



Surface Morphological Analysis of Differently Sulphonated Styrene -1, 6-Hexanediol Diacrylate Copolymer as Novel Cation Exchange Resin and as a Catalyst Support

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Abstract : This work describes the surface morphological analysis of differently sulphonated styrene -1, 6-hexanediol diacrylate copolymer. The copolymer beads were synthesised by suspension copolymerisation. It was chemically modified by sulphonating the polymer using con. Sulphuric acid. The differently sulphonated copolymer beads were obtained by varying the sulphonation reaction time. The sulphur content in the sample was first analysed by CHNS analysis. The sulphonic acid group attachment into the copolymer network was verified by infrared spectroscopy (FTIR). Ion-exchange capacity value of the sulphonated polymer was determined by salt splitting titration using standardised NaOH. The surface morphology of the copolymer beads were done by scanning electron microscopy analysis.

Introduction

A variety of polymer supported systems are available today and the polymeric support is used for immobilizing the bound species¹⁻⁶. The major advantage of using this polymer support is the simplification of the product work up, separation of the compound by simple filtration, ease of isolation, the possibility of regeneration of the polymers etc⁷. These polymer supports may be insoluble but swellable linear or crosslinked species. Crosslinked polymers are more useful because they can be easily cleaned off from soluble reactants and products. The polymer support should have significant mechanical stability. After the introduction of Merrifield resin there has been an intense activity on the modification of polymers by functionalization. The desired functional group can be introduced into support either by chemical modification of the polymer or by polymerisation of monomer containing the required functional group. Such functionalised polymeric systems possess the physical properties of the polymeric matrix as well as chemical reactivity of attached functional groups. Sulphonated aromatic polymers are well known for their mechanical, thermal and chemical stability. The introduction of -SO₃H group provides conductivity to the polymeric support. Sulphuric acid, acetyl sulphate, chlorosulphonic acid etc. are the popular sulphonating agents⁸⁻¹¹. Sulphonated polystyrene (PS)-divinyl benzene (DVB) resins have been used as ion exchange resin for many years. Utilisation of ion exchange resins in water processing has been one of the traditional techniques in industry. The sulphonated PS-DVB resins can be used as solid acid catalyst in many chemical processes such as dehydration of alcohols to olefin or ethers, alkylation of phenols, addition of alcohols to olefins manufacturing bisphenol and so on¹²⁻¹⁵. Resins based on PS-DVB support may be showing low metal ion uptake¹⁶. This may be due to rigid and hydrophobic nature of the polymer backbone. PS crosslinked with 1, 6-hexanediol diacrylate (HDODA) possess optimum hydrophobic hydrophilic balance and is more flexible than PS-DVB system. So HDODA crosslinked PS has been found to be convenient as catalyst support. Here we report the sulphonation, characterisation and surface morphology analysis of PS-HDODA resin.

Experimental

Materials

Styrene and HDODA were purchased from Sigma Aldrich. Acetone, methanol, toluene, DMF, DCM, benzoyl peroxide, PVA and sulphuric acid 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

Methods

Copolymerisation reaction

Free radical suspension polymerisation is used for the synthesis of crosslinked polystyrene. For the synthesis of 2% HDODA crosslinked polystyrene a mixture of styrene(98mmol), HDODA(2mmol), Toluene (8ml) and benzoyl peroxide (1g) was prepared. It is then suspended into 1% PVA solution. The above mixture is mechanically stirred at 80 °C. Polymerisation 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 °C. Beads were sieved into three different sizes using standard sieves.

Sulphonation processes

The copolymer was swelled in dichloromethane for 30 minutes. Fixed volume of concentrated sulphuric acid was added and heated to 50 °C. Periodic shaking is needed during sulphonation. The various degrees of sulphonation were obtained by varying the reaction time. The sulphonated resin was filtered, washed with distilled water and dried at 50 °C for 6 h. Fig 1 shows the sulphonation reaction pathway.

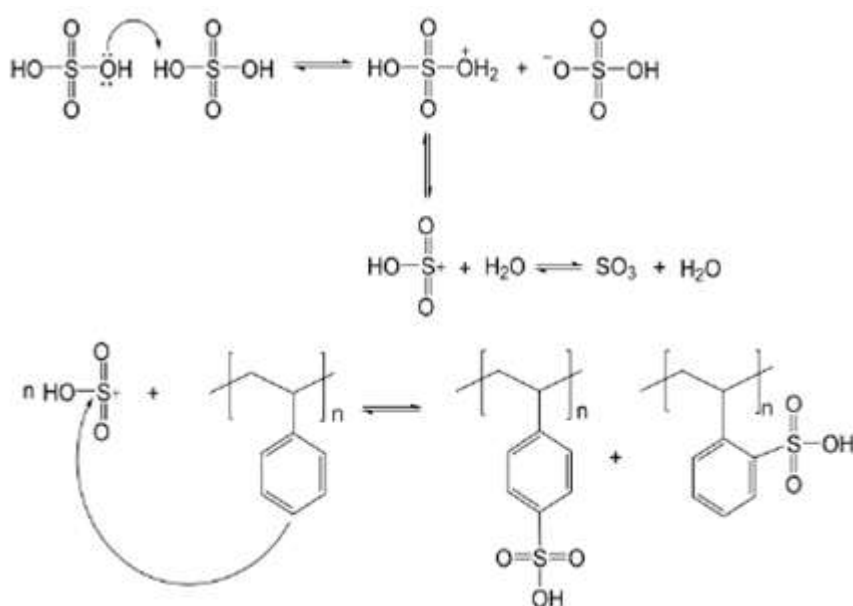


Fig 1. Sulphonation reaction pathway¹⁷

Characterisation

CHNS analysis was done by Perkin-Elmer 2400 Series CHNS analyser. Ion exchange capacity was determined by salt splitting titration. FTIR spectra were recorded on Perkin Elmer spectrometer. The surface morphology of crosslinked polystyrene and sulphonated polystyrene were studied in a scanning electron microscope.

Results and discussion

The copolymer beads were synthesised by suspension polymerisation and then sulphonated for varied reaction times into the differently sulphonated resins. The CHNS analysis, FTIR spectra and the ion exchange capacity of the obtained resins were determined. The resins were also characterised by scanning electron microscopy. After sulphonation all resins show swelling in polar solvents indicating the presence of hydrophilic group in the resin. The sulphur content in 10 min. sulphonated polymeric resin was determined by CHNS analysis (Table 1) gives clear evidence for the attachment of sulphur containing group.

Table 1. CHNS analysis of sulphonated resin

Sample No	Sample name	C%	H%	N%	S%
1	PS-HDODA SO ₃ H	60.00	60.18	0.18	5.86

Ion-Exchange capacity

The ion-exchange capacity of sulphonated resin was determined by the salt splitting titration. About 0.1 g of sulphonated resin was weighed and added into an Erlenmeyer flask containing 2 N sodium chloride solution. It was stirred for three hours, and then titrated with standardised sodium chloride solution using phenolphthalein as the indicator. The ion-exchange capacity of the sulphonated resin (IEC, meq/g) was calculated from

$$IEC = c \times v / w$$

Where c is the standardized concentration of sodium hydroxide, v is the volume (ml) at an end point of the NaOH solution and w is the weight (g) of determined sulphonated resin.

Table 2. Ion-Exchange capacity of sulphonated resins

Sample Name	Sulphonating time (Minute)	Volume sulphuric acid (mL)	of Temperature (°C)	Ion exchange Capacity (IEC) (meq/g)
PS	-	-	-	0.00
PS-10S	10 minute	2mL	60°C	0.94
PS-20S	20 minute	2mL	60°C	1.93
PS-30S	30 minute	2mL	60°C	2.96
PS-40S	40 minute	2mL	60°C	3.50

Table: 2 shows the ion exchange capacity of sulphonated copolymer beads which were determined by using standardized NaOH solution. The copolymer beads showed no ion-exchange capacity due to the absence of sulphonic acid group. The IEC increased with the longer sulphonating period. The highest value of ion exchange capacity was obtained for 40 minute sulphonated polymer. The attached sulphonic acid group was the ion exchangeable site of the polymeric resin and can interchange its counter ion with another cationic counter ion. With the increasing degrees of sulphonic acid group added in the polymeric resin, the greater the interchange of the counterions, thus showing the higher IEC.

In the FTIR spectrum (Fig 3-7) the copolymer beads exhibit characteristic bands around 1715.31-1729.73 cm⁻¹ due to carbonyl stretching frequency. The presence of carbonyl stretching frequency in the FTIR spectrum of all the copolymer beads clearly indicating the obtained polystyrene is crosslinked with HDODA

The sulphonic acid group attachment was confirmed by FTIR spectroscopy. The band around 1120-1250cm⁻¹ which was attributed to S=O symmetric stretching vibrations and the band above 3400cm⁻¹ related to OH stretching frequency in -SO₃H group

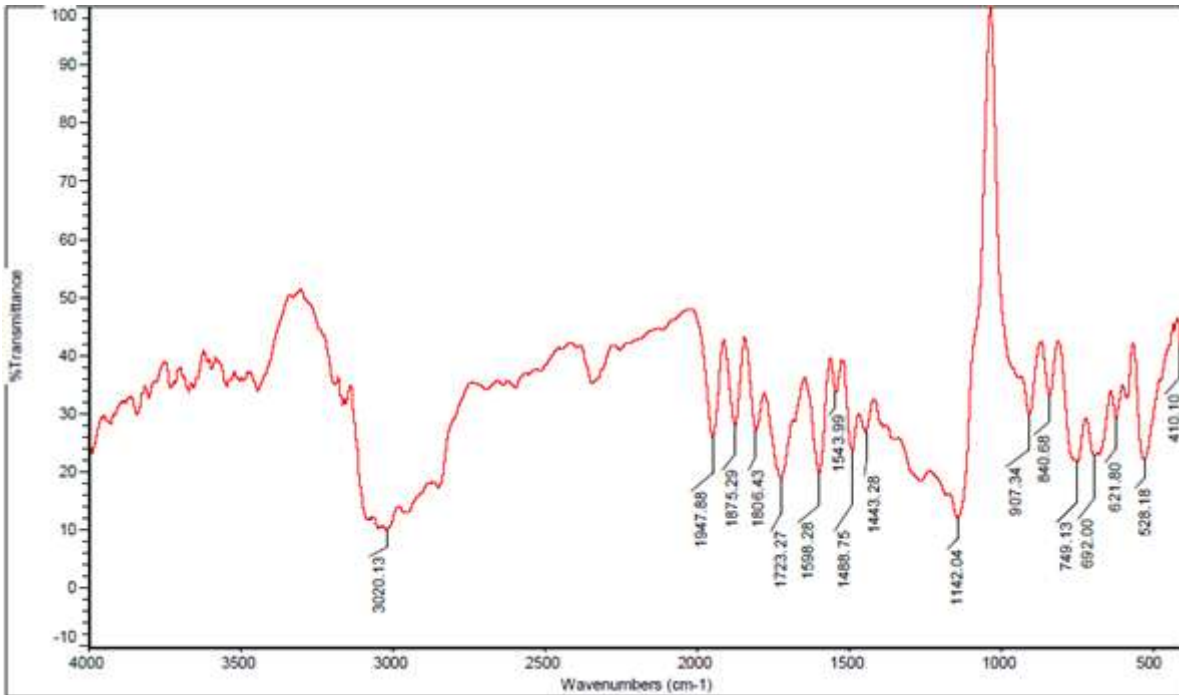


Fig 3.FTIR spectrum of 2 mol % HDODA crosslinked polystyrene.

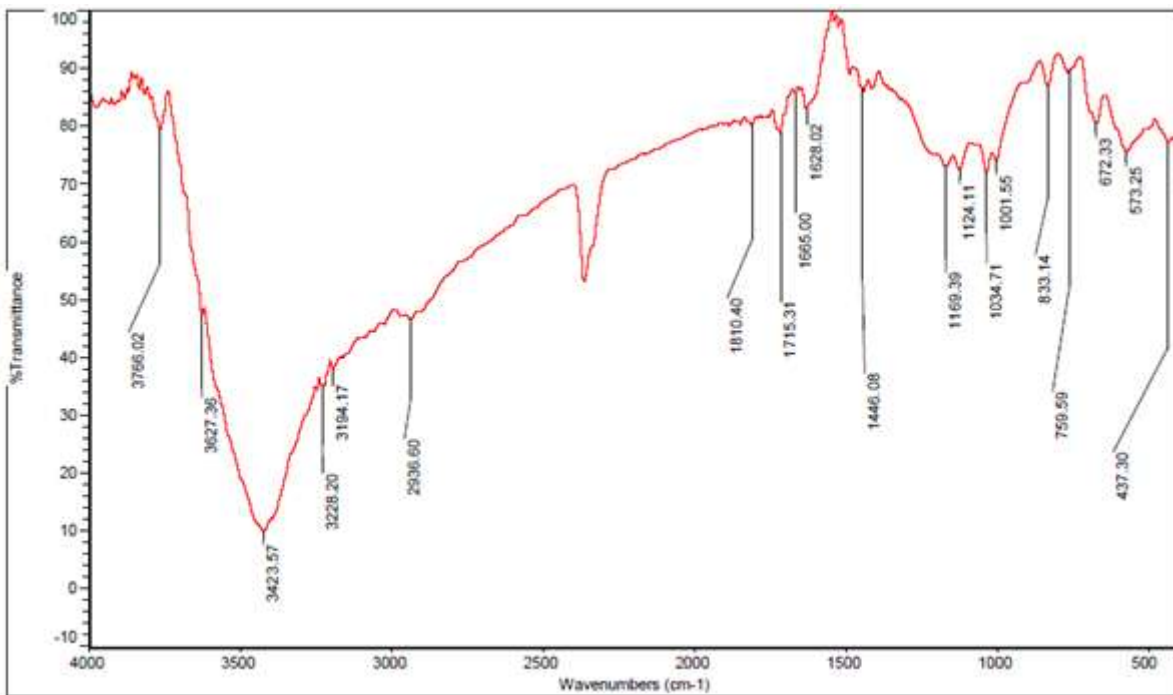


Fig 4.FTIR spectrum of 2 mol % HDODA crosslinked 10 minutes sulphonated polystyrene

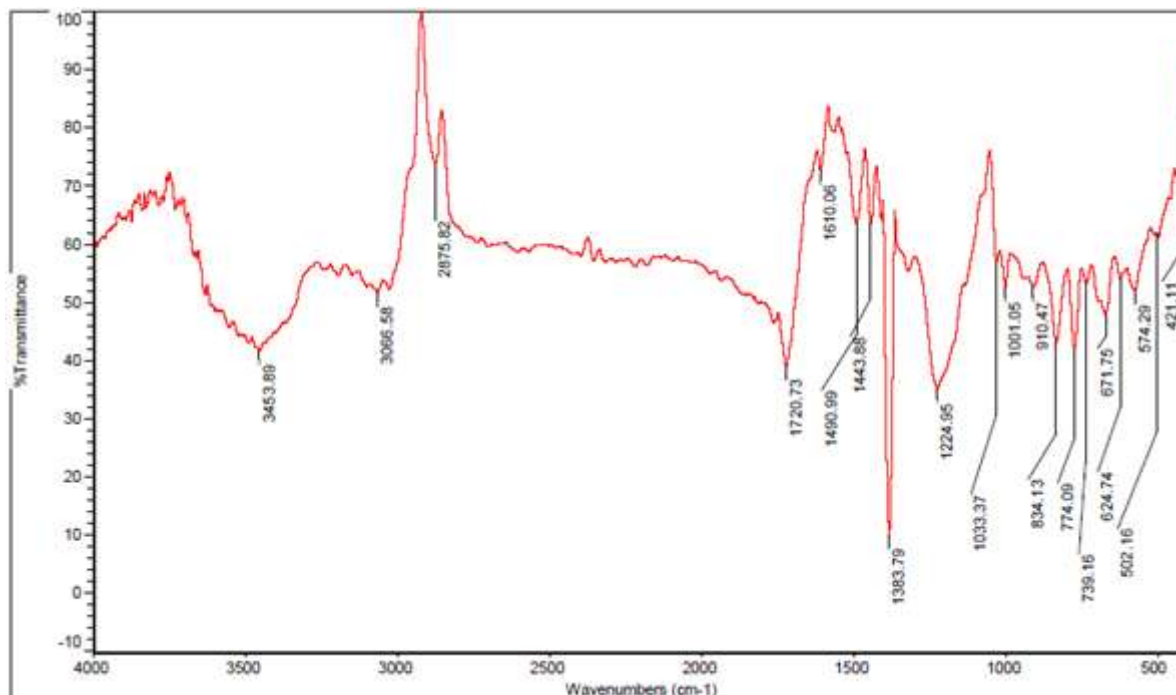


Fig 5 FTIR spectrum of 2 mol % HDODA crosslinked 20 minutes sulphonated polystyrene

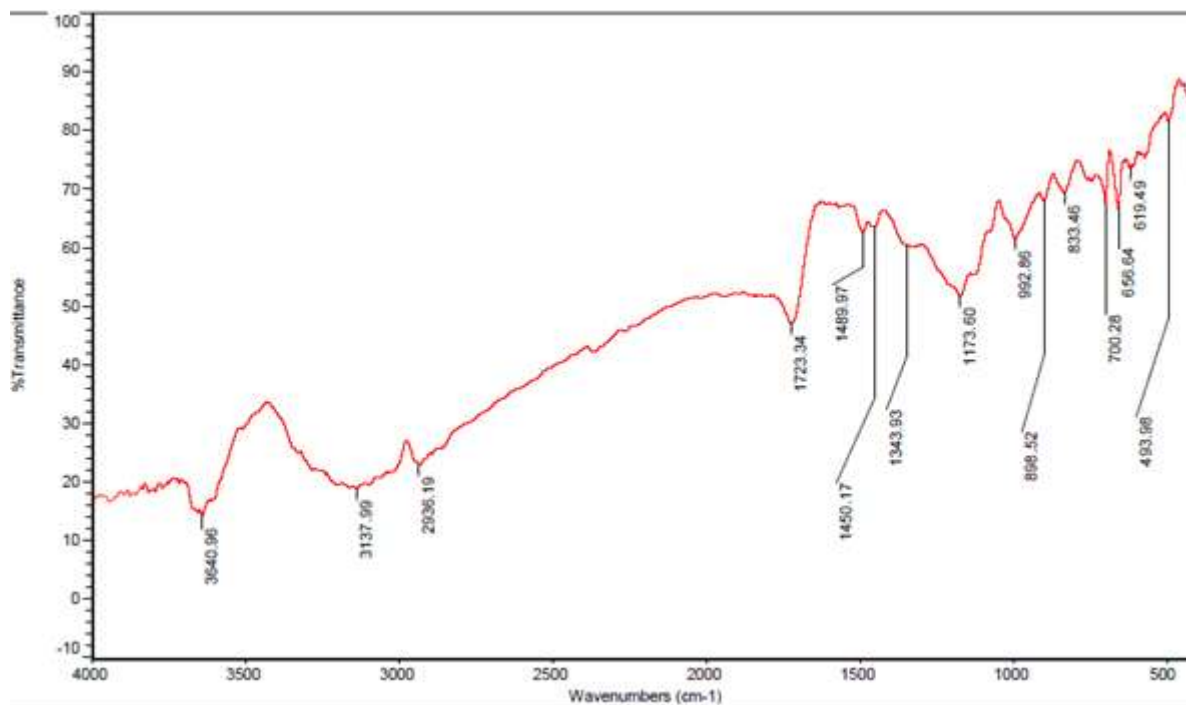


Fig 6. FTIR spectrum of 2 mol % HDODA crosslinked 30 minutes sulphonated polystyrene

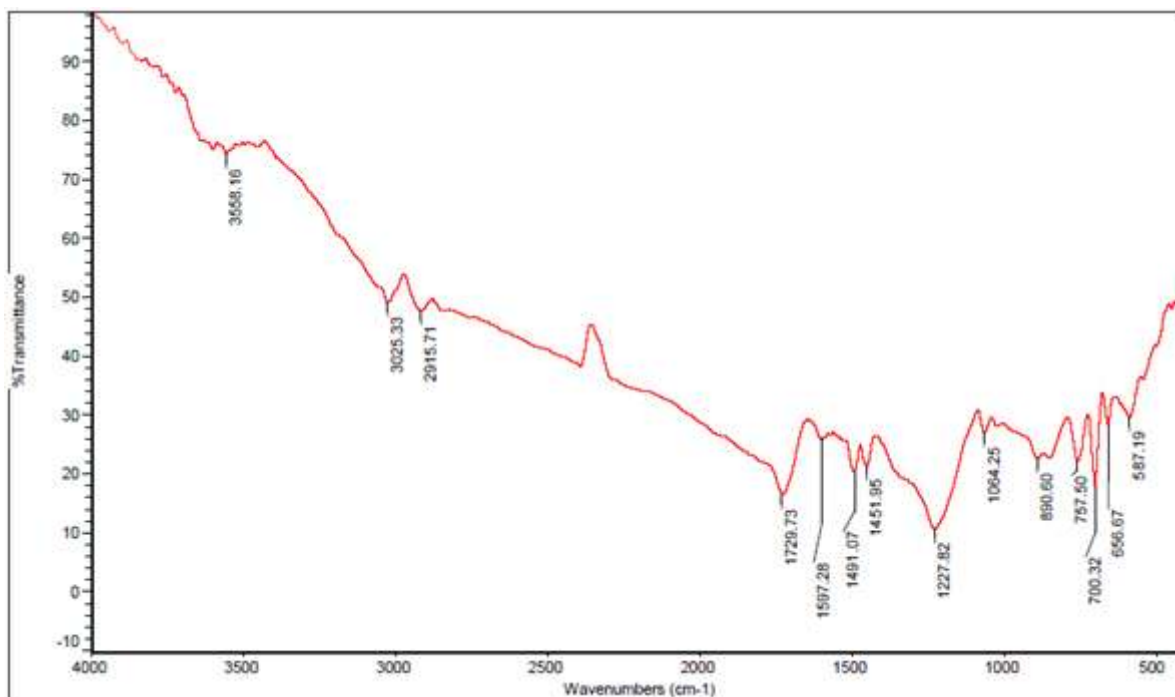
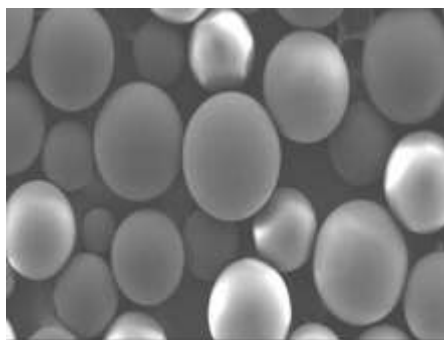
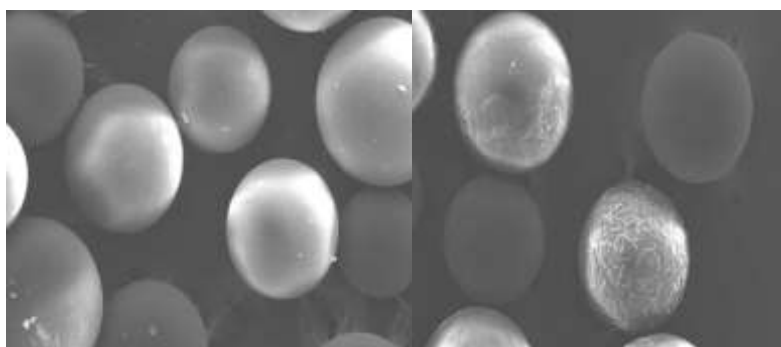


Fig 7. FTIR spectrum of 2 mol % HDODA crosslinked 40 minutes sulphonated polystyrene.

The surface morphology of the polymeric beads were analysed by SEM. These micrographs (Fig 8) show clearly that the spherical morphology of copolymer beads retained after sulphonation. But the external surface of the sulphonated copolymer beads show scales and cracks probably by the sulphonation process.



(a)



(b)

(c)

Fig 8. SEM image of (a) 2% PS-HDODA (b) 10 minutes sulphonated 2% PS-HDODA, (c) 40 minutes sulphonated 2% PS-HDODA

Morphological defects (cracks, scales) can be seen in highly sulphonated copolymer beads(c) In fact, even the commercial resins show defects in their surface¹⁸. After sulphonation the resin swell in polar solvent such as water indicate the presence of hydrophilic groups in the copolymer beads.

Conclusion

A novel functionalised resin is introduced both as an ion exchanger and as a catalyst supporter for heterogeneous catalysis. 2% PS-HDODA crosslinked resin is obtained by suspension polymerisation and functionalised by sulphonation using Conc.sulphuric acid. Sulphonation of PS-HDODA copolymer bead is relatively an easy process and is very stable. The degree of sulphonation can be controlled by varying the reaction time. The sulphonated PS-HDODA resin showed ion exchange property as evident from capacity measurements. Sulphonated resin is characterised by CHNS analysis and FTIR. Surface morphology of the sulphonated PS-HDODA is carried out by SEM analysis and showed that spherical morphology of the copolymer bead is maintained even at highly sulphonated system but the external surface shows scales and cracks. Thus flexible and hydrophilic sulphonated PS-HDODA could be effectively used as a cation exchange resin and as a catalyst support in heterogeneous catalysis. It can also be used for water softening and in drug delivery.

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References

1. Climent, M. J.; Corma, A.; Iborra, S., *Chem. Rev.*, 2011,111, 1072.
2. Vagin, S.I.; Reichardt, R.; Klaus, S.; Rieger, B. J., *Am. Chem. Soc.*, 2010, 132, 14367.
3. Signori, A. M.; Santos, K. O.; Eising, R.; Albuquerque, B. L. Giacomelli, F. C.; Domingos, J. B. *Langmuir.*, 2010, 26 (22),17772.
4. Yamada, Y. M. A.; Jin, C. K.;Uozumi, Y. *Org. Lett.*, 2010, 12, 4540.
5. Karimi, B.; Akhavan, P. F., *Inorg. Chem.*, 2011, 50, 6063.
6. Bergbreiter, D. E.; Yang, Y.C.; Hobbs, C. E. J., *Org. Chem.*, 2011, 76, 6912.
7. Kobayashi, S. *Chem. Soc. Rev.*1999, 28, 1.
8. D. Huang, M. Han, J. Wang, Y. Jin, *Chem. Eng. J.*, 2002, 88, 215.
9. P.J Dumont, J. S. Fritz, *J. Chromatogr., A*, 1995, 691, 123.
10. M. Struck, H. Widdecke, *Die Angew. Makromol. Chem.*, 1996, 235, 131.
11. T.K. Chambers, J.S. Fritz, *J. Chromatogr., A*, 1998, 797, 139.
12. M.A. Harmer, *Appl. Catal. A Gen.*, 2001, 221, 45-62.
13. H. Widdecke, *Design and Industrial Application of Polymeric Acid Catalysis*, in: D. C Sherrington, P. Hodge (Eds.), *Syntheses and Separations Using Functional polymers*, Wiley, Chichester, 1988, 149.
14. V.J. Frilette, E.B. Mower, M.K. Rubin, *J. Catal.* 1964, 3, 25-31.
15. A. Chauvel, B. Delmon, W.F. Hoelderich, *Appl. Catal. A.*, 1994, 115, 173-217.
16. K. Sivadasan chettiyar & K. Sreekumar, *Metal complexation on functionalised polymer support- An adsorption/ complexation phenomenon*, *Indian Journal of Chemical Technology*, 2004, Vol.11, 59-66
17. S. Mulijani, K. Dahlan and A. Wulanawati, *Sulphonated Polystyrene Copolyer: Synthesis, Characterisation and Its Application of Membranefor Direct Methanol Fuel Cell (DMFC)*, *International Journal of Materials, Mechanics and Manufacturing*, 2014, Vol. 2, No. 1.
18. Ana Jaqueline Barreto de Oliveiraa , Alcino Palermo de Aguiar , Mo`nica Regina Marques Palermo de Aguiarb , Luiz Claudio de Santa Maria, *How to maintain the morphology of styrene-divinylbenzene copolymer beads during the sulfonation reaction*, *Materials Letters* 2005,59, 1089 – 1094

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