

Effect of the Macromolecular Characteristics of the Polymer Support on the Reactivity of Polystyrene-Supported Chromates

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ABSTRACT: Polystyrene crosslinked with 2-20 mol% divinylbenzene (DVB), ethyleneglycol dimethacrylate (EGDMA) and hexanediol diacrylate (HDODA) was synthesized and functionalized to incorporate chromate function. The polymers were characterised FT-IR and ¹³C CP-MAS NMR spectroscopy and scanning electron microscopy. The efficiency of this reagent as a heterogeneous catalyst was investigated towards the oxidation of benzoic acid to benzil as a model reaction. The topographical nature of the polymer matrix exerts a significant influence on the reactivity of the attached functional groups. Among the three crosslinked systems the reactivity decreased in the order HDODA- > EGDMA- > DVB-crosslinked system. This is due to the increase in the flexibility of the HDODA- and EGDMA-crosslinked systems compared to rigid DVB system. The reactivity was found to be high for low crosslinked systems and decreased with increase in crosslinking. Studies revealed that the reactivity of the supported chromate function is highly dependent on the nature and degree of crosslinking.

KEYWORDS: polystyrene; crosslinked; supported; chromate; oxidation; structure- reactivity correlation

I. INTRODUCTION

Organic synthesis mediated by crosslinked polymer supports has been an active area of research during the last three decades. Polymeric reagents have been developed for use in oxidation [1, 2], halogenation [3], acylation [4], epoxidation [5]. A reagent covalently bound to a polymer acquires the physical properties of the latter and the reasonably crosslinked, functionalized polymer remains insoluble in common organic solvents. A polymeric organic reagent can provide an effective alternative to its low molecular weight counterpart if its design is such that it allows for an easier isolation of the desired product after the reaction and if the polymeric reagent can be regenerated and recycled for further use without loss of reactivity [6]. The feasibility of a polymer-supported reaction involving a crosslinked polymer support depends on the accessibility of the reactive groups in the polymer matrix, which in turn depends on the nature of the macromolecular backbone. The oxidation of primary alcohols by chromic acid leads to extra problems, the aldehydes formed are fairly easily oxidised, to the corresponding carboxylic acids [7]. But with the help of polymer-supported reagents, alcohols can be selectively oxidised to carbonyl compounds [8]. The present paper describes the synthesis, characterisation and oxidation behavior of 2 - 20mol% DVB-, EGDMA- and HDODA-crosslinked polystyrene-supported chromates. A study on the correlation between the rate of oxidation with the nature and degree of crosslinking was also carried out using the oxidation of benzoic acid to benzil as the model reaction.

II. EXPERIMENTAL

1. Materials and methods

Divinylbenzene (DVB), ethyleneglycol dimethacrylate (EGDMA), and hexanediol diacrylate (HDODA) were commercial products obtained from Aldrich Chemical Company, USA; styrene was purchased from E Merck, Germany. All low molecular weight compounds were commercially available samples and were purified by literature

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procedures. AR grade solvents were purified by distillation. IR spectra were recorded on a Shimadzu FT-IR-8400 S spectrophotometer. UV spectra were recorded using a Shimadzu UV- 2450 spectrophotometer. ¹³C CP-MAS spectra were recorded using a BRUKER DSX 300MHz NMR spectrometer and ¹H NMR spectroscopy using a BRUKER BZH 500MHz NMR spectrometer. Melting points were measured using a Buchi-530 melting point apparatus.

1. Preparation of DVB-, EGDMA- and HDODA-crosslinked polystyrenes

A free radical initiated, suspension polymerisation technique [11] was used to prepare crosslinked polystyrene. For the preparation of 2 mol% DVB-crosslinked polystyrene, polyvinyl alcohol (2.2g) was dissolved in 350ml of boiling distilled water and stirred for sometime on a water bath at 80°C. A solution of styrene (22.4ml) and DVB (0.896 ml) in toluene (30ml) was added to this solution with stirring. The polymerisation was allowed to proceed under nitrogen atmosphere at 80°C after the addition of benzoyl peroxide (500mg) for 6 h. The white shiny beads obtained were collected by filtration and washed with hot water, acetone, benzene, chloroform and finally Soxhlet extracted with methanol and acetone to remove all low molecular weight impurities, dried under vacuum at 50°C. The beads were meshed to 200-400µm range. 2, 5, 10, 15 and 20 mol% DVB-crosslinked polystyrenes were also prepared. 2-20 mol% EGDMA- and HDODA-crosslinked polystyrenes were also prepared using the same procedure by adjusting the composition of the monomers.

2. Chloromethylation of crosslinked polystyrene

Polystyrene (1 g) was allowed to swell in dichloromethane (6-10ml) for half an hour. 0 Anhydrous ZnCl₂ (.4 ml) and chloromethyl methyl ether (6 ml) were added. The mixture was kept in an oil bath at 50-55°C for 12h. The polymer was washed with THF, THF:HCl (4N)(1:1), THF:HCl: H₂O (1:1:1) and Soxhlet extracted using dichloromethane and with methanol. Dried in vacuum at 50°C.

3. Estimation of chloromethyl group (Volhard's method)

Chloromethylated polymer (100mg) was treated with pyridine (4ml) at 100°C for 8h. To the suspension concentrated HNO₃ (5ml), acetic acid-H₂O mixture (1:1v/v, 30ml) and AgNO₃ (0.05M, 5ml) were added and titrated against standard ammonium thiocyanate (0.1N) using ferric alum as indicator. A blank titration was also conducted. The IR spectrum of chloromethylated polymer showed a characteristic C-Cl stretching band at 680 cm⁻¹.

4. Conversion of chloromethyl polystyrene to triethylamino methyl chloride polymers: General procedure

The chloromethyl polystyrene (5g) was allowed to swell in DMF for 12h. Five molar excess of triethyl amine was added and heated to 80°C for 6 h. The polymers were washed with DMF, DMF: H₂O, H₂O and finally with acetone.

5. Preparation of crosslinked polystyrene-supported chromate complexes

The functionalized polymer (5g) was allowed to swell in acetonitrile for 12h. CrO₃ (5g) in acetonitrile: water (1:1v/v) was added and shaken for 6h. The polymer was filtered and washed with water until the filtrate was completely free from CrO₃. The polymer was then washed with methanol and acetone and dried in vacuum yielding polymer-supported chromate complex.

6. Determination of the capacity of crosslinked polystyrene-supported chromate complexes

The supported chromate complex was suspended in KOH solution (2N, 10 ml) overnight with occasional stirring. To the resulting solution 10% KI solution (5ml) and concentrated HCl (3ml) were added. It was diluted to 50ml and titrated against standard sodium thiosulphate solution using starch as indicator.

7. Investigation of the oxidation behavior of polystyrene-supported chromium complex: General procedure

A five fold molar excess of the reagent moistened with water was added to a solution of benzoin (100mg) in chloroform, THF or cyclohexane (10ml) and refluxed. 0.1ml each of the reaction mixture was withdrawn using a micropipette after definite time intervals and was made up to 5ml using appropriate solvent. Concentration of benzil

was measured on a UV spectrophotometer at 387nm. The experiment was repeated using the differently crosslinked polymers.

III. RESULTS AND DISCUSSION

Styrene crosslinked with 2 - 20mol% DVB/EGDMA/HDODA by free radical suspension polymerization (Scheme 1). The crosslinked polymer with 200-400 mesh size was functionalised by Friedel-Crafts chloromethylation reaction using anhydrous $ZnCl_2$ as catalyst [9] (Scheme 2). The chlorine capacities of DVB-, EGDMA- and HDODA-crosslinked polystyrenes are given in Fig.1.

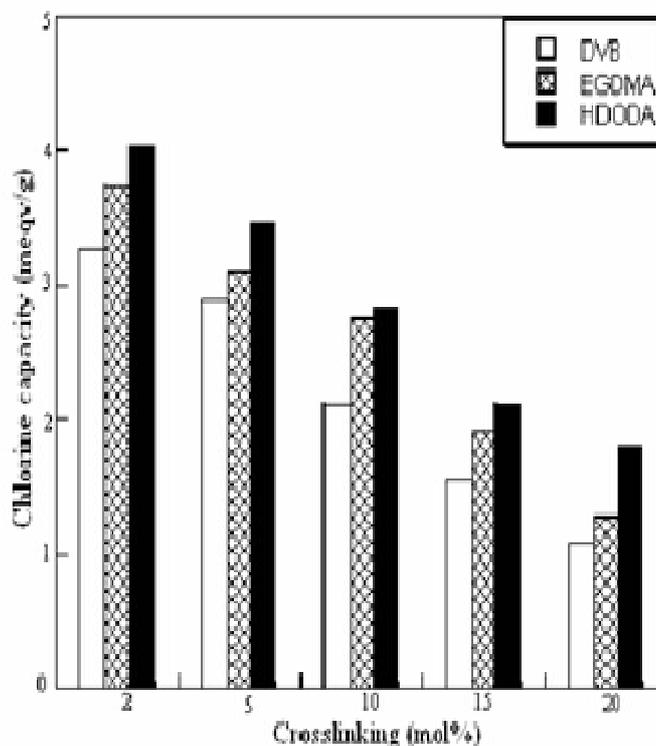


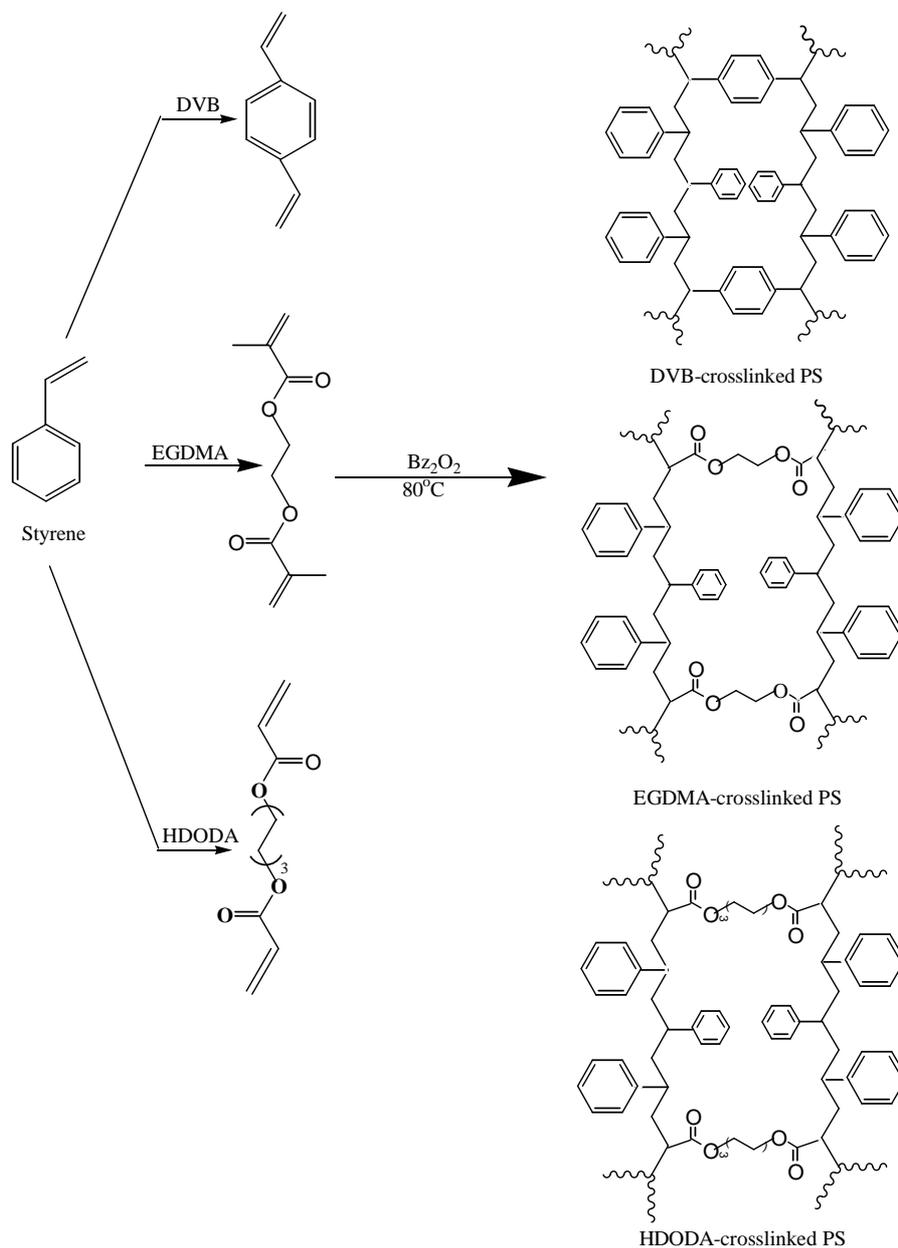
Fig. 1. Chlorine capacities of 2-20 mol% DVB-, EGDMA- and HDODA-Crosslinked chloromethyl polystyrenes

The FT-IR spectrum of crosslinked chloromethylated polystyrene showed the characteristic $C-Cl_{str}$ around $675cm^{-1}$. The extent of chloromethylation of polystyrenes was found to be highly dependent on the nature of crosslinking. With increasing flexibility of the crosslinking agent the extent of chloromethylation also increased. The higher chlorine capacity of HDODA-crosslinked polystyrene over DVB-crosslinked polystyrene is due to the flexibility of the crosslinking agent. The chloromethyl polystyrenes were converted into triethylamino methyl chloride by treating chloromethyl polystyrene with fivefold molar excess of triethylamine. The extent of quarternisation calculated on the basis of residual chlorine content was in the range of 92-94%.

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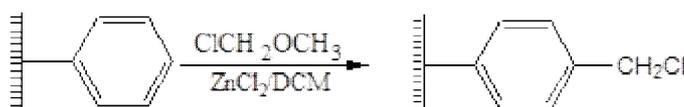


Scheme 1. Synthesis of DVB-, EGDMA- and HDODA-crosslinked polystyrenes

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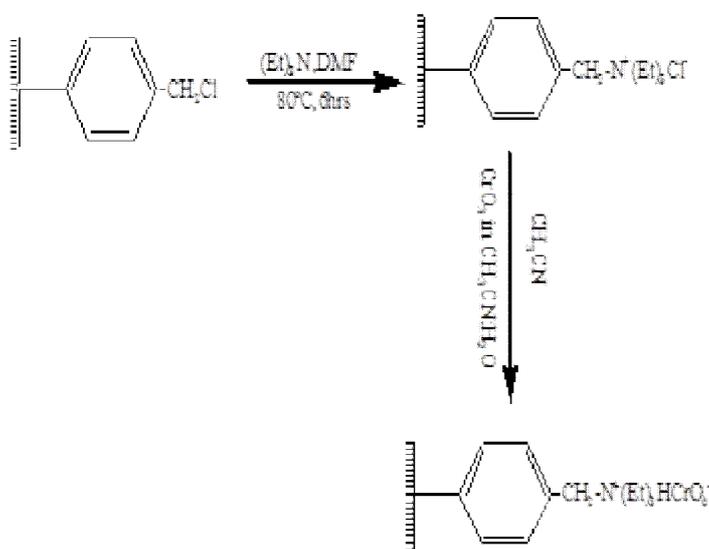
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Scheme 2. Chloromethylation of crosslinked polystyrene

The triethylamino methyl chloride of crosslinked polystyrenes were converted to their chromate functionalised polymer by treating the functionalised polymer with CrO_3 in acetonitrile-water mixture after swelling the polymer in acetonitrile (Scheme 3). HDODA-crosslinked polystyrene has the highest chromate capacity than EGDMA- and DVB-crosslinked polystyrenes. HDODA and EGDMA are relatively flexible due to the presence of the methylene groups [10]. With increasing number of methylene groups, the separation between the connecting polymer chains increases leading to less steric strain resulting in an increase in the hydrophilicity. This is the reason for the high functionality of HDODA- and EGDMA-crosslinked systems. The extent of functionalisation was found to be highly dependent on the degree of crosslinking. With increasing crosslink density the functional group capacity decreased.



Scheme 3. Incorporation of chromate function on DVB-, EGDMA- and HDODA-crosslinked chloromethyl polystyrenes

The crosslinked polystyrenes and the functionalised polymers were characterised using FT-IR and ^{13}C CP-MAS NMR spectroscopy and scanning electron microscopy. The characteristic FT-IR absorptions of aromatic rings were obtained at 2910, 1520 and 908 cm^{-1} . There was a strong band at 1452 cm^{-1} corresponding to $-\text{CH}_2-$ bending vibrations characteristic of polystyrene. EGDMA- and HDODA-crosslinked polystyrenes showed additional absorption of carbonyl stretching at 1720 cm^{-1} ($\text{C}=\text{O}$) and a broad band at 1110 cm^{-1} ($\text{C}-\text{O}-\text{C}$ str) characteristic of the ether linkages confirming the copolymer formation. In addition to the absorptions corresponding to styrene and crosslinking agents, the functionalised polymers showed absorptions characteristic of the chromate group at 942, 887, 854, and 762 cm^{-1} [11].

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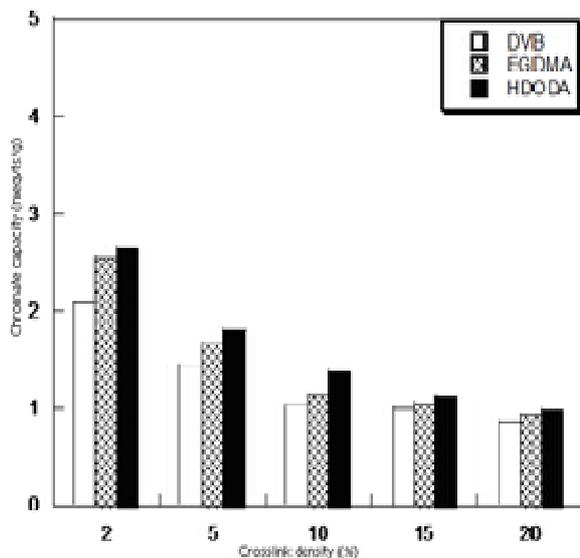


Fig. 2. Chromate capacities of 2-20 mol% DVB-, EGDMA- and HDODA- Crosslinked chloromethyl polystyrenes

The solid state ¹³C CP-MAS NMR spectra of 2% HDODA-crosslinked and functionalised polystyrenes showed an intense peak at 129.885ppm and a small peak at 147.418ppm corresponds to the aromatic carbons of the styrene (Fig.3&4). The methylene carbons of the polymer backbone gave a singlet at 42.33ppm.

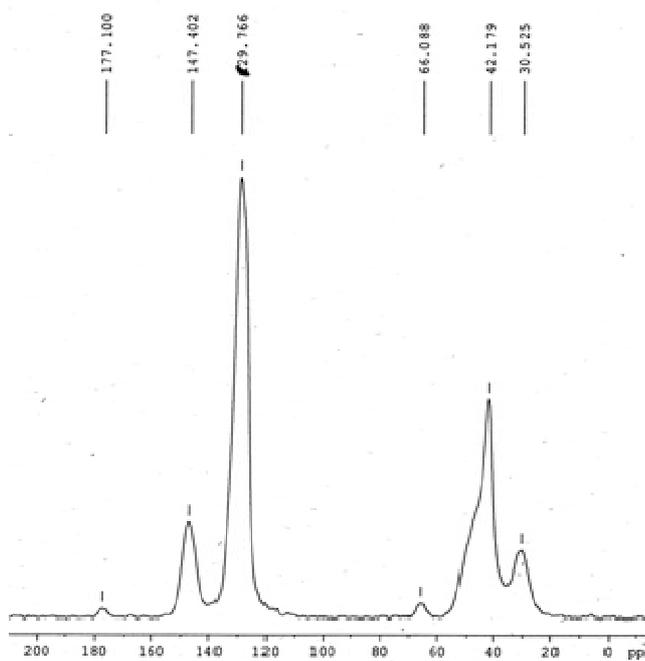


Fig. 3. ¹³C CP-MAS NMR spectra of 2mol% HDODA-PS

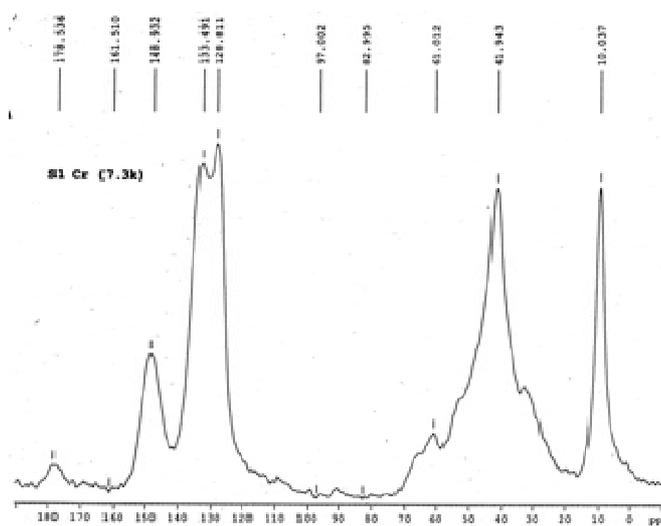


Fig. 4. ¹³C CP-MAS NMR spectra of 2mol% PS- chromate

The scanning electron micrograph showed that the surface of the functionalized polymer was rougher than the free polymer (Fig.5).

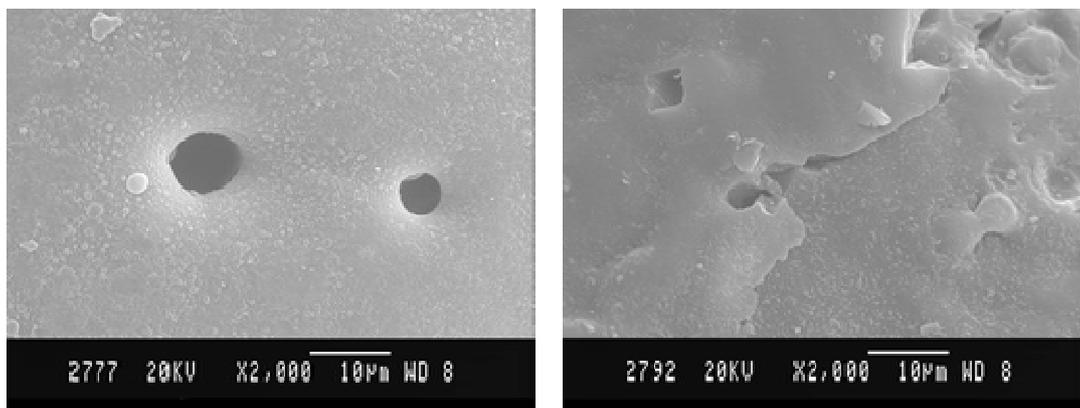


Fig. 5. Scanning electron micrographs of HDODA-crosslinked PS and PS-chromate

Swelling behavior is the most important property for amphiphilic networks. It not only reflects the structure of the networks, but also determines their potential applications. The solvation characteristics of the crosslinked polystyrenes with different crosslinking agents and with different crosslink densities were studied. The variation in equilibrium swelling ratio of different styrene polymers and their chromate complexes are graphically represented in Fig.5. Hydrophobic supports, like DVB-crosslinked polystyrene, swell to a great extent in nonpolar solvents like cyclohexane. On the other hand, hydrophilic polymers like EGDMA- and HDODA-crosslinked polystyrenes have good swelling properties in polar solvents like chloroform and tetrahydrofuran. This is due to comparable polarities of the solvents and the supports. From the swelling studies it is clear that the swelling is directly proportional to the crosslink density of the polymer support [12]. In the case of lightly crosslinked polymers, the polymer can form a gel by absorbing a considerable amount of solvent. But with highly crosslinked polymers, the polymer backbone becomes

more rigid and the polymer chains cannot expand appreciably by interacting with the solvent. As the crosslink density increases from 5 to 20% the equilibrium swelling ratio also decreases.

In the case of chromate supported on crosslinked polystyrenes, the extent of swelling was found to be less than that of the free polymer. The extent of swelling was maximum for 2% HDODA-, EGDMA- and DVB-crosslinked polystyrenes. For HDODA- and EGDMA-crosslinked PS, maximum swelling was observed in chloroform. DVB-crosslinked polystyrene is more hydrophobic and it swells more in cyclohexane, a nonpolar solvent. Fig.6 shows the dependence of nature of crosslinking on equilibrium swelling in different solvents.

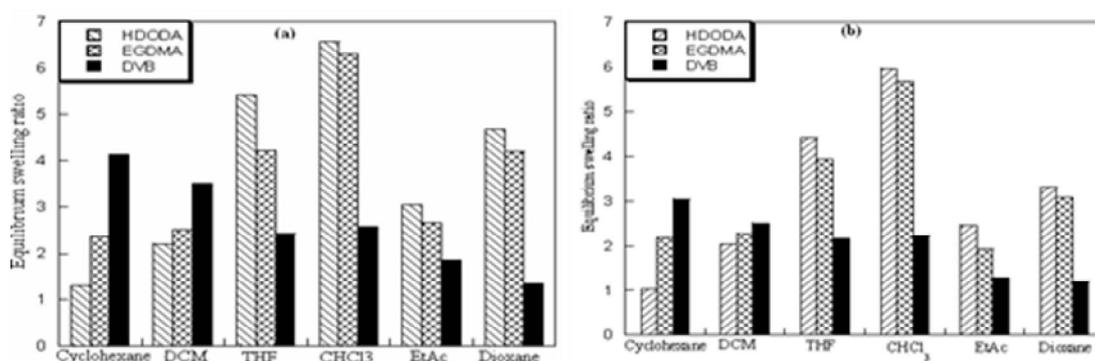


Fig.6. Dependence of the nature of crosslinking on equilibrium swelling ratio of (a) 2 mol% DVB-, EGDMA-, HDODA-crosslinked PS, and (b) chromate complexes

Structure-reactivity correlations of polystyrene-supported chromates

The nature of the polymeric backbone influences the kinetics and extent of functional group conversions in polymer-aided reactions [13]. The binding of a functional group to a polymer chain generally results in a new reagent with a different structure, reactivity and selectivity. Apart from the effect of possible heterogenization, polymer anchoring gives systems containing several active species per molecule, which can behave differently from the low molecular weight analogue because of cooperative interactions. The chemical reactivity of an immobilised functional group is governed by its distribution and accessibility on the polymer backbone [14]. The presence of other groups in the macromolecule can also be important for hydrophobic interactions with the substrates and the selectivity if groups with particular steric requirements are used [15, 16].

Effect of nature and degree of crosslinking

From the foregoing observations it is clear that, compared to DVB-crosslinked polystyrene, EGDMA- and HDODA-crosslinked copolymers showed significant increases in the reactivity of the bound functionality. The increased reactivity of HDODA- and EGDMA-crosslinked polymers is due to the flexibility of the crosslinking agents and also due to the increased compatibility with reagents and solvents.

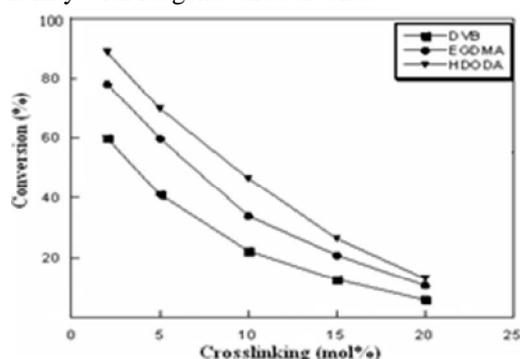


Fig. 7. Effect of the nature of crosslinking on oxidation of benzoin by PS-chromate

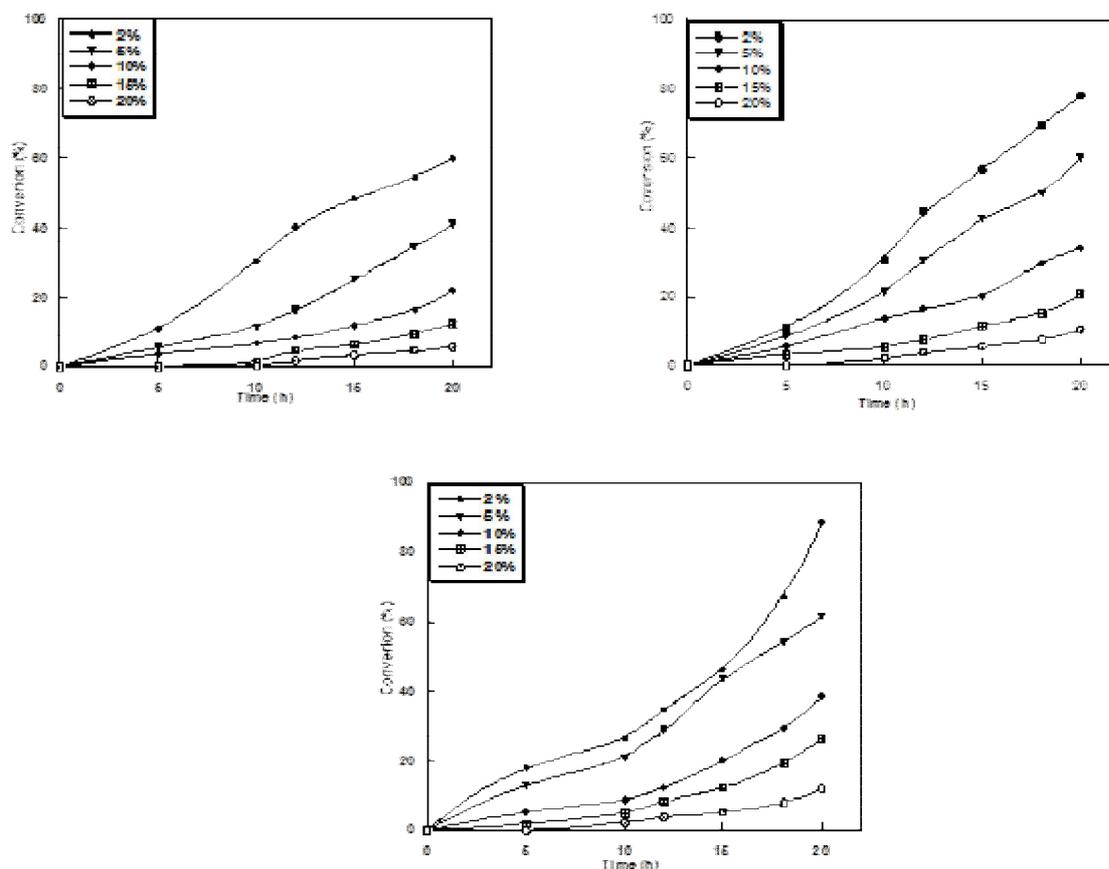


Fig. 8. Effect of degree of crosslinking on oxidation of benzoin by 2 mol% DVB-, EGDMA- and HDODA-crosslinked PS-chromate

Fig. 7 & 8 indicates the effect of nature and degree of crosslinking on the oxidation of benzoin to benzyl. The nature and degree of crosslinking of the polymer support is detrimental in deciding the net polarity of the polymeric reagent system. As the crosslink density increases, hydrophobicity attains prominence. The accessibility of the reactive groups in highly crosslinked networks are considerably diminished due to the reduction of intermolecular spaces accessible to the reactive molecules.

Among the three crosslinked polystyrene-supported chromates, 2mol% crosslinked systems exhibited maximum oxidising efficiency. At lower crosslink densities the polymer becomes more swollen and the reactive sites become more accessible. Highly crosslinked networks are unsuitable as supports since they are very difficult to functionalise, due to the presence of dense crosslinks and inaccessible domains. Even if functionalisation is achieved, the access of reactants to the active sites is slow and typically diffusion controlled. Similarly at higher crosslink densities, swelling may be too low to give effective access to the reactive groups.

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IV. CONCLUSION

A series of polymeric chromate derivatives based on differently crosslinked polystyrenes were developed and their chemistry investigated. The reactivity is maximum for 2% HDODA-crosslinked polystyrene-supported chromates than the EGDMA- and DVB-crosslinked systems. As the crosslink density increases from 2 to 20mol%, the reactivity decreases due to decreased diffusion of low molecular weight reagents into the polymer matrix. By the proper choice of the crosslinking agent and by adjusting the crosslink density, a polymeric reagent can be tailor made and a specific microenvironment can be developed which may induce certain selectivity and specificity at the reaction site.

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