

# Synthesis of Photoconducting Polymer of Triarylamine Moiety.

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## Abstract:

4,4'-dimethyl-4''-nitro triphenyl amine was synthesized by treating 4,4'-dimethyl diphenyl amine with 1-fluoro-4-nitro benzene in presence of sodium hydride in the solvent medium of DMF stirring for 24h. 4,4'-dimethyl-4''-aminotriphenyl amine was prepared by reducing 4,4'-dimethyl-4''-nitro triphenyl amine with tin and acetic acid under reflux for 10h. Vinyl monomer was synthesized by treating 4,4'-dimethyl-4''-amino triphenylamine with methacryloyl chloride in presence of pyridine in the solvent medium of THF at 0°C for 3h and then at room temperature for 50h. Polymerization was carried out by treating the vinyl monomer with styrene in the solvent medium of DMF at 110°C for 80h.

**Keywords:** 4,4'-dimethyl-4''-nitro triphenyl amine, 4,4'-dimethyl-4''-amino triphenyl amine, vinyl monomer, polymerization.

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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), carbazole-containing derivatives became the subject of numerous investigations for applications in electrophotography. 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.

Photo refractive 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 photorefractive 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 photoconducting polymer based on heteroaromaticdoner moiety like carbazole and indole.

Another family of materials with strong electron donating nature are poly (triarylamine) s. They stand out due to their excellent hole transporting mobilities and good electro chemical stability. The corresponding monomer triphenyl amine (TPA) is used in commercial xerographic applications because of its excellent physical, photochemical and electrochemical properties of this hole conductor. With in 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 or TPD units can be incorporated either in the main chain or in the side chain of a polymer with a non-conducting backbone e.g. Poly styrene. These polymeric analogues are used in HTMs, OLEDs, OPVs. In order to realize the solubility of TPA main chain polymers either methyl groups, alkyl, alkoxy chains have to be attached.

## **II. Experimental:**

### **2.1. Synthesis of 4,4'-dimethyl-4''-nitro triphenyl amine**

To a cooled in ice-bath suspension of sodium hydride (60% dispersion in oil)(1.82g 0.042 mol) in 10ml DMF 4,4'-dimethyl diphenyl amine(3.94g,0.02mol)in 5ml of DMF was added dropwise under argon. The mixture was allowed to warm to room temperature and stirring continued for 1h. Then 1-fluoro-4-nitro benzene (3.0g,0.021mol) was added and the mixture was stirred for 24h. Then reaction mixture was poured onto ice, the precipitate was filtered off, washed with water and dried compound was recrystallized from MTBE.

### **2.2 Synthesis of 4,4'-dimethyl-4''-amino triphenyl amine:**

To a solution of 4,4'-dimethyl-4''-nitro triphenyl amine (3.18g,0.01mol)in 90ml acetic acid, tin (3g) was added, and the mixture was heated to reflux for 10h. Water (120ml) and dichloromethane (200ml) were added and the mixture was shaken with 40% sodium hydroxide solution till the aqueous layer became alkaline. DCM layer was separated, washed with water and dried over magnesium sulphate. The solvent was partially removed (till the volume of solution 30ml), and 50ml of hexane was added. Precipitate was filtered and dried.

### **2.3 Synthesis of vinyl monomer:**

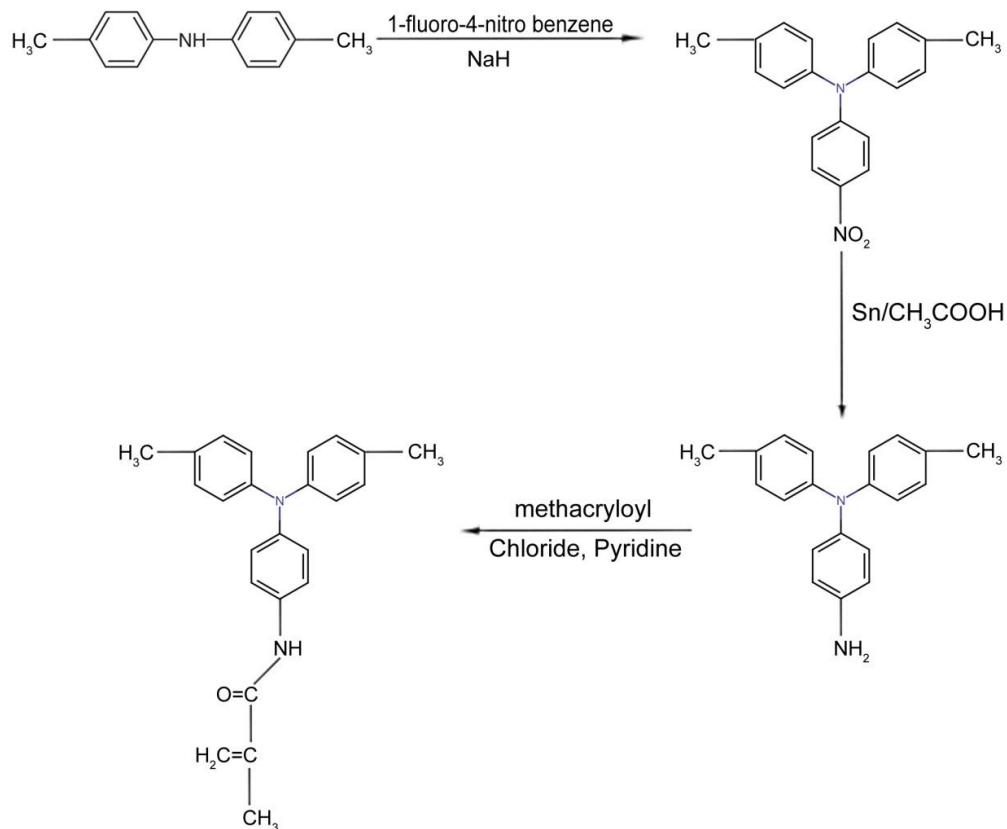
4,4'-dimethyl-4''-amino triphenyl amine (2.926g,10.16m mol) was dissolved in 25ml of dry THF under nitrogen. To the solution, pyridine (0.1g,1.26mmol) and methacryloyl chloride (1ml, 10.26 mmol) were added dropwise simultaneously. The reaction was carried out at 0<sup>o</sup>with magnetic stirring for 3h. and then at room temperature for 50h. The resulting mixture was washed with hydrochloric acid (0.1M), sodium carbonate(5%)and finally with distilled water . The excess solvent was evaporated under reduced pressure. The organic layer was dried over anhydroussodiumsulphate. The reaction product obtained was purified by column chromatography using methylene dichloride.

### **2.4 Polymerization:**

Vinyl monomer (1.342g,3.77mmol), styrene (0.39g,3.75mmol) and AIBN(2g,12.19mmol) were dissolved dry DMF(40ml). The reaction was carried out at110<sup>o</sup>c for 80h, under nitrogen. The polymer was precipitated out in methanol, filtered and dried under vacuum.

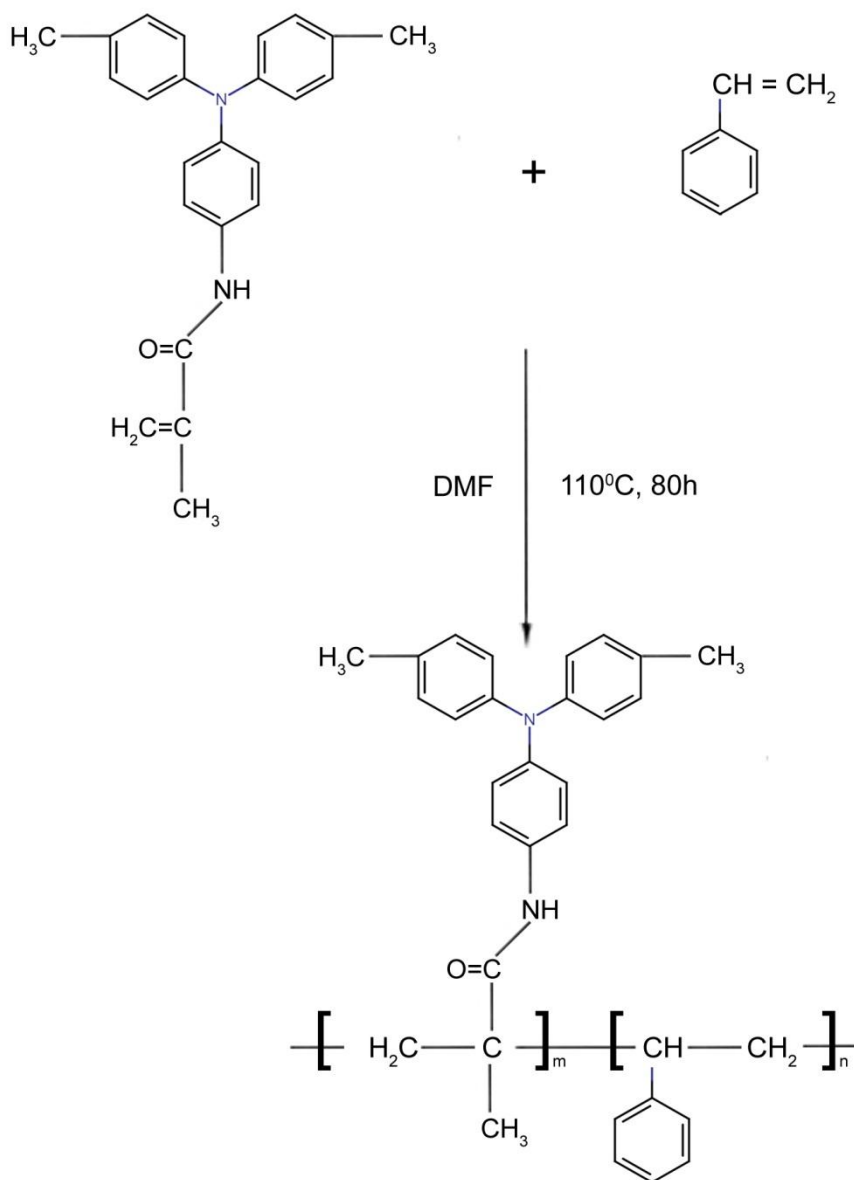
## **III. Result and discussion :**

IR, UV and NMR spectra revealed the successful preparation of the polymer. The monomer was synthesized as follows: Firstly, 4,4'-dimethyl-4''-nitro triphenyl amine was synthesized by treating 4,4'-dimethyldiphenyl amine with 1-fluoro-4-nitro benzene in presence of sodium hydride in the solvent medium of DMF stirring for 24h.The reaction mixture was then poured onto ice, the precipitate was filtered off, washed with water and dried compound was recrystallized from MTBE. Secondly,4,4'-dimethyl-4''-amino triphenyl amine was prepared by reducing 4,4'-dimethyl-4''-nitro triphenyl amine with tin and acetic acid heated to reflux for 10h. Water and dichloromethane were added and the mixture was shaken with 40% of sodium hydroxide solution till the aqueous layer became alkaline. DCM layer was separated, washed with water and dried over magnesium sulphate. The solvent was partially removed and hexane was added. Precipitate was filtered and dried. Lastly, the vinyl monomer was synthesized by trating 4,4'-dimethyl-4''-aminotriphenyl amine with methacryloyl chloride in presence of pyridine in the solvent medium of THF at 0<sup>o</sup>c for 3h and then at room temperature for 50h. The resulting mixture was washed with hydrochloricacid(0.1M), sodium carbonate(5%) and finally with distilled water. The excess solvent was evaporated under reduced pressure. The organic layer was dried over anhydrous sodium sulphate. The reaction product obtained was purified by column chromatography using methylene dichloride . The synthetic route of monomer was represented in scheme-I.



Scheme-I

The polymer was synthesized as follows: Vinyl monomer, styrene and AIBN were dissolved in dry DMF. The reaction was carried out at 110<sup>0</sup>c for 80h, under nitrogen. The polymer was precipitated out in methanol, filtered and dried under vacuum. The synthetic route of polymer was represented in scheme-II.



Scheme-II

#### IV. Conclusion:

Polymers based on triphenylamine with well-defined structure and characteristics were successfully synthesized. The monomer and the polymer were characterized by IR, UV and NMR spectra. The polymer have good optical 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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