

Synthesis of Electro-optic Copolymer of 3,3', 5,5'-tetra methyl-4,4'-dimethacryloyloxy stilbene With Methyl methacrylate.

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Abstract: Celite supported silver carbonate was prepared by the general procedure. 2,4,6- trimethyl phenol was oxidized with silver carbonate by refluxing the mixture in benzene for 2h which ultimately formed 3,3' 5,5'-tetramethyl stilbenequinone in 93% yield. After that stilbenequinone was reduced with zinc dust and acetic acid which ultimately formed 3, 3', 5, 5'-tetramethyl-4,4' dihydroxystilbene as yellow crystals. 3,3', 5,5'-tetramethyl dihydroxystilbene was then treated with methacryloyl chloride in THF solvent medium for 50h at room temperature which formed 3,3' 5,5'-tetramethyl -4,4'-dimethacryloyl oxy stilbene. Then the monomer 3,3' 5,5'-tetramethyl-4,4'-dimethacryloyloxy stilbene was co-polymerized with methyl methacrylate in DMF solvent medium at 110⁰c for 80h by using free radical initiator benzoyl peroxide. All the monomers and co-polymer were investigated by studying UV,FT-IR, NMR spectroscopy.

Key words: 3,3' 5,5'-tetramethyl stilbenequinone, 3,3' 5,5'-tetramethyl -4,4'-dihydroxy stilbene, 3,3' 5,5'-tetramethyl-4,4'-dimethacryloyloxy stilbene, copolymerization.

I. Introduction

Photoconducting polymers are the subject of intense study owing to their potential applications in photo refractive devices, light emitting diodes, photo voltaic and many other optoelectronic devices. The possibility of adjusting the properties by modifying the structure is the attractive feature of polymeric systems .photoconductivity in polymeric systems is a complex process involving absorption of radiation, generation of charge carrier, injection , transport, recombination and trapping.

One of the necessary requirements for photo refractivity is photoconductivity. The polymeric photoconductor used in practise are based on two type of systems. In the first, the charge transporting unit is a part of the polymer chain and in the second , low molecular weight charge generating and charge transporting molecules are embedded in a polymeric matrix .These are called molecularly doped polymers. A large number of polymers with charge-transporting units in the side chain and main chain, polymers with pi-conjugated and sigma conjugated main chain were extensively studied. Molecularly doped systems have attracted great attention because of their importance in the construction of transport theories in amorphous photoconductors. The main drawback with these systems is phase separation due to presence of large number of low molecular dopants in the inert polymer host matrix. Hence, the application of molecular doping towards stable photorefractive polymer system is limited. In order to decrease the chances of phase separation, polymers were synthesized with charge transporting units chemically attached to main chain or as side chain

Lot of reports are there in the literature about the synthesis and properties of conjugated polymer systems. However, less attention was given to non-conjugated polymers. In non-conjugated polymers, the semiconducting property is based on the charge hopping from one localized site to another in the direction of electric field. In this chapter, the monomer 3, 3', 5,5'-tetramethyl -4, 4' dimethacryloyl oxy stilbene was synthesized and then it was co-polymerized with methyl methacrylate via radical initiated polymerization technique. The synthesized polymer has good thermal stability and mechanical strength. The synthesized polymer was characterized by FT-IR and NMR spectroscopy .After the discovery of photoconductivity in PVK, most of the photorefractive studies were done on systems based on PVK. Since then several high speed photorefractive polymer systems with PVK as photoconducting polymer matrix werereported. Various photoconducting polymers other than PVK were designed, synthesized and are extensively used as hole transport conductors for the preparation of photo refractive systems.

Similarly a photorefractive system containing poly (3, 3', 5, 5'-tetramethyl-4, 4'-dimethacryloyloxy stilbene-co-methyl methacrylate) as charge transporting polymer host can be developed. The second- order non-linear optical chromophore, disperse red-1(DR 1), the plasticizer, N-isopropyl carbazole and the charge generator C60 can be dispersed into the charge transporting polymer host and photorefractivity can be measured.

II. Experimental

2.1. Preparation of Celite-supported Silver carbonate:

The celite was purified by washing it successively with methanol containing 10% concentrated hydrochloric acid and then with distilled water until neutral. It was finally dried at 120^oc. Purified Celite (30 g) was added to mechanically stirred solution of silver nitrate (34 g, 200 m mol) in distilled water (200 ml). A Solution of sodium carbonate decahydrate (30 g, 105 m mol) in distilled water (300 ml) was then added slowly to the resulting homogeneous suspension. when the addition was complete, stirring was continued for a further 10 minutes. The yellow –green precipitate which was formed was then filtered off and finally dried in a rotary evaporator over a period of several hours. The silver carbonate/ Celite reagent contains about 1 m mol of silver carbonate in 0.57 g.

2.2. Synthesis of 3, 3', 5, 5'- tetramethylstilbenequinone:

6.8g (0.05 mol) 2, 4, 6- trimethyl phenol and 0.22 mol silver carbonate was mixed with 300 ml of benzene and refluxed for 2 h. At the end of the reaction (determined by t.l.c. monitoring), the solid phase was filtered off and the solvent evaporated. The product is highly pure and recrystallisation is unnecessary.

2.3. Preparation of 3,3' 5, 5'-tetramethyl-4,4'-dihydroxy stilbene:

A solution of 3,3' 5, 5' –tetramethylstilbenequinone (0.05 g) in acetic acid (100ml) was shaken with zinc dust (4g) for about 1h. The colourless mixture was filtered and the filtrate neutralized with sodium hydrogen carbonate. Extraction with ether and evaporation of solvent gave 3, 3', 5,5'-tetramethyl-4, 4'-dihydroxy stilbene as yellow crystals. The product was characterized by IR, UV and NMR spectroscopy.

2.4. Synthesis of 3, 3', 5, 5'- tetramethyl- 4, 4'-dimethacryloyloxy stilbene:

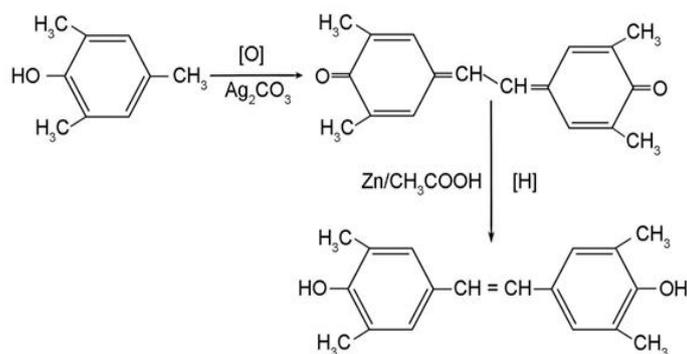
3, 3', 5, 5'- tetramethyl-4, 4'- dihydroxystilbene (5.36g, 20 m mol) was dissolved in 50 ml dry THF under nitrogen. To this solution, pyridine (0.4 g, 5.04 m mol) and methacryloyl chloride (4ml, 20.52 m mol) were added dropwisesimultaneously. The reaction was carried out at 0^oc with magnetic stirring for 3h and then at room temperature for 50h. The resulting mixture was washed with hydrochloric acid (0.1 M), sodium carbonate (5%) and finally with distilled water. The excess solvent was evaporated under reduced pressure. The organic layer was dried over anhydrous magnesium sulphate. The reaction product obtained was purified by column chromatography using methylene dichloride. The monomer was characterized by IR, UV and NMR spectroscopy.

2.5. Polymerization

3, 3', 5, 5'-tetramethyl-4, 4'-dimethacryloyloxy stilbene (1.616 g, 4 m mol), methyl methacrylate (0.80 g, 8 m mol) and benzoyl peroxide (2.26 g, 10 m mol) were dissolved in dry DMF (40 ml). The reaction was carried out at 110^oc for 80 h under nitrogen. The resulting solid was dissolved in DMF and reprecipitated from methanol. The polymer was collected by filtration, dried under vacuum and stored. The polymer was characterized by IR, UV and NMR spectroscopy.

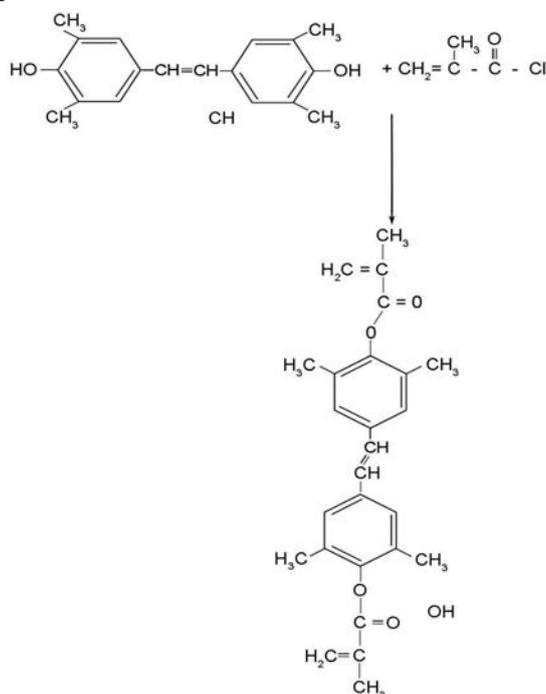
III. Result And Discussion:

IR, UV and NMR spectra revealed the successful preparation of the polymer. The first monomer namely 3, 3', 5,5'-tetramethyl-4,4'-dihydroxy stilbene was prepared as follows. At first the compound 2,4,6,-trimethyl phenol was oxidized with celite supported silver carbonate which subsequently formed 3,3', 5,5'-tetramethyl stilbenequinone which was further reduced with zinc dust and acetic acid to form 3, 3',5,5'-tetramethyl-4,4'-dihydroxystilbene. The synthetic route of the first monomer was represented in scheme-I.



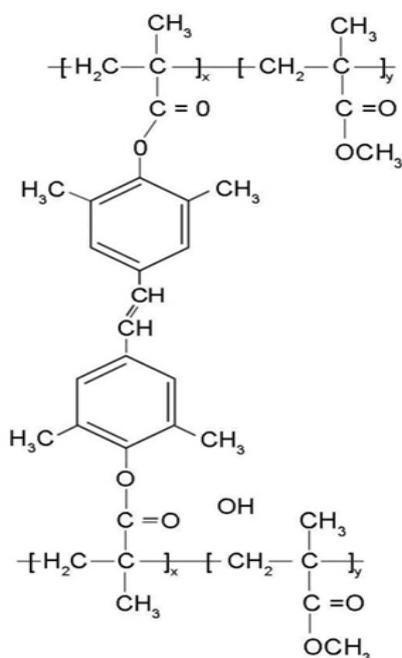
Scheme – I

The second monomer was synthesized as follows. The first monomer namely 3,3',5,5'-tetramethyl-4,4'-dihydroxy stilbene was treated with methacryloyl chloride in THF solvent at room temperature for 50h which subsequently formed the product 3,3',5,5'-tetramethyl-4,4'-dimethacryloyloxy stilbene. The synthetic route of the second monomer was represented in scheme-II.



Scheme – II

Ultimately the second monomer namely 3,3',5,5'-tetramethyl-4,4'-dimethacryloyloxy stilbene was co-polymerized with methyl methacrylate in DMF solvent at 110⁰c via radical initiated polymerization using benzoyl peroxide as catalyst. The polymer was identified by the characterization of IR,UV and NMR spectra. The polymer obtained in good yield. The co-polymer was soluble in most common organic solvent. The synthetic route of the polymer was represented in scheme-III.



Scheme - III

The non-conjugated polymer namely poly (3,3,5,5'-tetramethyl-4,4'-dimethacryloyloxy stilbene-co-methylmethacrylate) has good thermal property and mechanical strength. The polymer has good photoconducting properties and opto-electric properties. The co-polymer can be doped with C₆₀ to enhance the photoconductivity. A photorefractive system can be developed by using the co-polymer as a charge transporting medium, the second –order non-linear optical chromophore, namely DR-1, the plasticizer, namely-isopropyl carbazole and the charge generator C₆₀.

IV. Conclusion

The polymer namely poly(3,3', 5,5'-tetramethyl-4,4'-dimethacryloyloxy stilbene-co-methylmethacrylate) was synthesized by treating the monomer 3,3' 5,5'-tetramethyl-4,4'-dimethacryloyloxy stilbene with methyl methacrylate in 1:2 molar ratio via radical initiated polymerization . The polymer was characterized by IR,UV and NMR spectroscopy. The co-polymer has good opto-electric and photoconducting properties. The polymer can also be used as a photorefractive NLO chromophore. The polymer has good mechanical properties and thermal stability. The polymer can be doped with C₆₀ to enhance the photoconductivity and quenching of photoluminescence.

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