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# Synthesis Of Photoconducting Polyester Of Triphenylamine-Benzoxazole Moiety.

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***Abstract :***
*4,4' –diformyl-4''-methoxytriphenylamine was synthesized by the treatment of 4-methoxy triphenyl amine with $POCl_3$ and DMF mixture with stirring and then heated the mixture for 7h at $95^0$-$100^0$c. After cooling, the mixture was poured into crushed ice and neutralized till $P^H$=8.4,4'-bis [6-hydroxy benzoxazol-2-yl] -4''-methoxy triphenyl amine was synthesized by the treatment of 4,4'-diformyl-4''-methoxy triphenyl amine with4-amino resorcinol in presence of 50 wt% of silica supported sodium hydrogen sulphate in the solvent medium of THF refluxed for 16h. Polyester was prepared from polycondensation of 4,4'-bis [6-hydroxy benzoxazol-2-yl] -4''-methoxy triphenyl amine with terephthaloyl dichloride in presence of triethyl amine in the solvent medium of DMF first at $0^0$c then stirred for 6h at room temperature.*

***Keywords:****4,4'-diformyl-4''-methoxy triphenyl amine, 4,4'-bis[6-hydroxy benzoxazol-2-yl] -4''-methoxytriphenyl amine, polycondensation.*

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## I. Introduction

Carbazole derivatives are well- known to exhibit good electro and photoactive properties due to their high hole transporting mobility, strong absorption in the ultra violet spectral region and blue-light emission. Since the discovery of photoconductivity in poly( 9-vinyl carbazole) , carbazolecontaining derivatives became the subject of numerous investigations for applications in electro photography .The second wave of interest in carbazole-based CTMs is connected mostly with the discovery of organic light emitting diodes and photorefractive materials, carbazole-containing transporting materials are studied as the components of photo-voltaic devices and field effect transistors. Commercial availability and relative cheapness of the starting materials, simple synthesis, number of sites available for easy functionalization, good charge drift mobility and solubility in common organic solvents make these precursors attractive building blocks for the construction of more complex materials for optoelectronic applications.

Photorefractive polymers have attracted considerable attention owing to their potential applications including high-density optical data storage, optical image processing, phase conjugation, lasing, dynamic holography, optical computing and pattern recognition. The necessary characteristics for a materials to be regarded as potentially photorefractive are photoconductivity. Polymer can be made by either incorporating these properties directly into polymer (fully functionalized polymer) or doping guest molecules into the polymer (guest-host polymer composite) to produce these properties. Most of the photo refractive polymers reported to date are based on guest-host polymer composite, which normally consist of four components (Photoconducting polymer host, NLO chromophore, plasticizer, and photosensitizer). We have synthesized and reported various photoconductingpolymer based on heteroaromaticdoner moiety like carbazole and indole.

Another family of materials with strong election donating nature are poly (triaryl amine)s. They stand out due to their excellent hole transporting mobilities and good electrochemical stability. The Corresponding monomer triphenylamine (TPA) is used in commercial xerographic applications because of its excellent physical, photochemical and electrochemical properties of this hole conductor. Within the functional TPA moiety, the nitrogen centre can be easily oxidized resulting in effective transport of positive charge carriers via a radical cation species. The unsubstituted TPA can undergo dimerization to tetra phenyl benzidine (also triphenyldiamine, TPD). Low molecular weight TPDS showed high hole transport mobility. The TPA and TPD units can be incorporated either in the main chain or in the side chain of apolymer with a non-conducting backbone e,g. polystyrene. These polymeric analogues are used in HTMS, OLEDs, OPVs. In order to realize the solubility of TPA main chain polymers either methyl, alkyl, alkoxy chains have to be attached.

## II. Experimental

**Synthesis of 4,4'-diformyl-4"-methoxy Triphenylamine:**

DMF (36.8 ml, 0.48 mol) was cooled in an ice-bath to $0^0$c, and $POCl_3$ (48ml, 0.52 mol) was added dropwise with stirring not allowing temperature above 10°c. Vilsmeir-Haack reagent was solid at room temperature, so it was warmed to $30^0$-40°c and compound mixture of 4-methoxy triphenylamine was added in portion with stirring. The mixture was heated for 7h at 95° -$100^0$c under argon atmosphere. After cooling, it was poured into crushed ice and neutralized till pH-8 with 40% solution of sodium hydroxide keeping temperature below $20^0$c by external cooling and adding crushed ice. At the end of neutralization bulk precipitate formed, Water (500 ml) was added in order to dissolve inorganic salts, and precipitate was separated by filtration and thoroughly washed with water. The crude product dried on air.

**Synthesis of 4.4'-bis [6-hydroxy benzoxazol-2-yl]-4"- methoxytriphenylamine:**

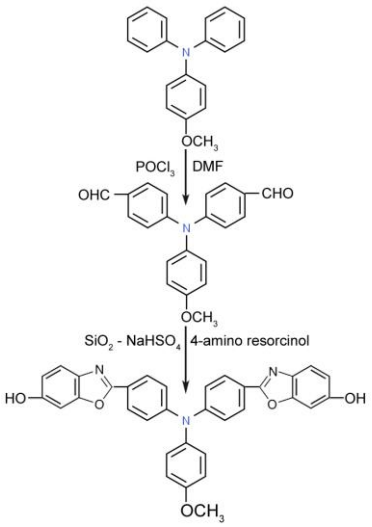
A mixture of 4-amino resorcinol (2 mmol), 4,4'-diformyl-4"methoxytriphenyl amine (1mmol) and silica- supported sodium hydrogen sulphate (50wt%) in THF was placed in a round bottom flask and stirred at reflux for 16h. After completion of the reaction, the reaction mixture was cooled and diluted with ethyl acetate and the catalyst was removed by filtration. The filtrate was washed with brine solution and dried over sodium sulphate and evaporated under vacuum. The obtained crude product was purified by column chromatography.

**Synthesis of polyester:**

A typical synthesis procedure for the preparation of polyester was conducted in three-necked round-bottom flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer bar. The flask was charged with 4.4'-bis [6-hydroxy benzoxazol- 2-yl] -4"-methoxy triphenylamine (1.034g ,2 mmol) in 20 ml of DMF and 0.8 ml of triethyl amine. A solution of terephthaloyldichloride (0.406g, 2 mmol) in 10 ml DMF was added dropwise at $0^0$c. The reaction was stirred for 6h at room temperature. The solution was then poured into water, and the precipitate was filtered and washed several times with the solution of sodium bicarbonate. The solid product was then dried in a Vacuum oven at 60°c.

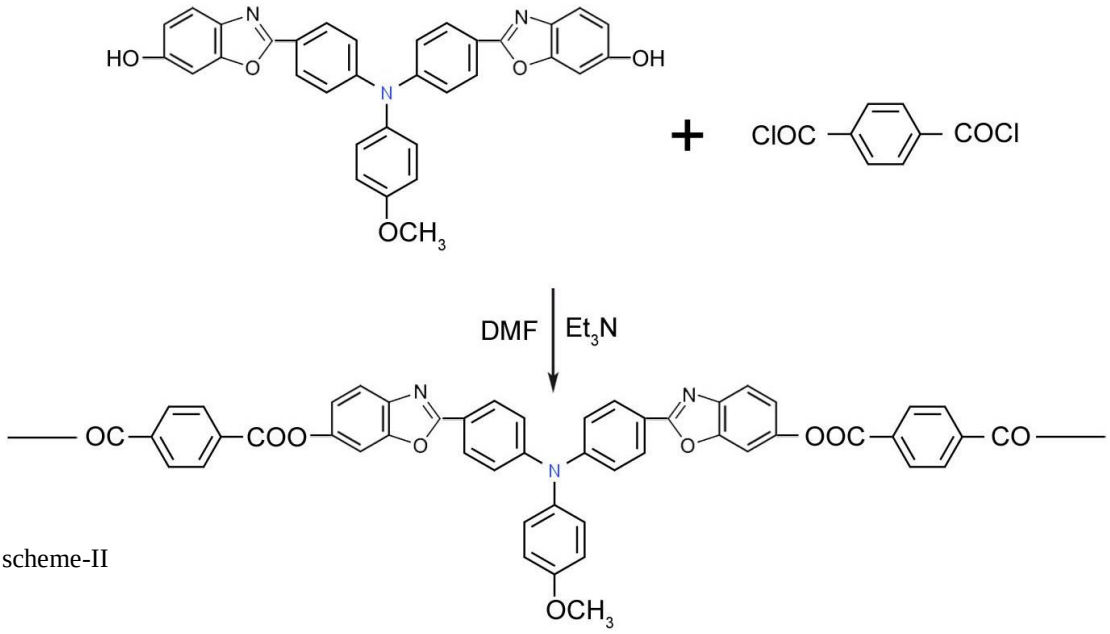
## III. Result and discussion

4,4'-diformyl-4"-methoxy triphenylamine was synthesized by the treatment of 4-methoxy triphenyl amine with Vilsmeir- Haack reagent and the mixture was heated for 7h at $95^0$-$100^0$c under argon atmosphere. After cooling, it was poured into crushed ice and neutralized till $p^H$=8 with 40% solution of sodium hydroxide keeping temperature below $20^0$c by adding crushed ice. At the end of neutralization bulk precipitate formed. Water was added in order to dissolve inorganic salts, and precipitate was separated by filtration. 4,4'-bis[6-hydroxy benzoxazol-2-yl]-4"-methoxy triphenyl amine was synthesized by adding a mixture of 4,4'-diformyl-4"-methoxytriphenyl amine and 4-amino resorcinol in presence of 50 wt% of silica-supported sodium hydrogen sulphate in the solvent medium of THF under reflux for 16h. After that, the reaction mixture was cooled and diluted with ethyl acetate and the catalyst was removed by filtration. The filtrate was washed with brine solution and dried over sodium sulphate and evaporated under vacuum. The obtained crude product was purified by column chromatography. The synthetic route of monomer was represented in scheme-I.




**scheme-I**

A typical synthesis procedure for the preparation of polyester was conducted. The flask was charged with 4,4'-bis [6-hydroxy benzoxazol- 2-yl]-4"-methoxytriphenyl amine in DMF and triethyl amine. A solution of terephthaloyl dichloride in DMF was added dropwiseat $0^0$c. The reaction was stirred for 6h at room temperature. The solution was then poured into water, and the precipitate was filtered and washed several times with the solution of sodium bicarbonate. The solid product was then dried. The synthetic routeof polyester was represented in scheme-II.




scheme-II

## IV. Conclusinon

Polyester based on triphenylamine with well-defined structure and characteristics was successfully synthesized. The monomer and polymer were characterized by IR, UV and NMR spectra. The polymer have good optical, thermal and electro-chemical properties. The synthesized polymer leading to a conductive film with electrochromic property and stable colour changes with coloration efficiency and high contrast of optical transmittance.

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