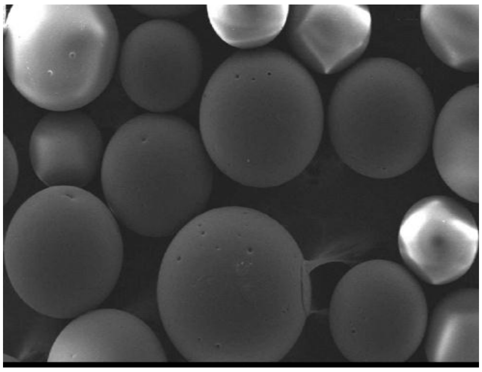


Figure 2: FTIR spectra of crosslinked polystyrene

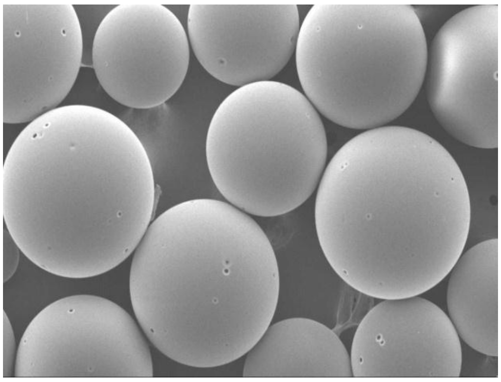
In the FTIR spectrum the copolymer beads exhibit characteristic bands at 3053.64 cm^{-1} and 1726.44 cm^{-1} due to aromatic –CH stretching and ester carbonyl stretching respectively. This clearly indicated the formation of crosslinked polymer.



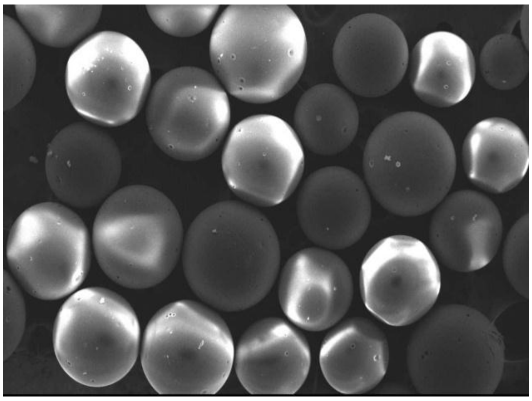
(a)



(b)



(c)



(d)

Figure 3: SEM images of (a) 2% PS-HDODA (b) 4% PS-HDODA (c) 6% PS-HDODA (d) 8% PS-HDODA

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 crosslinking was investigated using this technique. In the present study SEM was used to probe the change in morphological features of HDODA crosslinked polystyrene. A comparison of SEM patterns of the different mol% HDODA crosslinked systems (Figure 3) indicated that the surface of the 8% HDODA crosslinked system is more roughen than the other three. This is due to the contraction of the polymer matrix by increased crosslinking. With increasing crosslinking the rigidity of the polymer increased and hence the swelling in different solvent also varied. Swelling capacity measurements of the crosslinked polymers is carried out in DCM, DMF, and NMP (Table 2). The graphical representation of swelling characteristics is given in figure 1. 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. We have obtained greater swelling in DCM, which was 10.01-6.44 mL/g. With all solvents 2% crosslinked polymer shows greater swelling. With increasing crosslinking percentage, swelling capacity gets decreased. This reduction arises from contraction of polymeric chains with increased crosslinking resulting in decreased intake of solvent. In all the above solvents as the crosslinking density increases, the swelling capacity decreased. This may be due to with the increasing crosslinking lead to additional chain contraction results in decreased swelling.

CONCLUSION

Crosslinked polymers can be used as catalyst support. They are experimentally more useful because of their ease of filtration and recyclability. The degree of crosslinking determines the solubility, extent of swelling and mechanical stability of the polymer. The degree of swelling is inversely proportional to the degree of crosslinking. Even though the support is inert it has a profound influence on the overall reactions carried on it. Design and development of polymer supports having optimum hydrophobic-hydrophilic balance is the key factor in polymer supported reactions. Here polystyrene crosslinked with 1, 6-hexanediol diacrylate (PS-HDODA) is introduced as a support for polymer supported catalytic applications. In the present work a systematic investigation of change in surface morphology and swelling capacity of different mol% HDODA crosslinked polystyrene has been presented. From the swelling capacity studies, we have obtained the highest value for 2% HDODA crosslinked polystyrene system and hence higher the degree of penetration of the reagent, helps in ease of the reaction. The SEM images of the polymeric systems show that 2% HDODA crosslinked polymer has the smoothest surface than the others. As the crosslinking density increases the smooth nature of the polymer surface disappeared and surface became more irregular. In the present SEM analysis different8% HDODA crosslinked system has found to be having rougher surface. Thus from the swelling and surface morphological studies of various crosslinks of PS-HDODA system a 2% crosslinked polymer has optimum properties and which could be used solid support in heterogeneous catalysis.

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