

N-ethyl-3-nitro indole reduction using 0.5 (N) sodium hydroxide and sodium dithionite solutions, followed by the preparation of N-ethyl-3-amino indole

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Abstract

By reacting 3-nitro indole with ethyl iodide in the presence of sodium hydride, N-ethyl-3-nitro indole was created. By reducing N-ethyl-3-nitro indole with sodium dithionite and 0.5 (N) sodium hydroxide solutions in the solvent medium of ethanol at 500°C, N-ethyl-3-amino indole was created. The reaction of N-ethyl-3-amino indole with 4-fluoronitro benzene in the presence of cesium fluoride in the solvent medium of DMSO under reflux at 1200C for 20 hours produced N-ethyl-3-(4,4'-dinitro diphenyl amino) indole. N-ethyl-3-(4,4'-dinitrodiphenyl amino) indole was reduced with palladium-carbon under reflux at 1300°C for 12 hours to produce N-ethyl-3-(4,4'-diamino diphenyl amino) indole. N-ethyl-3-(4,4'-diamino diphenyl amino) indole and 6FDA were combined in a 1:1 molar ratio and heated for 24 hours at 400°C to create polyamic acid which was subsequently treated with acetic anhydride and pyridine at 1000c for 24h in the solvent medium of DMF.

Keywords: N-ethyl-3-nitro indole, N-ethyl-3-amino indole, N-ethyl-3-(4,4'-dinitro diphenyl amino) indole, N-ethyl-3-(4,4'-diamino diphenyl amino) indole, 6FDA, polyimide.

Introduction

Due to their high hole-transporting mobility, robust UV absorption, and blue-light emission, carbazole derivatives are well recognized to display good electro and photo active characteristics. Since poly(N-vinyl carbazole) was shown to be photoconductive, derivatives containing carbazole have been the focus of various studies for use in electro photography. The development of organic light-emitting diodes and photorefractive materials is primarily responsible for the second wave of interest in carbazole-based CTMS. In addition to electro photographic photoreceptors, light-emitting diodes, and photo-refractive materials, transporting materials containing carbazoles are being researched for use as field-effect transistors and photo-voltaic device components. Commercial availability, relative affordability of the raw ingredients, ease of synthesis, accessibility of a large number of fictionalization sites, strong charge drift mobility, and solubility in common organic solvents are all positive attributes building blocks for the construction of more complex materials for optoelectronic applications.

Photorefractive polymers have attracted considerable attention owing to potential applications including high-density optical data storage, optical image processing, phase conjugation, lasing, dynamic holography, and optical computing and pattern recognition. The necessary characteristics for a material to be regarded as potentially photorefractive are photoconductivity. Polymer can be made 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 photorefractive polymers reported to date are based on guest-host polymer composite, which normally consist of four components (photo conducting polymer host, NLO chromophore, plasticizer and photo sensitizer). We have synthesized and reported various photo conducting polymers based on hetero aromatic doner moiety like carbazole and indole.

Indole is another heteroaromatic molecule which is easily available from coal-tar and has doner moiety like carbazole . Indole, the heteroaromatic structure like carbozole was designed to work as photoconducting moiety as well as electron doner. Indole was adopted over carbazole for this purpose, because indole provides better poling efficiency owing to the more compact size compared with carbozole. Indole has good thermal and mechanical properties. It easily formed C.T. complex with TNF and crystal violet and forming hole that will migrate the polymer chain. Diphenylamine like triphenylamine has also electron donating

ability.

In this article, we have synthesized polyimide of indole diphenylamine moiety. It is a guest-host system polymer where the host polymer matrix can be doped with guest molecule like TNF. A good photorefractive system can be developed by conjugation the polymer with a second order NLO chromophore, plasticizer and photosensitizer.

Experimental

Synthesis of N-ethyl-3-nitro indole:

To a three necked round-bottom flask equipped with nitrogen purge and reflux condenser was added 3.24g(0.02mol) of 3-nitro indole along with 75 ml of anhydrous DMF. To the stirred solution was added 0.72g (0.03 mol) of sodium hydride. Immediately a precipitate formed with evolution of hydrogen gas. This was stirred for further 15 minutes to dissolve the indole anion Then 4.68g(0.03 mol) of iodoethane was added in one portion. After 10h, 200ml of water was added to give a precipitate. The product was recrystallized from chloroform.

Synthesis of N-ethyl-3-amino indole:

A solution of 3.0 g of sodium dithionite in 15 ml 0.5(N) sodium hydroxide solution was added to a solution of 0.50g of N-ethyl-3-nitro indole in 35 ml of ethanol and 10ml (N) sodium hydroxide solution at 50^oc . The mixture was then filtered hot, and the filtrate was evaporated to dryness. The residue was dissolved in 5% hydrochloric acid solution, filtered and made basic with cold 30% sodium hydroxide. The basic solution was extracted with ether and then evaporated to dryness.

Synthesis of N-ethyl-3-(4,4'-dinitro diphenyl amino) indole:

In a round-bottom flask 250ml with a magnetic bar, 4.8g (0.03mol) of N-ethyl-3-amino indole, 8.46g(0.06mol) of 4-fluoro nitrobenzene and 9.20g (0.06mol) of cesium fluoride in 80ml of DMSO were refluxed to 120^oc for 20h. The final solution was stream into 200ml solution of methanol/water (1:1) to get precipitate . After filtration which was washed with methanol and water several times and recrystallized from DMF/methanol to give crystals.

Synthesis of N-ethyl-3-(4,4'-diamino diphenyl amino) indole:

In a 250ml stirred round bottom flask, 10.05g(0.025mol) dinitro intermediate, 0.20g 10wt% Pd/C, 10ml of hydrazine hydrate in 120ml of ethanol are refluxed at 130^oc for 15h. Then the Pd/C powder was separated by filtration of the hot crude. The filtrate was cooled and poured into water. The precipitate was filtered and dried.

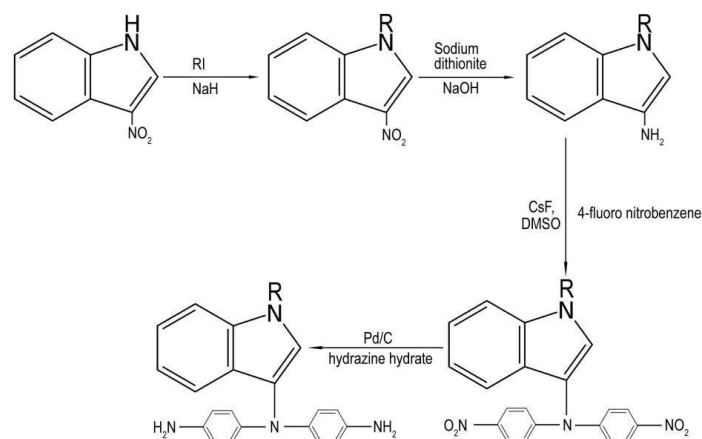
2.5 synthesis of polyimide:

Monomer, N-ethyl-3—(4,4'-diamino diphenylamino) indole (1mmol) and 6FDA (1mmol) were dissolved in DMF (20ml). The solution was stirred at 40^oc under nitrogen for 24h yielding a viscous polyamic acid solution. To this solution acetic anhydride (12ml) and pyridine (6ml) were added. The stirring was continued at 100^oc for 24h. Then the reaction mixture was poured into methanol, the polymer was filtered and purified by washing with methanol.

Results and Discussion

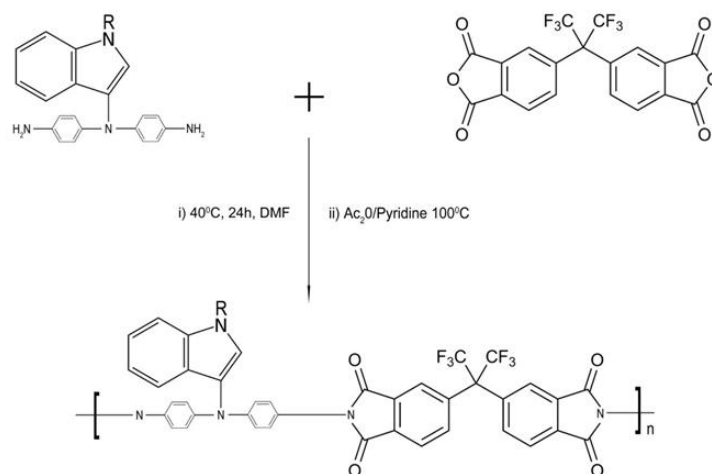
IR, UV and NMR spectra revealed the successful preparation of the polymer. N-ethyl-3-nitro indole was prepared by the reaction of 3-nitro indole with ethyl iodide in presence of sodium hydride in the solvent medium of DMF. After subsequent reaction, water was added to get precipitate which was recrystallized from chloroform. N-ethyl-3-amino indole was synthesized by the treatment of N-ethyl-3-nitro indole with sodium dithionite in presence of (N) sodium hydroxide in ethanolic medium at 50^oc. The mixture was filtered hot and the filtrate was evaporated to dryness. The residue was dissolved in 5% hydrochloric acid, filtered and made basic with cold 30% sodium hydroxide. The basic solution was extracted with ether and evaporated to dryness. N-ethyl-3(4,4'-dinitro diphenyl amino) indole was synthesized by the treatment of N-

ethyl-3-amino indole with 4-fluoro nitro benzene in presence of cesium fluoride in DMSO solvent refluxed at 120°C 20h. The final mixture was stream into (1:1) methanol/water to get the precipitate and recrystallized from DMF/methanol to get crystals. N-ethyl-3-(4,4'-di amino diphenyl amino) indole was synthesized by the reduction of dinitro intermediate with 10 wt% Pd/C and hydrazine hydrate in the solvent medium of ethanol under reflux at 130°C for 15h. After filtration hot, the filtrated was cooled and poured into water. The monomer was filtrated and dried . The synthetic route for the preparation of monomer was represented in scheme-I.



Schem-I

Polymer was synthesized by the treatment of N-ethyl-3-(4,4'-diamino diphenyl amino) indole with 6FDA at(1:1) ratio in the solvent medium of DMF stirring at 40°C for 24h yielding a viscous polyamic acid solution. Then this solution was mixed with acetic anhydride and pyridine and stirring was continued at 100°C for 24h. The reaction mixture was poured into methanol to get the precipitate. Indole is electron doner heteroaromatic molecule. Diphenyl amine has also electron donating ability. Thus indole-diphenylamine is a good photoconducting candidate. It is a guest-host system polymer matrix. The polymer matrix can be doped with TNF and photoconducting properties can be measured. The synthetic route of the polymer was represented in scheme-II.



Schem-II

Conclusion

Our method of obtaining high Tg polyimide of the indole diphenyl amine moiety was successful. By using IR, UV, and NMR spectra, the monomer and polymer were examined. Polyimide based on indole demonstrated excellent thermal stability with a high Tg and good solubility. This polymer's intrinsic viscosity and appealing characteristics make it appropriate for a wide range of applications. Polyimides made from indoles often have outstanding thermal, mechanical, electrical, and chemical characteristics. As a result, it may be used to a variety of things, including composite materials, electronics, coatings, and adhesives.

References

1. Kippelen B, Tamura K, Peyghambarian N, Padias AB, Hall Jr. HK. Phys. Rev B 1993, 48 (15): 10710.
2. Yu L, Chan WK, Peng Z, Gharavi A. Acc. Chem. Res. 1996, 29:13.
3. Zhang Y, Wada T, Wang L, Aoyama T, Sasabe H. Chem. Commun. 1996, 2325
4. Barrett C, Chowdhury B, Natansohn A, Rochon P. Macromolecules 1998, 31, 4845
5. Wright D, Diaz- Garcia MA, Casperson JD, DeClue M, Moerner WE, Twieg RJ. Appl. Phys. Lett. 1998, 73(11), 1490.
6. Cox AM, Blackburn RD, West DP, King TA, Wada FA, Leigh DA. Appl. Phys. Lett. 1996, 68(20), 2801.
7. Zhang Y, Ghosal S, Casstevens MK, Burzynski R. J. Appl. Phys. 1996, 79 (12), 8920.
8. Silence SM, Scott JC, Stankus JJ, Moerner WE, Moylan CR, Bjorklund GC, Twieg RJ. J. Phys. Chem. 1995, 99, 4096.
9. Moon H, Hwang J, Kim N, Park SY. Macromolecules 2000, 33(14), S116.
10. Moon H, Kim N, Park SY. Nonlinear Optics 1999, 20, 347.
11. Meerholz K, Volodin BL, Sandalphon, Kippelen B, Peyghambarian N. Nature 1994, 371(6), 497.
12. Bolink HJ, Krasnikov VV, Malliaras GG, Hadziioannou G. J. Phys. Chem. 1996, 100, 16 356.
13. Zhang Y, Spencer CA, Ghosal S, Casstevens MK, Burzynski R, Appl. Phys. Lett. 1994, 64, 1908.
14. Walsh CA, Moerner WE. J. Opt. Soc. Am B 1992, 9, 1642
15. Centore R, Panunzi B, Roviello A, Sirigu A, Villano P. J. Polym. Sci. Part A Polym. Chem. 1996, 34, 3203.