CHAPTER VII

EXPERIMENTAL

The monomers, styrene, DVB, EGDMA, and methyl methacrylate (Aldrich) were purified by low pressure distillation. Styrene-divinyl benzene, styrene-ethyleneglycol dimethacrylate and methyl methacrylate-NN' methylene bis acrylamide copolymer supports were prepared by adopting procedures reported for parallel cases. Commercially available low molecular weight compounds were purified by distillation or recrystallisation unless otherwise stated. Microanalyses were done at Regional Sophisticated Instrumentation Centre, I I T, Madras and Central Drug Research Institute, Lucknow. The spectrophotometric measurements were done on Milton and Roy Spectronic 21D spectrophotometer. IR spectra were recorded on a Perkin-Elmer-397 spectrometer using KBr pellets.

1. Preparation of Styrene-Divinyl Benzene Copolymer (1a)

The monomers were washed with sodium hydroxide solution (1%,3 times) and water (3 times) to remove the inhibitors. Crosslinked polymers were prepared by suspension polymerisation technique using poly (vinyl alcohol) as the suspension stabilizing agent. PVA (150 mg) was dissolved in water (100 ml) and heated to 80-90°C. The mixture of monomers, say, styrene (18.68 ml) and DVB (0.95 ml ), for 2% crosslinked resin, and benzoyl peroxide (200 mg) as initiator were added to the hot solution with vigorous stirring. The mixture was heated at 90°C with stirring for 12h. The polymer formed was filtered, washed with hot water (15 ml x 3 times), carbon tetrachloride (15 ml x 2 times), benzene (15 ml x 2 times) and ethanol (15 ml x 2 times) and dried at 70°C in vacuum.
Polymers with crosslink densities 2,5,10,15 and 20 were prepared by varying the monomer ratio.

2. Preparation of Styrene-Ethylene glycol dimethacrylate Copolymer Support (1b)

The monomers were washed with sodium hydroxide solution (1%, 3 times) and with water (3 times) to remove the inhibitors. Poly (vinyl alcohol) (150 mg) was dissolved in water (100 ml) and heated to 70-80°C. The mixture of monomers, say, styrene (18.68 ml) and EGDMA (0.63 ml), for 2% crosslinked polymer and benzoyl peroxide (200 mg) as initiator were added to the hot solution with vigorous stirring. The mixture was heated to 90°C with stirring for 12h. The precipitated polymer was filtered, washed with hot water (15 ml x 2 times), carbon tetrachloride (15 ml x 2 times), benzene (15 ml x 2 times), ethanol (20 ml x 2 times) and dried at 60°C in vacuum. Polymers with crosslink densities 2,5,10,15 and 20 mole% were prepared by varying the monomer ratio.

3. Friedel Crafts Reaction of Polystyrene (1) with Chloromethyl Methyl Ether. Preparation of Chloromethyl Polystyrene (2)

Polystyrene beads (10g), preswollen in dichloromethane (20 ml) were added to a well stirred mixture of anhydrous SnCl₄ (3g) and chloromethyl methyl ether (10 ml) at 0°C. The temperature was allowed to rise to 30°C during a period of 1h. The mixture was then stirred for 10h. Finally, the reaction mixture was filtered at the pump and washed successively with dioxane-water (1:1), dioxane-water-HCl, water and methanol (15 ml x 2 times each). The resin was then dried in vacuum. A portion of the resin when tested for chlorine indicated the presence of chlorine. The chlorine content was determined by Volhard’s method.
4. Estimation of Chlorine Capacity in Chloromethyl Polystyrene Resins: General Procedure

The chloromethyl polystyrene (200 mg) was suspended in pyridine (5ml) and digested at 100°C for 12h. The product was then transferred into a clean conical flask by washing with 50% acetic acid. Nitric acid (6N, 10ml) and silver nitrate (0.1N, 20 ml) were added to the resulting mixture. Toluene was then added till it was half inch high over the solution. The excess silver nitrate was then titrated against standard ammonium thiocyanate (0.1N) using ferric alum as the indicator till a reddish brown colour was developed. A blank was also conducted. From the two titre values, chlorine capacity was determined.

5. Preparation of Polystyrene Carboxylic Acid Resins (3)

(a) Carboxylic Acid Resins with Zero Methylene Spacer

Chloromethyl polystyrene (10g), preswollen in acetone, was treated with potassium permanganate (15 g) in presence of anhydrous sodium carbonate (7g) in distilled water at refluxing temperature for 15h. After the reaction, the mixture was cooled and acidified with conc.HCl (10ml) in presence of sodium sulphite (7g). The reaction mixture was filtered at the pump. The resin was washed successively with acetone (10ml x 3 times), water (20 ml x 6 times), dioxane (20ml x 3 times), ethanol (20ml x 2 times) and dried in vacuum to constant weight.

b. Carboxylic Acid Resin with One Methylene Spacer

Chloromethyl polystyrene (10g) was reacted with potassium cyanide (6g) in DMF (50ml) at 120°C for 12h. After the reaction, the mixture was filtered at the pump, washed with water, ethanol and acetone (20ml x 3 times each) and dried in vacuum. Cyanomethyl
polystyrene (7 g) was hydrolysed using acetic acid - sulphuric acid mixture (1:1, v/v, 50 ml) at 100°C for 8h. After the reaction, it was filtered at the pump, washed with water ethanol and acetone (20 ml x 3 times each), dried in vacuum and weighed.

c. Carboxylic Acid Resin with Three Methylene Spacer

Polystyrene beads (10 g) was added to a previously prepared Lewis acid complex, comprising of anhydrous AlCl₃ (20 g) and succinic anhydride (14 g) kept at 0°C in dichloromethane-carbon disulphide mixture (1:4, v/v, 50 ml). The mixture was heated to reflux for 8h. After the reaction, the mixture was filtered, washed with water, ethanol and acetone (20 ml x 3 times each), dried in vacuum and weighed.

The carbonyl group of the ketonic acid resin (10 g) so obtained was reduced with previously prepared Zn-Hg (30 g) and conc. HCl (75 ml). The reaction mixture was refluxed for 30 h, after adding toluene (100 ml). It was filtered, washed with water, ethanol and acetone (30 ml x 3 times each), dried in vacuum and weighed.

d. Carboxylic Acid Resin with Five Methylene Spacer

Polystyrene (10 g) was added to Lewis acid complex, prepared from anhydrous AlCl₃ (20 g) and adipoyl chloride (15 ml) kept at 0°C in dichloromethane-carbon disulphide mixture (1:4 v/v, 50 ml). The temperature of the mixture was slowly raised to 30°C and stirred for 2 h. The mixture was then heated to reflux for 8 h. After the reaction, the mixture was filtered, washed with water, ethanol and acetone (20 ml x 3 times each), dried in vacuum and weighed.
The ketonic acid resin (10g) obtained from the above experiment was subjected to Clemmensen reduction using Zn-Hg (30g) and conc.HCl (75 ml). The reaction mixture was heated to reflux for 30h with toluene (100ml). It was then filtered, washed with water, ethanol and acetone (30ml x 3 times each), dried in vacuum and weighed.

6. Estimation of Acid Capacity of the Carboxylic Acid Resins. General Procedure

The carboxylic acid resin (200 mg), preswollen in acetonitrile (5ml) was treated with standard alcoholic potassium hydroxide solution (0.5 N, 20ml) for 12h. The resin was filtered off, washed with water and the excess potassium hydroxide present in solution was titrated against standard oxalic acid (0.5N) using phenolphthalein as the indicator. A blank was also conducted. From the titre values, acid capacity was determined.

7. Preparation of Carbethoxy Polystyrene Resin

Polymeric carboxylic acid resin (10g), preswollen in THF (20ml), was esterified using absolute ethanol (30ml) in presence of conc.H$_2$SO$_4$ (2ml) at 80°C for 12h. The mixture was filtered at the pump, washed with water, ethanol and acetone (20ml x 3 times each), dried in vacuum and weighed.

8. Estimation of Ester group Capacity. General Procedure

The carbethoxy polystyrene resin (200mg), preswollen in acetonitrile (5ml) was refluxed with standard KOH solution (0.1N, 20 ml), for about 6h. The resin particles were filtered off, washed with water and the unreacted alkali was titrated against standard oxalic acid (0.1N) using phenolphthalein as the indicator. A blank was also conducted. From the titre values, acid capacity was determined.
9. Preparation of Polystyrene Bound 1, 3 Diketones

Polymeric ester resin (10g), preswollen in THF (20ml), was refluxed with acetophenone (15ml) in presence of sodium ethoxide (5g) for 12 h. The mixture was cooled to room temperature and dil. H₂SO₄ (20ml) was added and stirred for 30 minutes. It was then filtered at the pump, washed with water, ethanol and acetone (20ml X 3 times each), dried and weighed.

10. Estimation of Enolic (–OH) Capacity of 1,3-Diketo Resins. General Procedure

The 1,3 diketo resin (200mg) was mixed with acetylating mixture (10ml) and stirred for 10h. The liberated acetic acid was then titrated against alcoholic KOH (0.5N) using phenolphthalein as indicator. A blank was also conducted. From the titre values, the enolic capacity was determined.

11. Preparation of Polymeric Isoxazole Resin

Polymeric β-diketo resin (10g) was heated to reflux with hydroxylamine hydrochloride (4g) in presence of pyridine (10ml) for 12h. The mixture was cooled to room temperature and water (10ml) was added, filtered at the pump, washed with water, acetonitrile, ethanol and acetone (20ml x 3 times each), dried and weighed.

12. Preparation of Polymeric Pyrazole Resin

Polystyrene supported 1,3-diketones (10g) was stirred with hydrazine sulphate (8g) in presence of pyridine (10ml) at room temperature for 12h. The resin particles were collected by filtration at the
pump. The resin was washed successively with water, acetonitrile, ethanol and acetone (20ml x 3 times each) and dried and weighed.

13. Preparation of Methyl methacrylate-DVB Copolymer Support

The monomers were washed with sodium hydroxide solution (1%, 3 times) and water (3 times) to remove the inhibitor. The crosslinked polymers were prepared by suspension polymerisation technique. Poly (vinyl pyrrolidone) (150 mg) was dissolved in distilled water (100 ml) and heated to 80-90°C. The mixture of monomers say, methyl methacrylate (20ml) and divinyl benzene (1.09 ml) for 2% crosslinked resin and benzoyl peroxide (200mg) as initiator were added to the hot solution with vigorous stirring. The mixture was heated at 80°C with stirring for 12h. The polymer so obtained was filtered, washed with hot water, carbon tetrachloride, benzene, ethanol and methanol (20 ml x 3 times each) and dried at 60°C in vacuum. Polymers with crosslink densities 2,5,10,15 and 20 were prepared by varying the monomer ratio.

14. Preparation of Methyl methacrylate-EGDMA Copolymer Support

The monomers were washed with sodium hydroxide solution (1%, 3 times) and with water (3 times) to remove the inhibitor. The crosslinked polymers were prepared by suspension polymerisation technique. Poly (vinyl alcohol) (150 mg) was dissolved in water (100 ml) and heated to 80°C. The mixture of monomers, say, methyl methacrylate (20ml) and EGDMA (0.72 ml) for 2 percent crosslinked polymer and benzoyl peroxide (200mg) as initiator were added to the hot solution with vigorous stirring. The mixture was heated at 80°C with stirring for 12h. The polymer so obtained was filtered, washed with hot water, CCl₄, benzene, ethanol and methanol (20ml x 3 times) and dried at 60°C in vacuum.
Polymers with crosslink densities 2, 5, 10, 15 and 20 were prepared by varying the monomer ratio.

15. Preparation of Methyl methacrylate-NN'MBA Copolymer Support

The monomers were washed with sodium hydroxide solution (1%, 3 times) and with water (3 times) to remove the inhibitor. The crosslinked polymers were prepared by solution polymerisation technique. The mixture of monomers, say, methyl methacrylate (20ml) and NN'MBA (0.59g) for 2 percent crosslinked polymer and benzoyl peroxide (200 mg) as initiator were added to ethanol (40 ml). The mixture was heated at 80°C with stirring for 12h. The precipitated polymer was filtered, washed with hot water (15 ml x 3 times), carbon tetrachloride (15ml x 3 times) and dried at 60°C in vacuum. Polymers with crosslink densities 2, 5, 10, 15 and 20 were prepared by varying the monomer ratio.

16. Preparation of Poly(methyl methacrylate) Bound 1,3-Diketones

The poly (methyl methacrylate) resin (10g) preswollen in acetonitrile (20ml) was heated with acetophenone (20ml) and sodium ethoxide(5g) at the refluxing temperature for 12h. Finally, the reaction mixture was cooled in an ice bath, acidified with sulphuric acid (2N, 20ml) solution. The product resin was collected by filtration, washed with water ethanol and acetone (20 ml x 3 times each) and dried in vacuum to constant weight.

17. Preparation of Poly(methyl methacrylate) Bound Isoxazoles

Poly(methyl methacrylate) supported 1,3 diketone (10g), preswollen in acetonitrile (20ml) was stirred with hydroxylamine hydrochloride (8g) in presence of pyridine (10ml) to reflux for 12h. The
mixture was cooled to room temperature and water (10ml) was added, filtered at the pump, washed with water, acetonitrile, ethanol and acetone (20ml x 3 times each), dried and weighed.

18. Preparation of Poly (methyl methacrylate) Bound Pyrazole

Poly(methyl methacrylate) supported 1,3 diketones (10g) preswollen in acetonitrile (20ml) was stirred with hydrazine sulphate (10g) in presence of pyridine (10ml) at room temperature for 12h. The reaction mixture was cooled and the resin particles were collected by filtration at the pump. The resin was washed successively with acetonitrile, dioxane-water (1:1), ethanol, methanol and dried in vacuum to constant weight.


The nitrogen containing resin (100 mg) was mixed with K₂SO₄-CuSO₄-HgO mixture in 15:2:1 ratio (0.7g) in a Kjeldahls' flask and was digested for 4h after addition of conc.H₂SO₄ (2ml). When the solution attained a blue colour and was clear, it was transferred quantitatively into an ammonia distillation unit. Sodium hydroxide solution (60%, 10ml) and a pellet of sodium thiosulphate were added to the solution. A stream of steam was passed through the solution and the liberated ammonia was collected in a saturated boric acid solution (20ml). It was then titrated against HCl (0.1N) using methylene blue-methyl red indicator till the colour of the solution changed from green to blue. From the titre values, the percentage of nitrogen in the resin was estimated.

20. Quaternisation of Polymeric Isoxazole and Pyrazole Resins with Methyl iodide

Polymeric isoxazole/pyrazole resin (10g), preswollen in acetonitrile (20ml) was reacted with methyl iodide (10ml) at the refluxing
temperature for 10h. After the reaction, the mixture was filtered, washed with water, ethanol and acetone (20ml x 3), dried and weighed.

21. Estimation of Iodide in Isoxazolinium and Pyrazolinium Iodide Resins

A definite amount (0.5g) of quaternised resin, preswollen in acetone (10ml), was allowed to react with silver nitrate (20ml) for 5h. The excess silver nitrate was then titrated against standard ammonium thiocyanate solution (0.1N) using ferric alum as the indicator till a reddish brown colour was developed. A blank experiment was also conducted. From the two titre values, amount of iodide ions present in the resins was determined.

22. Preparation of Polymeric Isoxazolinium and Pyrazolinium Permanganate Resins

Quaternised polymeric isoxazole/pyrazole resin (10g) was reacted with potassium permanganate (2g) in acetone-water mixture (2:1, v/v, 25 ml) at 0°C for 4h. After reaction, the mixture was filtered, washed with water, ethanol and acetone (20ml x 3 times each), dried and weighed.

23. Estimation of Permanganate in the Functionalised Resins: General Procedure

A definite amount (0.5g) of the functionalised resin was accurately weighed and suspended in H₂SO₄ (2N, 30ml) containing acetone (10ml). The resin was allowed to swell in the medium for about 1h. A known excess of standard ferrous ammonium sulphate solution was added and stirred until the dark colour of the resin was completely disappeared and turned to almost white. The unreacted ferrous ammonium sulphate
solution was titrated against standard KMnO₄ solution. From the titre values, the permanganate equivalent of isoxazolinium/pyrazolinium permanganate was calculated.

24. Preparation of Polymeric Isoxazolinium and Pyrazolinium Chromate Resins

Quaternised polymeric isoxazole/pyrazole resin (10g) preswollen in acetonitrile (10ml) was stirred at 30°C with CrO₃ (3g) dissolved in water (10ml) for a period of 10h. The resin was filtered and washed with distilled water until the filtrate was clear. It was then washed with acetone, dried and weighed.

25. Preparation of Polymeric Isoxazolinium and Pyrazolinium Chlorochromate Resins

Polymeric isoxazole/pyrazole resin (10g) preswollen in acetonitrile (20ml) was suspended in acetonitrile-water mixture (1:1v/v), (20ml), CrO₃ (4g) and conc.HCl (10ml) were then added. The mixture was stirred at room temperature for 10h and filtered, the resin was washed with distilled water until the filtrate was clear. Finally it was washed with acetone (10ml) and dried.

26. Preparation of Pyrazole-CrO₃ Complex Resin

Polymeric pyrazole resin (10g) preswollen in dichloromethane (20ml) was added to a suspension of CrO₃ (3g) in dichloromethane (20ml) and the mixture was stirred at room temperature for 10h. The resulting dark brown resin was filtered, washed with dichloromethane, chloroform, acetonitrile, water and acetone (20mlx 3 times each) and dried.
27. Estimation of Chromate, Chlorochromate and CrO₃ Complex in the Functionalised Resins

A known weight (0.5g) of functionalised resin, preswollen in acetone, was treated with alcoholic KOH (0.5N, 10ml) for about 24h. The polymer particles were filtered off. To the filtrate containing K₂CrO₄, KI (10%, 10ml) was added followed by H₂SO₄ (IN, 3ml ) and the liberated iodine was titrated against standard sodium thiosulphate solution using starch as the indicator.

28. Oxidation of Alcohols: General Procedure

The alcohol (1m mol) was dissolved in chloroform (10 ml). A two fold molar excess of the polymeric reagent was added and the reaction mixture was stirred. H₂SO₄ (10%, 1ml) was also added in the case of CrO₃ complex reagents. The reaction was followed by thin layer chromatography. After the completion of the reaction, resin was filtered and washed with chloroform. The combined filtrate and washings on evaporation of the solvent afforded the corresponding carbonyl compounds. The products were identified and characterised by comparison (m.p/b.p and IR) with authentic samples.

29. Study of the Effect of Length of Spacer arm and Degree of Crosslinking on the Extent of Oxidation Reactions

In order to study the effect of crosslink density on the reactivity of the prepared polymeric oxidising reagents having different spacer groups, reagents with 0,1,3 and 5 methylene spacer arm were prepared from (2-20%) DVB and EGDMA crosslinked polystyrene and used for the oxidation of alcohols to the corresponding carbonyl compounds. In the present study, oxidation of benzoin was taken as the model reaction.
The amount of benzil formed was determined and the reactions were followed spectrophotometrically and by tlc.

30. Investigation of the Effect of Solvent on the Efficiency of Oxidation Reactions

To study the effect of solvents on the yield of products obtained during oxidation, oxidation of benzoin was taken as the model reaction. The oxidation reaction was conducted in different solvents like chloroform, benzene, dichloromethane, tetrahydrofuran, acetonitrile, dioxane and cyclohexane using the polymeric oxidising reagents having 0, 1, 3 and 5 methylene spacer groups. The substrate to resin ratio was fixed at 1:2. In all the cases, time for complete conversion was noted.

31. Effect of Temperature on the Oxidation Reactions

In order to study the effect of temperature on the oxidation reaction, oxidation of benzoin to benzil was taken as the model reaction. Oxidation reactions were conducted at temperatures ranging from 20-60°C. In all the cases, time for maximum conversion was noticed.

32. Study of Influence of Concentration of the Reagents on the Extent of Oxidation Reactions

To study the dependence of the reactivity of isoxazolinium and pyrazolinium chromate, chlorochromate and permanganate on their concentration, oxidation of benzoin was taken as the model reaction. The reagent to substrate ratio used were 1:1, 2:1, 3:1, 4:1 and 5:1. The amount of benzil obtained after a particular time interval (10h) was noted by spectrophotometric method.
33. Kinetics of Oxidation of Differently Substituted α-Phenyl Ethanois by the Polymeric Oxidising Reagents

α-Phenyl ethanol or substituted α-phenyl ethanol (1 mol) was dissolved in chloroform (20 ml). The resin (2 mol) was added to the alcohol solution and shaken well, at 30°C. An aliquot of the solution (1 ml) was withdrawn after regular intervals of time, diluted to 10 ml and the concentration of the ketone formed was measured spectrophotometrically. The experiment was repeated at different intervals of time and at refluxing temperature. The rate constant for the reaction was calculated.

34. Recycling and Reuse of the Spent Permanganate Resins

The spent polymeric reagent (5 g) collected from different experiments, was stirred for 2 h with 2N solution (50 ml) of ferrous ammonium sulphate in the presence of 2N H₂SO₄ (20 ml) to remove all oxides of manganese. The resin was filtered, washed with water, and dried. The regenerated polymer was functionalised with permanganate following the procedure described earlier. The regenerated and refunctionalised permanganate resin was used for oxidation of alcohols as described earlier.

35. Recycling of the Spent Chromate, Chlorochromate and CrO₃ Complex Resins

The spent polymeric reagents collected from different oxidation reactions were treated with alcoholic KOH solution to remove the unreacted chromate function, filtered, and washed successively with chloroform, methylene chloride, THF, methanol and acetone (20 ml x 3 times each) and dried in vacuum. The dried resin was refunctionalised as described earlier.
II. Preparation of Polystyrene Supported Dioxirane Containing a Five Methylene Spacer

(a) Preparation of the Acid chloride Resin

Polymeric carboxylic acid resin (10g) containing a five methylene spacer was suspended in toluene (20 ml) for 12h. Dimethyl formamide (1 ml) and thionyl chloride (40 ml) were added and refluxed on a water bath for 6h until the evolution of HCl ceased. The reaction mixture was cooled and filtered at the pump, washed with toluene, chloroform, benzene and acetone (20 ml x 3 times each) and dried in vacuum. Chlorine content was determined by Volhard’s method.

(b) Determination of Chlorine in Acid Chloride Resin: Volhard’s Method.

The acid chloride resin (200 mg) was digested with pyridine (10ml) for 3h. The pyridinium chloride formed was extracted by glacial acetic acid (30ml) and conc. HNO₃ (5ml). Standard silver nitrate solution (20ml) was added and the excess silver nitrate was back titrated against standard ammonium thiocyanate solution using ferric alum indicator. A blank was also run with the carboxylic acid resin under the same conditions. From the volume of the AgNO₃ consumed, the amount of chlorine present in the resin was calculated.

(c) Preparation of 2-Oxoalkyl Resin

(i) Preparation of Ethoxymagnesium Diethyl Malonate

Magnesium turnings (5.4 g, 0.22 g atom), absolute ethanol (5ml) and carbon tetrachloride (0.5 ml) were heated on a steam bath. After 15 minutes, dry ether (50ml) was added cautiously with stirring. A solution of diethylmalonate (35.2g, 0.2 mol), ethanol (20ml, 0.34 mol) and ether (25 ml) was added with stirring at such a rate that rapid boiling was
maintained. The mixture was refluxed on steam bath for 3h when all magnesium turnings were dissolved.

(ii) Preparation of Polymeric Acyl Malonate Resin

Polymeric carboxylic acid chloride resin (10g), preswollen in THF (20ml) was added slowly with stirring to the ethoxymagnesium diethyl malonate, from the above step. Heating under reflux was continued for another 5h. The mixture was cooled and shaken with dil H₂SO₄ (25ml conc.H₂SO₄ in 200 ml water). The acyl malonate resin was collected on a sintered glass filter, washed with water, methanol, chloroform and acetone, dried and weighed.

(iii). Hydrolysis of Polymeric Acyl Malonate Resin : Preparation of 2-Oxoalkyl Resin

The polymeric acyl malonate resin, (10g) was suspended in THF (20ml) for 12h. It was treated with a solution of glacial acetic acid (60ml), conc.H₂SO₄ (7.6ml), water (40ml) and THF (50ml). The reaction mixture was refluxed for 4h until the evolution of carbon dioxide was ceased. After cooling, the resin was filtered at the pump, washed with water, sodium bicarbonate solution, water, ethanol and acetone (20ml X 3 times each), dried in vacuum and weighed.

d. Estimation of Keto group in 2-Oxoalkyl Resin

The keto resin, preswollen in acetonitrile (10 ml), was suspended in NaOH (0.1N, 20 ml) for 2h. It was treated with iodine solution and stirred well for 10h. The unreacted iodine was back titrated with sodium thiosulphate solution using starch as indicator.
e. Conversion of Carbonyl group of 2-Oxoalkyl Resin to Dioxirane Function: Preparation of Dioxirane Resin

A suspension of 2-oxoalkyl resin (10 g) in THF (20 ml) was added to a solution of sodium bicarbonate (5 g) in water (10 ml). It was kept at 0°C. Potassium permonosulphate (6 g) was added to the above mixture slowly and stirred for about 12h. After the reaction, it was filtered, washed with water, methanol, ethanol and acetone (20 ml x 3 times each), dried and weighed.

f. Estimation of Dioxirane Function in the Resin

The dioxirane resin (500 mg), preswollen in acetonitrile (10 ml), was allowed to react with acetic acid-acetone mixture (3 : 2) for about 5 h. Potassium iodide solution (10 ml) was then added and kept for another 5 h. The liberated iodine was then determined using standard solution of sodium thiosulphate using starch as indicator. A blank experiment was also conducted. From the titre values, dioxirane equivalent present in the resin was calculated.

g. Oxidation and Expoxidation Reaction Using Polymeric Dioxirane

The substrate (1 mmol) dissolved in chloroform (5 ml) was added to a suspension of resin (2 mmol) in chloroform (5 ml) and stirred with H₂SO₄ (2N, 1 ml). The reaction was followed by thin layer chromatography. After the completion of the reaction, resin was filtered and washed with chloroform. The combined filtrate and washings on evaporation of the solvent afforded the product. The products were identified and characterised by comparison (m.p/b.p and IR) with authentic samples.
h. Effect of Solvents on the Reactivity of the Polymeric Dioxirane

In order to study the effect of solvents on the reactivity of polymeric dioxirane, oxidation of aniline was taken as the model reaction. The oxidation reaction was conducted in different solvents like chloroform, dichloromethane, benzene, benzene--dichloromethane mixture, acetonitrile, THF and dioxane. The substrate to resin ratio was fixed at 1 : 2. In all cases, time required for maximum conversion and yield obtained were noted. All reactions virtually proceeded to completion and the final products were isolated and characterised by comparison with authentic samples.

(i). Effect of Temperature on the Oxidation Reaction

To study the effect of temperature, the oxidation of aniline was done at temperatures 20, 30, 40, 50 and 60°C with a resin to amine ratio 2 : 1. The reactions were allowed to go completion. The reaction was followed by thin layer chromatography. The products, after reaction, were isolated and identified by comparing their physical constants (m.p/b.p) with authentic samples.

(j). Recycling of Spent Dioxirane Resin

The spent reagent collected from different experiments was washed thoroughly with solvents like chloroform, dichloromethane and acetone (20ml x 3 times each). It was then functionalised using potassium peroxymonosulphate adopting the procedure described earlier.