

Note

Advanced polymers for high technology applications

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The present paper describes the synthesis of organic conjugated polymers of pyrrole and formaldehyde. The reaction is catalyzed by strong acid, weak acids, organic acids and also by Lewis acids. Spectroscopy reveals that the polymers formed are long organic chains that are not only held together by the usual C-C sigma bonds that are found in ordinary polymers, but the electrons are delocalized in the conjugate structures forming intensively coloured polymers.

Keywords: Organic conjugated polymers, pyrrole, formaldehyde

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Over the past few years, a thorough study has been made on reactive polymeric materials having significant impact on mankind and also having applications in various areas of chemistry and biotechnology¹⁻³. In day-to-day life, an increasingly large number of polymeric materials have been investigated to provide interesting facilities in organic synthesis⁴. This has resulted into gradual increase in their study by many researchers and scientists⁵⁻⁷ to prepare products having unique physical and chemical properties. E.g. phenolic resins, have excellent insulation properties, high strength of weight ratio, excellent resistance to chemicals and better flammability resistance compared to most of the other polymeric materials⁸. Conjugated polymers^{9,10} have received a great deal of attention because of their potential applications such as biosensors, non linear optics, solid state batteries, semi conducting devices, to make composites or blends of conducting polymers and insulating polymers. Like phenolic resins pyrrolic resins can also adjust to the ever changing requirement of our industrial society and find diverse applications such as protective coatings, fibres, adhesives, packaging^{11,12} etc.

Presence of plasticizers increasing the solubility of polymers is well known. Kim DY *et al.*¹³ and MacDiarmid *et al.*¹⁴ synthesized polypyrroles using

pyrrole monomer with the dopants dodecylbenzenesulfonic acid and di-(2-ethylhexyl)sulfosuccinate respectively with increased solubility in organic solvents. All pyrrole-formaldehyde polymerizations are less thoroughly understood than that of radical polymerization reactions¹⁵. Reaction systems are often heterogeneous involving acid catalyst and organic monomers and generally a large effect may be produced by a third component that is present in a very low concentration. Pyrrole-formaldehyde polymerization often leads to very-high-molecular weight polymer at an extremely high rate. A visible activation spectra maxima of pyrrole-formaldehyde reaction in the presence of strong acid, weak acids, organic acid and Lewis acids is reported in this study (**Table I**).

Experimental Section

All the reagents used were of analytical grade and obtained from commercial sources. Pyrrole was purified by vacuum distillations before use. In a fume hood, to freshly distilled pyrrole (0.05 mole) added 40% by weight aqueous formaldehyde solution containing 10-14% methanol in order to prevent polymerization of formaldehyde. Carefully to this resultant mixture few drops of acid was added directly through the top of the beaker with a capillary. The colour of the complex turned bright violet/purple/red. The solution was refluxed for 30 min on a water-bath. The mixture was cooled at room temp. and then placed mixture in an ice-bath for 0.5 hr and collected the beautiful dark red coloured polymer was collected which becomes hard and brittle on standing. A small portion of polymer was dissolved in DMF solution for UV-visible spectroscopic study showing absorption

Table I—Visible activation spectra of pyrrole-formaldehyde reaction

Sr No.	Catalyst	λ_{\max} (nm)	Absorption	Energy KJ/mole
1	HCl	547.5	3.9500	21.80
2	CH ₃ COOH	390.0	1.6000	30.00
3	C ₆ H ₅ COOH	531.0	4.2000	22.00
4	FeCl ₃	425.3	4.0880	28.11
5	ZnCl ₂	372.8	4.6018	32.00
6	AlCl ₃	547.5	0.3375	21.80

peak at a longer wave length ($> 370\text{nm}$). The study of literature on organic polymer chemistry has revealed that whenever double bonds are introduced into the planer molecule, it helps to increase flexibility of molecule and conjugation makes the molecule more rigid and raises the softening point of the molecule.

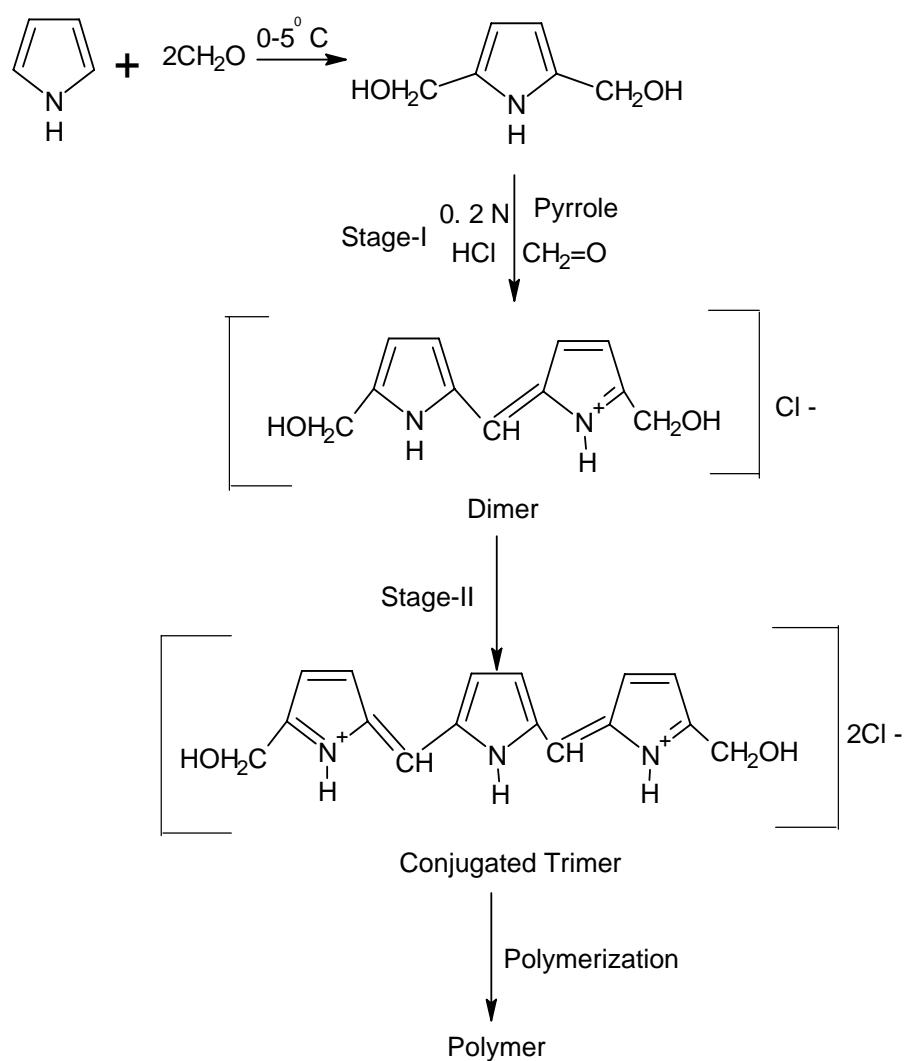
Similar procedure is adopted for different catalytic reagents for the formation of coloured polymer of pyrrole and formaldehyde due to the presence of conjugation single-double bond and $\pi \rightarrow \pi^*$ absorption that shifts the absorption to higher wavelength. On storage slow reaction occurs leading to the hardening of polymer (**Scheme I**).

Resonance stabilized conjugated cation under appropriate conditions (linear dimer) undergoes chain polymerization and the reaction gets activated after which a chain of repeating units adds up

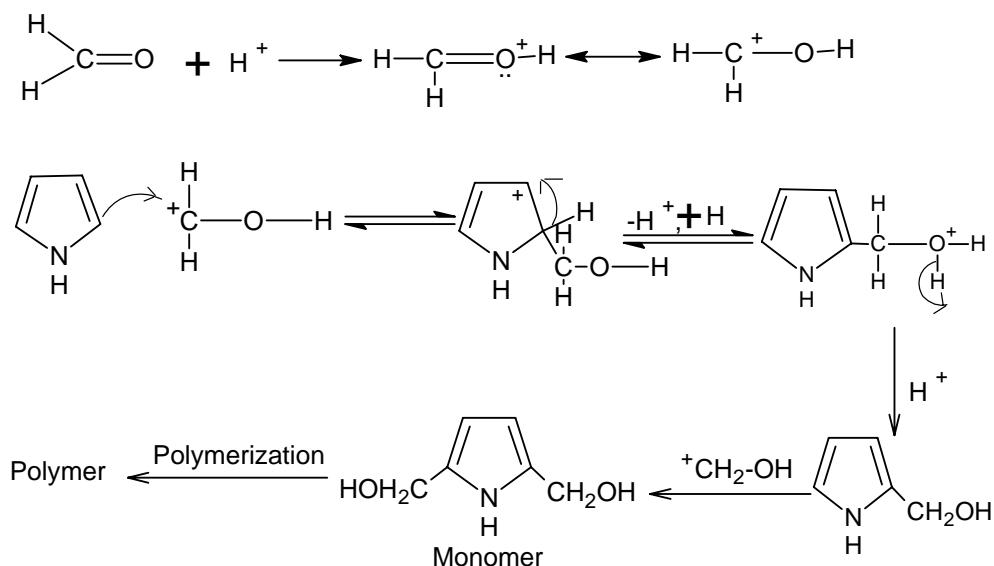
spontaneously thus building up the chain length gradually.

Acid catalyzed mechanism

Pyrrole reacts with wide range of electrophiles because of its electron rich character affording 2 and 3 substituted pyrroles with 2 isomer being predominant and sometimes polysubstitutions of pyrrole ring also occur¹⁶. As shown the reaction (**Scheme II**) is an electrophilic addition reaction in which a monomer is formed and each activated pyrrole molecule is added in a similar fashion to the another pyrrole molecule and the process continues leading to the formation of polymer. 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.



Scheme I



Scheme II

The observations made during the spectroscopy of polymer are included in **Table I**.

IR spectra (KBr) 3310 (weak NH) stretching, C = C (stretching vibration), 1620, 1605, C = N (ring) 1520, 1505, C—N (stretching) 1260 cm^{-1} ; ^1H NMR (DMSO- d_6) 2.93 (pyrrole NH), 8.70 (pyrrole CH).

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