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Synthesis & Characterization of Novel Aniline—Formaldehyde-- α - Napthol Terpolymers

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ABSTRACT

The present manuscript reported the synthesis of organic terpolymers of aniline, formaldehyde & α-naphthol. The reaction is catalyzed by strong acids, weak acids, organic acids and also by Lewis acids. The composition of terpolymers has been determined by elemental analysis and spectral studies such as UV, IR and NMR have been carried out to elucidate the structure of the terpolymers. The polymer exhibit high temperature resistance better thermal properties as evident from the TGA data. The polymer undergo degradation under inert atmosphere at increasing temperature provides good for nature. Spectroscopic data revels that long chain polymer hold together not only by C-C bond, but also the electrons are delocalized in conjugation showing coloured aniline- formaldehyde-α-naphthol terpolymers.

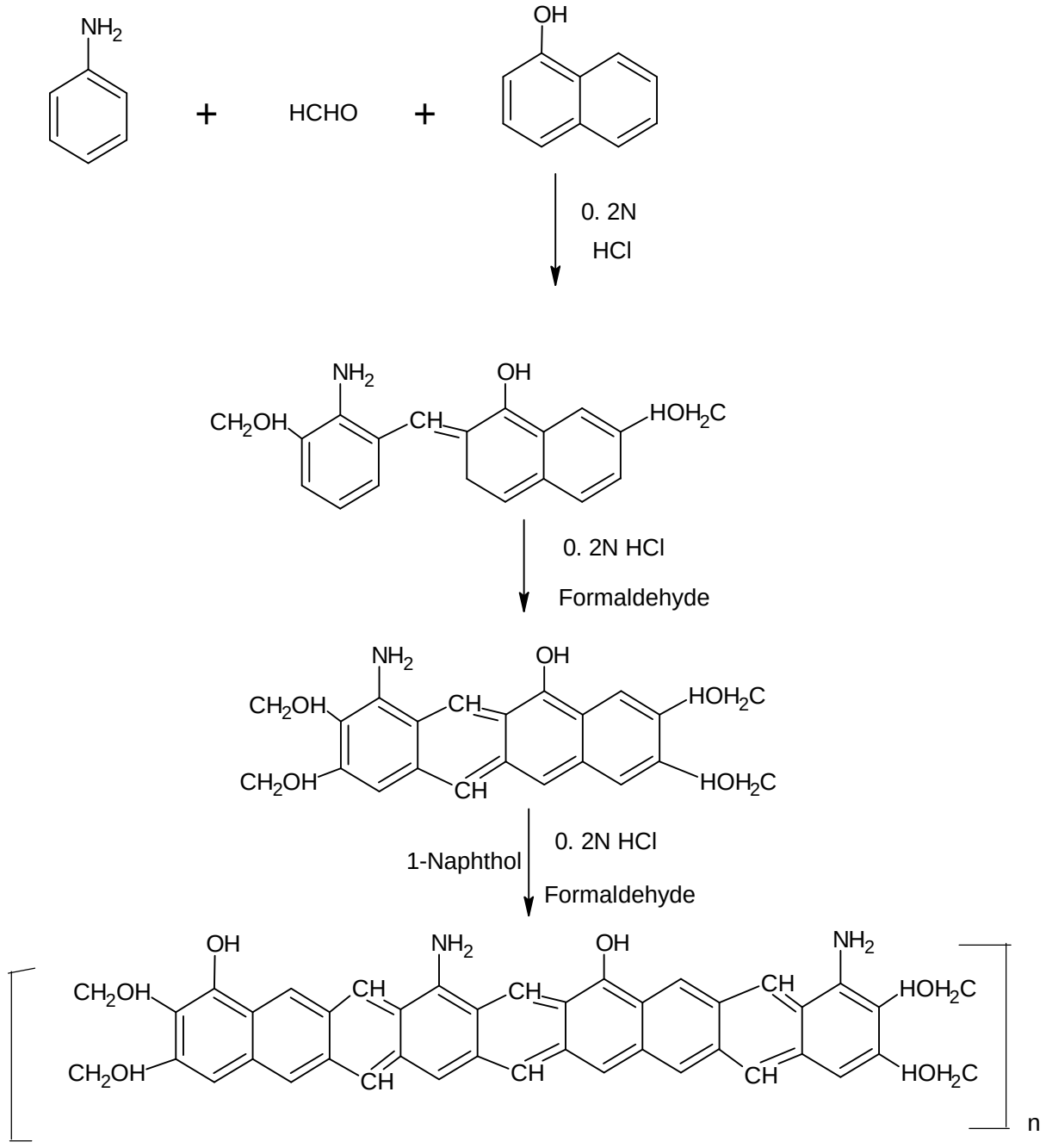
Keywords: Terpolymerization, aniline, formaldehyde, α-naphthol.

INTRODUCTION

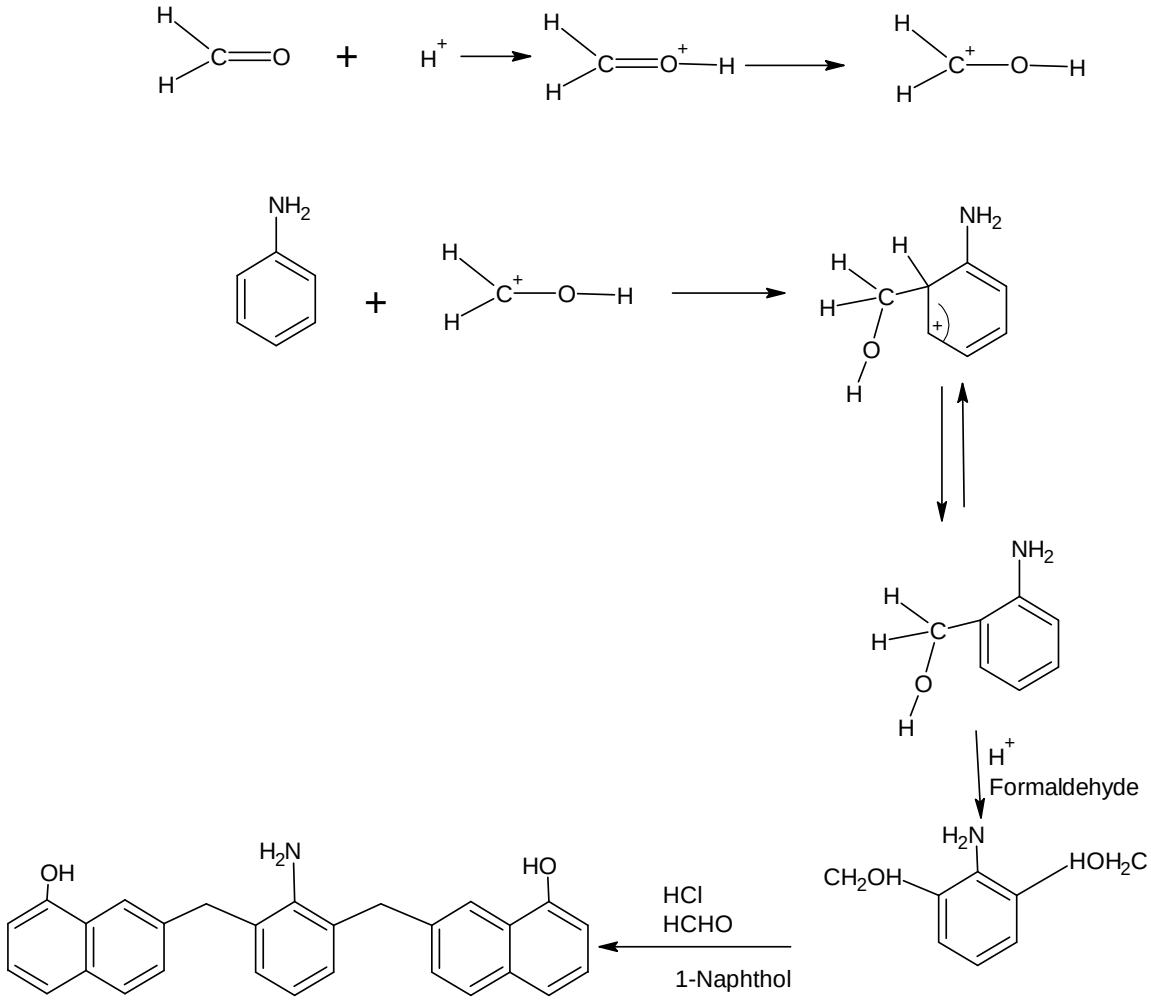
Polymer science[1-9]has emerged as active discipline of materials science. This field impinges on areas of commodity, engineering and speciality polymers thereby stimulating interest all over the globe in exploiting newer domains. One such branch that has emerged is polymermetal complexes comprising an organic polymer containing co-ordinating sites, complexed with metals. This is of relatively recent origin and an interdisciplinary approach taking into its fold areas viz; chemistry, metallurgy, environmental and material sciences Terpolymerization of 2-

ethoxyethyl methacrylate, styrene and malefic anhydride initiated by benzoyl peroxide was carried out in acetone as common solvent for three monomers. For the last two decades, an acceptor–donor–acceptor monomer system is an effective method for the synthesis of functional macromolecules with given composition, structure and properties Terpolymers are used in Stucco, Exterior Insulation, Finish Systems, Insulated Concrete Form coatings, Tile installation products, Decorative stamped and spray-applied concrete finishes Joint compounds and texture finishes The complex-radical terpolymerization of methacrylate, with vinyl aromatic i.e. styrene, gives an alternating copolymer. Terpolymer powders provide superior hydrolytic stability and water resistance due to the bulky and hydrophobic co monomers. The result is a UP range that is highly suitable for use in formulations containing Portland cement. Each product has been developed to provide end users specific benefits, which include excellent workability, no sticking to tools, and hydrophobic. In day to day life result interesting facilities with the formation of polymers. The most important of the synthetic polymers used on tonnage scales, are polyethylene, polypropylene polyvinyl chloride, nylons, polyesters, polyacrylonitriles, styrene-butadiene rubber, butyl rubber. The synthetic polymers are made from petrochemicals[10-13]. Some polymers can be derived an modification of natural polymers. The important properties in the synthetic polymers are low density, resistance to attack by chemicals. Thermal and especially electrical insulators, flexibility or softer and less brittle, good plasticity, Elasticity, ability to absorb shock, sound, vibrations some are transparent live gas, some can act as very good adhesives. Some plastics can be converted into strong fibers. They can be given attractive colours. They can be strengthened by reinforcement; Proteins, cellulose (wood), polyphosphates (bones), polysilicates (rocks), DNA, etc. are the natural polymers. Man stinted mullein of synthetic polymers in the twentieth century and the commercially the products are in are form polymers have gained today such importance that the modern life style cannot be imagined with out them. Most of the synthetic polymers are in the form of plastics and rubbers. Plastics are the substances of very high molecular weight. They are early molded with the aid of pressure heat and moulds. The rubbers are also such type of elasticity. The synthetic polymers find uses as the substitute or alternative materials for a) Metals b) wood c) cotton and wool d) gums e) glass f) conductors / insulators, g) ceramics. some special polymers have very high thermal stability, very high conductivity. However, the synthetic polymers are disadvantages as they are combustible softer, costly. How service temperature limitation, limited mechanical strength, not bio degradable early and pose problem of pollution. Polymerization is chemical process in which a large number of monomer molecules get joined to form the polymer molecules large number of ethylene molecule (monomer) get joined by chemical bonds to form polyethylene. This new heterocyclic compound was thiophene. Thiophene and its derivatives occur in petroleum, sometimes in concentrations up to 1-3%. The thiophenic content of oil and coal is removed via the hydrodesulphurization (HDS) process. In HDS, the liquid or gaseous feed is passed over a form of molybdenum disulfide catalyst under a pressure of H_2. Thiophenes undergo hydrogenolysis to form hydrocarbons and hydrogen sulfide. Thus, Thiophene itself is converted to butane and H_2S. More prevalent and more problematic in petroleum are benzothiophene and dibenzothiophene. Reflecting their high stabilities, thiophenes arise from many reactions involving sulfur sources and hydrocarbons, especially unsaturated ones, e.g. acetylenes and elemental sulfur, which was the first synthesis of thiophene by Viktor Meyer in the year of its discovery. Thiophenes are classically prepared by the reaction of 1,4-di ketones, diesters, or dicarboxylates with sulfiding reagents such as P_4S_{10}. Specialized thiophenes can be synthesized similarly using or Lawesson's reagent as the sulfiding agent, via the Gewald

reaction, which involves the condensation of two esters in the presence of elemental sulfur. Another method is the Volhard-Erdmann cyclization. Naphthols, 1- and 2-naphthol[13-15], recently have been suggested as route-specific biomarkers for exposure to airborne polycyclic aromatic hydrocarbons. For the proper application of naphthols as biomarkers, we studied effects of lifestyle on naphthol levels in 119 Japanese male workers.



Scheme-I



Scheme-II

MATERIALS AND METHODS

SYNTHETIC METHOD FOR PREPARATION OF ANILINE-FORMALDEHYDE-α-NAPTHOL TERPOLYMERS : All the reagents used were of analytical grade and obtained from commercial sources. Aniline was purified by vacuum distillations before use. In a fume hood, to freshly distilled. Aniline (0.05 moles) added 40% by weight aqueous formaldehyde solution containing 10.14% methanol in order to prevent polymerization of formaldehyde. Carefully to this resultant mixture add α-naphthol (0.05 moles) and few drops of acid was added directly through the top of the beaker with a capillary. The colour of the complex turned bright violet / pink/ dark red. The solution was refluxed for 30 min on a water bath. The mixture was cooled at room tamp, and then placed mixture in an ice-bath for 0.5 hr. and collected the beautiful dark pink coloured polymer was cold which becomes hard brittle on standing. A small portion of polymer was dissolved in DMF solution for UV-Visible spectroscopic study showing absorption peak at a longer wave length (>400hm). The

study of literature on organic polymer chemistry has reveled that whenever double bonds one introduced in to the planer molecule, it helps to increase flexibility of molecule and conjugation makes the molecule move rigid and raises the softening point of the molecule. Simple procedure is adopted for different acid to the formation of coloured aniline-formaldehyde-α-naphthol terpolymers.

RESULTS AND DISCUSSION

ACID CATALYZED MECHANISM : Aniline reacts with wide range of electrophilies because of its electron rich character affording 2 and 3 substituted aniline with 2 isomer being predominant and sometime poly substitutions of aniline ring also occur. As shown the reaction **(Scheme II)** is an electrophilic addition reaction in which a monomer is formed and each activated aniline molecule is added in a similar fashion to the another thiophene molecule and the process continues leading to the formation of aniline—formaldehyde--α-naphthol terpolymers.. On the basis of spectral-structure correlation, the polymers have been developed that are useful in predicting the type and degree of substitution on the conjugated system. The observations made during the spectroscopy of polymer are included in **Table I&II.**

Table 1. Spectral Data of Newly Prepared aniline-formaldehyde-α-naphthol terpolymer

Compounds	**Spectral data**
AFN Terpolymer	IR (KBr); 3645 (-OH), 3330(-NH_2), 2954.7 (CH), , 1614.3
	1444.6(Ar-H);
	^{1}HNMR (300 MHz DMSO) δ7.47 (4H, m, CH),
	7.24 (2H, m, NH_2), 5.43 (10H, m, Ar-H).

Table II: UV Visible spectra value of aniline—formaldehyde--α-naphthol terpolymers

Sr.	Catalyst	□max (nm)	Absorption	Energy(KJ/ Mole)
1	HCl	542.1	3.9500	21.00
2.	H_2SO_4	380.6	1.6000	30.00
3.	HNO_3	532.1	4.2000	22.00
4.	$FeCl_3$	426.3	4.0880	28.11
5	CH_3COOH	372.8	4.6018	32.00
6.	C_6H_5COOH	547.5	0.3375	21.00
7.	HCOOH	430.1	2.93	146.7
8.	$H_2C_2O_4$	500.1	3.10	1.61
9.	$H_2SO_3^-$	445.1	4.91	100.05
10	HNO_2	340.1	3.70	102.75

APPLICATIONS

Terpolymer powders provide superior hydrolytic stability and water resistance due to the bulky and hydrophobic co monomers. The result is a UP range that is highly suitable for use in formulations containing Portland cement. This Polymer can be prepared in a short reaction time with good yield.

CONCLUSION

On the basis of polymerization process a simple and general method has been developed for the synthesis of aniline- formaldehyde-α-naphthol. A long chain polymer hold together not only by C-C bond, but also the electrons are delocalized in conjugation showing coloured aniline-formaldehyde-α-naphthol terpolymers with good to excellent yields after short reaction time. Consequently, the present method can be as a viable alternative to the existing procedures for applicable terpolymers.

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