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Synthesis of Photorefractive Polymer of Carbazole Ring.

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Abstract:*4-nitro benzene diazoniumsulphatewas prepared by the diazotization reaction of 4-nitro aniline with sodium nitrite and concentrated sulphuric acid at 0^0c.Thenthe diazonium salt was coupled with 3-amino-9-ethyl carbazole dissolved in acetic acid at 0^0c.The obtained azodye namely 4-azo-(4˜nitro-1'-phenyl) 3-amino-9-ethyl carbazole was purified and characterized by IR,UV and NMR spectroscopy. 2-methacryloyl-3-(4-azo-4'-nitro-1'-phenyl) amino-9-ethyl carbazole was synthesized by the reaction of 4-azo-(4'-nitro-1'-phenyl)-3- amino-9-ethyl carbazole with methacryloyl chloride in the solvent medium of THF under stirring for 50h.Lastly,the polymer was synthesized by the radical polymerization of 2-metharyloyl-3(4-azo-4'-nitro-1'-phenyl)-3-amino-9-ethyl carbazole with methylmethacrylate by using AIBN as radical initiator under stirring at 110^0c in the solvent medium of DMF for 80h. All the monomers and polymer was characterized by IR,UV and NMR spectroscopy.*

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I. Introduction:

In the last years the aromatic azo polymers have been widelyused due to their application in different optical fields. After the photorefractive effect of organic compounds was discovered, several polymers which containing carbazole have become attractive from the point of view of their photoconductivity.The photoconductive and electro-opticfunctionalites in the side chain of those polymers can be considered as potential materials for photorefractive applications. Therefore,the azo benzene photochemistry continue to produce unexpected phenomena because the azobenzene group is incorporated into the polymer, and in this respect thephotoisomerization phenomenon can have unexpected possible consequences.It is well known that in the polymer materials with carbazole can appear the possibility of building several variable spacers between the azo group and the main chain which can increase the order degrees as well as the azo group becomes much decoupled from the main chain motion.

The photorefractive polymers with carbazole ring and azo moieties in the side chain have all the necessary elements for photorefractivityproperties(electro-optic chromophore and charge trappers).The azo containing carbazole groups provided both the photoconductivity and non-linear optical(NLO) activity, and the aliphatic chain attached on the nitrogen atomof the carbazole ring acts as spacer.Hence, the photorefractive polymer exhibit equally photoconductivity and optical non-linerity.They have concerned substantial interest due to their potential applications in optical computing,optical correlation, 3D data or image storage.

The ability of non –liner optical materials to transmit process and store information forms the basis of emerging optoelectronic and photonic technologies. Organic chromophore containing polymers, in which the refractive indexcan be controlled by light or anelectric field,are expected to play a important role.NLO is an important component of photorefractive system.Organic moieties with delocalized pi- electrons distribution have been extensively investigatedfor their potential applications in optical signal processingoptical switching and optical power limiting,each which require large and fastnonlinearities for the purpose.The NLO response of many organic materials is extremelyrapid, because the effects occur primarily through electronic polarization, and hence there has been afocus of attention on NLO properties of the pi conjugated system.

Dye chromophores are a class of organic moleculeswith multiple pi-conjugated bonds,which can exhibits large optical non-linerities and fast response time,as a result the case of polarization of their extended mobile pi-electroncloud over long distances.Strong absorption of dyes in the visible region makes them particularlysuited for non-liner optical investigations.It has also beenshownthat embedding dye chromophores in suitable host matrices enhance the life time and stability of the dyes entrapped within it.

The aim of this research was to synthesize a fully functionalized NLO polymer,So we have synthesized the monomer 2-methacryloyl-3-(4-azo-4'-nitro 1'–phenyl) amino-9-ethyl carbazole and its polymerization with methylmethacrylate.In this monomer,achromophoric dye molecule has been attached chemically with the charge transporting media (Polymer chain).

II. Experimental:

2.1. **Synthesis of 4-azo-(4'-nitro-1'-phenyl)-3-amino-9-ethyl carbazole:**

4-nitro aniline (2.76g,0.02mol) was mixed with water.The amine was diazotized in 10ml of concentrated sulphuric acid by adding sodium nitrite (2.76g,0.04mol) solution in 20ml of water dropwise at 0^0-5^0c,and stirred for 20mins at this temperature.Excess nitrous acid was destroyed by the addition of urea(approximately,0.2g). The diazo liquor obtained was added slowly to a vigorously stirred solution of 3-amino-9-ethyl carbazole(4.9g 0.025mol) in glacial acetic acid(10ml).The reaction mixture was thenstirred for 2h and the resulting product was filtered,washed with water,dried and recrystallised from ethanol to give the titled compound. Theazo dye was characterized by IR,UV,and NMR spectroscopy.

2.2 Synthesis of 2-methacryloyl-3-(4-azo-4'-nitro-1'-phenyl) amino-9-ethyl carbazole:

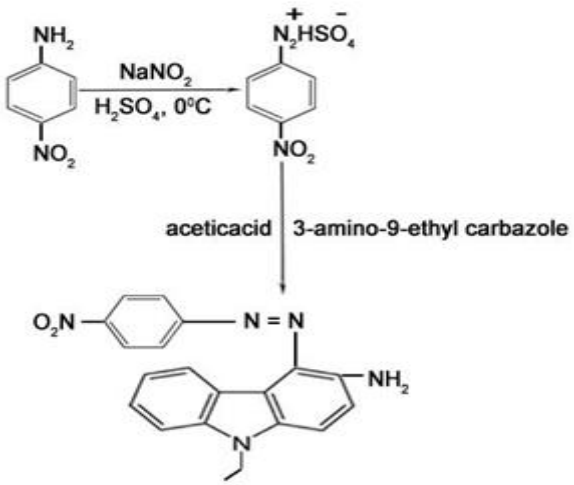
4-azo-(4'-nitro-1'-phenyl)-3-amino-9-ethyl carbazole(3.45g,0.01mol)was dissolved in 30ml of dry THF under nitrogen.Tothe solution pyridine (1.0g) and methacryloyl chloride(1.05g,0.01mol)were added dropwisesimultenusly.The reaction was carried out at 0^0c with magnetic stirring for 3h then at room temperature for 50h.The resulting mixture was washed with HCl(0.1M),Na_2CO_3 (5%) and finally with distilled water.The excess solvent was evaporated under reduced pressure.The organic layer was dried over anhydrous Na_2SO_4.The reaction product obtained was purified by column chromatography usingdichloromethane.

2.3. **Polymerization:**

2-methacryloyl-3-(4-azo-4'–nitro-1'-phenyl)amino-9-ethyl carbazole(1.239g,3mmol),methylmethacrylate(0.3g,3mmol)and azobisisobutyronitrile(2g,12.19m mol) were dissolved in dry DMF(40ml).The reaction was carried out at 110^0c for 80h,under nitrogen.The resulting solid was dissolved in DMF and reprecipitated from methanol.Polymer was collected by filtration,dried under vacuum.The polymer was characterized by IR,UV and NMR spectroscopy.

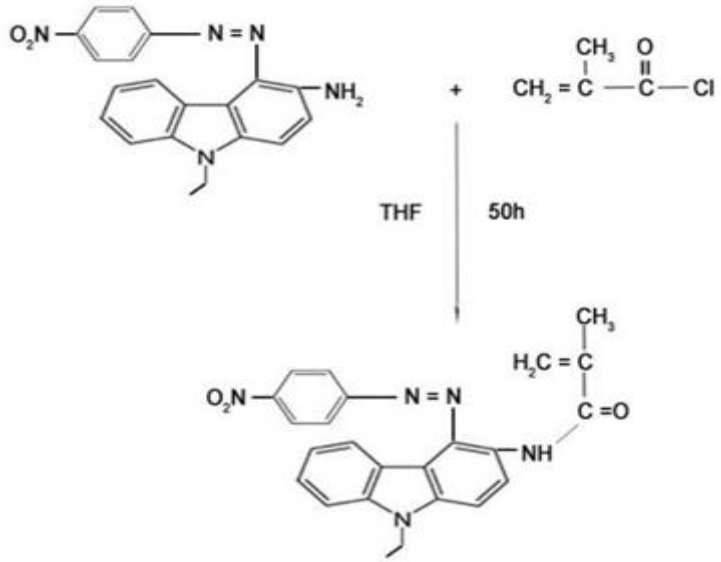
III. Result and Discussion:

The study of IR,UV and NMR spectra reveled the successful prepraration of the polymer.The monomer namely 4-azo-(4'-nitro-1'-phenyl)amino-9-ethyl carbazole was prepared as follows. At first the azo dye namely 4-azo-(4'-nitro-1'-phynyl)-3-amino-9-ethyl carbazole was prepared.The azo dye was prepared by following way.At first 4-nitroaniline was diazotized by using sodium nitrite and concentrated sulphuric acid at 0^0c.Then diazonium salt that is 4-nitrobenzene diazoniumsulphate was coupled with 3-amino-9-ethyl carbazole in acetic acid.The dye was recrystallized from ethanol and characterized by IR,UV and NMR spectra.The synthetic route for the prepration of azo dye was depicted in scheme-I



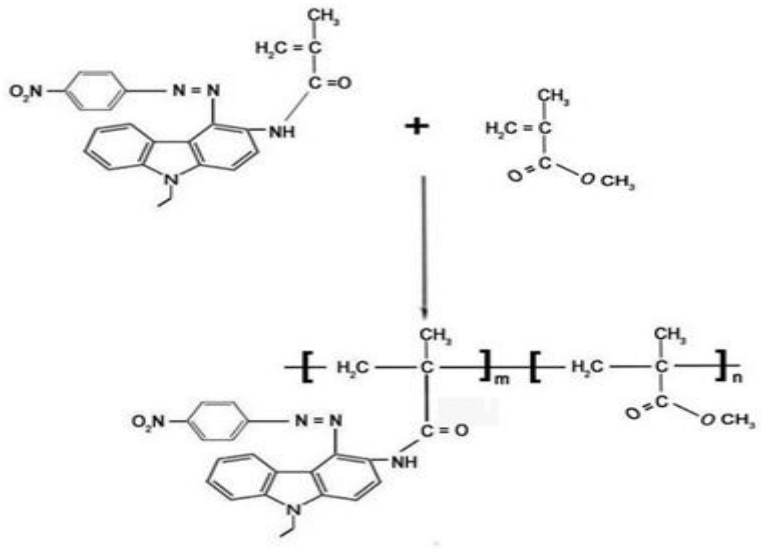
scheme-I

Then the azo dye namely,4-azo-(4'-nitro-1''-phenyl)-3-amino-9ethyl carbazole was treated with methacryloyl chloride in the solvent medium of THF and magnetically stirred for 50h.The mixture namely,2-methacryloly-3-(4-azo-4'-nitro-1'-phenyl) amino-9-ethyl carbazole synthesized was washed with HCl 1(M),5% Na_2CO_3 andlastly with distilled water.The excess solvent was removed under reduced pressure.The organic layer was dried over sodium sulphate and the monomer was purified by column chromatography using dichloromethane.The monomer was characterized byIR,UV, and NMR spectroscopy.The synthetic route of the monomer was depicted in scheme-II.



Scheme-II

Lastly the polymerization of the monomer namely,2-methacryloyl-3-(4-azo-4'-nitro-1'-phenyl)amino-9-ethyl carbazole was treated with methylmethacrylate(MMA) in1:1 ratio in the solventmedium of DMF at 110^0c for 80h by using a radical initiator AIBN.The polymer was precipitated out in methanol.The unreacted monomer was removed by reprecipitation method.The polymer was characterized by IR,UV and NMR spectroscopy.The synthetic route of the polymer was depicted in scheme-III.The polymer has good thermal,mechanical and photochemical properties due to carbazole backbone.It is a fully functionlized NLO polymer.The polymer has good photorefractive property.The azo dye based with carbazole ring has good stability and good chromophoricazogroup.The polymer has pi-conjucation and push-pull structure.Carbazole itself aheteroaromatic nucleus and has good donating character.Itfroms C.T complex with TNF (0.2 wt%).The polymer has also good photoconducting and photorefractive property.The photorefractive composite can be prepared by doping the polymer with 0.2 wt% of TNF.



Scheme-III

IV. Conclusion:

In this study was synthesized a new carbazolederivative 2-methacryloyl-3-(4-azo-4'-nitro-1'-phenyl)amino 9-ethyl carbazole and its co-polymer with methylmethacrylate which can be used in obtaining of new photorefractive materiacls.This polymer has photoconductive and photorefractive functionality (i.e.3-amino-9-ethyl carbazole)as well as photochromic group such as azo which can be used innon-liner optical(NLO) field.All the monomers and polymer were characterized by FT-IR,UV and NMR

spectroscopy.Due to carbazole backbone the polymer has good thermal,mechanical and photochemical stability.The electron donor moiety i.e. carbazole ring can easily form C.T Complex with TNF or crystal violet.The polymer can also be used NLO field.It is a fully functionalized polymer and can be used as a photofractive composite by doping the polymer with 0.2 wt% of TNF.

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