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Synthesis and characterization of conducting polypyrrole by γ – radiation

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Abstract:

Conducting polypyrrole (Ppy) has been synthesized by γ – radiation from Co60 source. The important advantage of this method is oxidant materials like $FeCl_3$ can be avoided and therefore the Ppy obtained is in highly pure form. These particles were characterized using FTIR and XRD. The electrical conductivity was determined by using two probe methods.

Key words: Pyrrole, gamma – radiation, structure, mode of bonding.

Introduction:

Electrical conducting polymers have assumed a great importance in recent years due to novel exotic properties. In general Ppy and PANi are synthesized by chemical method using oxidants, such as FeCl3 and APS, or by electrochemical technique [1-4]. Intensive research from our group as well as other has shown that electrical conductivity can be raised by trying to increase the conjugation length and use of suitable dopants [5-7].

Ppy has been studied in detail due to several advantages such as ease of synthesize, good electrical conductivity, good environmental stability and possibility of commercial applications like Rechargeable batteries, Microwave EMF shields, Chemical sensors, Conducting fabrics etc [8-11].

Of the several polymerization methods used to produce Ppy, chemical oxidation, electrochemical synthesis occupy the important place. However both these methods introduce impurities in the terms of oxidant chemicals or dopant ions [12]. Also the methods of UV radiation [13], microwave radiation [14] and radiolysis polymerization [15] have been reported. However it has been reported that for efficient polymerization, it is required to have some oxidants molecules to induce the reaction which once again can lead to impurities [16].

On account of the good possibilities of using Ppy as actuator materials, attempts have been made to synthesis Ppy materials on a porous substrate [17]. This results in formation of tubular or wire like materials, and the possibilities of one dimensional change of size. However the need for removal of the porous substrate at a later time proves to be a difficult process.

In the present studies, we report the synthesis of Ppy under the γ – radiation from Co60 source. The resultant material was analysis using FTIR and XRD. The electrical conductivity was measured by two probe method and was found to be comparable to that produced from other methods. The main advantage of this method was found to have Ppy in the pure form. The globular particles formed are of uniform size and much smaller in size, probably in the range of nanometers. The mechanism of polymerization seems to be bonding through 2, 4 instead of 2, 5 as seen normally.

Material and methods

Pyrrole monomer was obtained from Sisco Research laboratory (99% pure) and was distilled before use. A γ – radiation source (Gamma Chamber 900) having Co60 source giving out radiation dose of 2 kGy/ hr. was installed at IIT, SAIF Bombay was used. In a typical experiment monomer Pyrrole was kept in a polyethylene bottle that was sealed and radiated by γ – radiation for 24 hrs under normal pressure and temperature conditions. On some occasion the monomer solution was spared over glass plate/ Copper plate/ Teflon sheet uniformly and subjected to irradiation.

The samples obtained were washed with distilled water before used. The black powder or film obtained was dried under vacuum at room temperature for 48 hrs.

The following instruments were used for the characterization. The chemical bonding was analyzed using FTIR spectroscopy by FTIR spectrometer model Perkin-Elmer Ltd. system 2000 using KBr pellets. XRD machine of PANalytical (Philips), model XpertPro was used. The XRD patterns were recorded in the range of 2θ = 100 to 400. The X – ray diffractometer uses CuK □ radiation of λ =1.5418 A0 generated at 40kV/ 20 ma. The Polypyrrole was tested for conductivity by preparing its pellets of area of cross section of 1 sq.cm. and 1mm. thickness. The conductivity was tested by two probe method at room temperature in the voltage range from 0 to 12 V.

Results and Discussions

The interaction of radiations can induce many ions, radicals and radical cations. The main reaction can be

Ppy0 → Ppy+ + e-
Ppy+ + Ppy+ → Diamer of Ppy

The electrons produced in the process can recombine with Pyrrole monomer and induce additional reactions. Such reactions can initiate polymerization of monomer and polypyrrole is formed.

Longer polymer chains are desirable for better electrical conduction. However the chains can also grow on sides, leading to branching and cross linking process which is difficult to avoid. However formation of conjugated bonds and interchain bonding can lead to electron/hole hopping across the chains. If more Ppy cations are available, more electron/hole pairs can be formed leading to higher conductivity. The conductivity of such oxides Ppy chains can rise to yet higher level, depending on the conditions of preparation and doping ions.

During chain propagation whether the chains are formed through 2, 5 bonding of the Pyrrole molecules, a mechanism normally seen, or through 2, 4 bonding is a question of concern. In either case, coplanarity of chains and good cross linking can lead to better conjugation and conduction within the plane. However from the point of minimization of energy, helical growth of chain and intermolecular bonding could be a distinct possibility.

FTIR Studies were carried out to understand this mechanism and bonding. The FTIR spectrum of Ppy prepared is represented in Fig.1 It shows strong absorption bands at around 3260cm-1 corresponding to N-H stretching. Other low intensity peaks are observed at around 2927 cm-1 - 2814 cm-1 which can be attributed to aromatic C-H stretching vibrations. The absorption band at 1553 cm-1 is related to C=C / C-C stretching vibrations of the Pyrrole ring, which are absent in our spectra. The band at 1470 cm-1 reflects the C-N stretching vibrations of the ring which are also absent. The region at 1250 cm-1 - 1100 cm-1 corresponds to breathing vibrations of the Pyrrole ring. The peak at 1310 cm-1 attributable to C-N in plane deformation vibration modes is shifted in our spectra to 1346 cm-1. The bond of C-H in plane deformation vibration is situated at 1043 cm-1 and of the C-C out of plane ring deformation vibrations or C-H rocking is at 681 cm-1 which occurs at 695 cm-1 in our spectrum. The C-H out of plane deformation vibration band of the ring has a peak at 915 cm-1, which is absent in our spectrum.

In order to determine the mode of bonding, we used the bands at 788 cm-1 , 730 cm-1 and 820 cm-1. When α – α` bonding i.e. 2, 5 coupling exists a strong absorption band occurs at 788 cm-1 . On the other hand when α – β` bonding i.e. 2,4 coupling occurs, we get absorption band at 730 cm-1 and 820 cm-1 . It was indeed observed that when $FeCl_3$ or APS were used as oxidants in chemical polymerization method we observed only 788 cm-1 band[18]. However in the case of γ – radiation samples we observed strong absorption band at 732 cm-1 and a weak absorption band at 825 cm-1. Additionally a shoulder is noted at 794 cm-1. This shows that predominantly α – β` bonding exist with some admixture of α – α` bonding.

Another noteworthy change in the γ – irradiated samples is the absence of absorption bands at 1558 cm-1 and 1488 cm-1 corresponding to ring vibrations of Pyrrole. Instead a very strong absorption band is observed at 1702 cm-1 (which is near to 1685 cm-1 assigned to C=N bond). Thus breaking of C=C in the ring can lead to formation of C=N. Possibility such rapid changes on γ – radiation may lead to formation of α – β` type of polymerization.

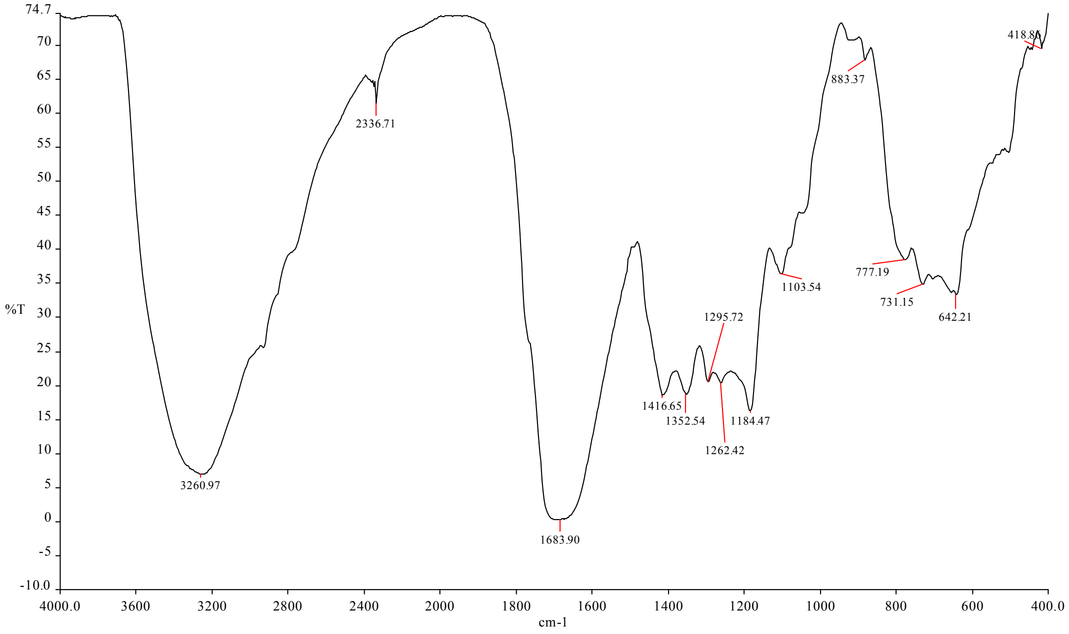

Fig. 1 : FTIR Spectra of Ppy prepared by γ – radiation

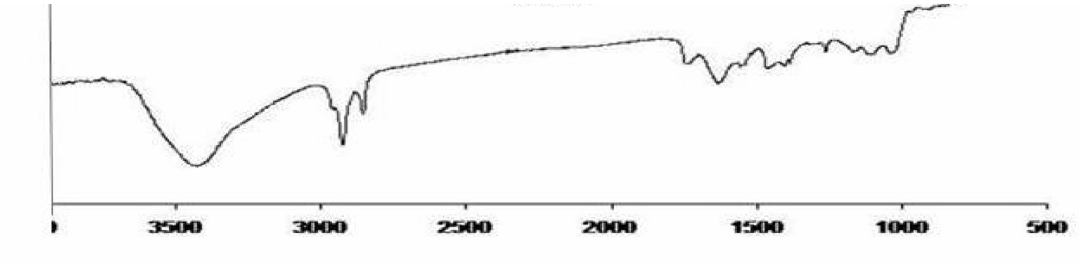

Fig. 2 : FTIR Spectra of Ppy monomer

XRD studies (Fig . 3) shows a broad peak at 2 = 240 to 260 spread over 150 to 350 .The broad peak corresponds to scattering from bare polymer chains at their normal inter planer spacing. In general XRD provides information on the crystalline and amorphous structure of the polymers, its spatial order and orientation of chains.

It has been reported that most of the Ppy synthesized by Chemical and electrochemical methods, doped by inorganic counter ions (Cl-, ClO_4-, TS- etc.) are essentially amorphous. It is seen in these as well as the present studies that the scattering curve is highly asymmetrical around the peak position. The curve at lower 2θ angles has a high scattering component, where as the curve at 2θ values greater than 260 shows nearly Gaussian shape.

Table 1 Peak positions of FTIR

Peak position	Assignments
3260 cm-1	N-H stretching
2927 cm-1- 2814 cm-1	Aromatic C-H stretching vibrations of benzene ring
1683 cm-1	C=N bond
1346 cm-1	C-N in plane deformation vibration modes
1250 cm-1- 1100 cm-1	Breathing vibrations of the Pyrrole ring.
1043 cm-1	C-H in plane deformation vibration
732 cm-1	α – β` bonding exists with some admixture of α – α` bonding.
695 cm-1	the C-C out of plane ring deformation vibrations or C-H rocking

The range of 2θ values (i.e. half width) gives us the range of d spacing. Since this d spacing is resulting from the inter chain distance of amorphous Ppy, it tells us about the distances involved in the interchain spacing. Our calculations show that d values vary from 3.862A0 to 4.595A0 i.e. the chains are placed at different distances from each other and do not have a unique space. This is due to inter chain interaction and cross-linking.

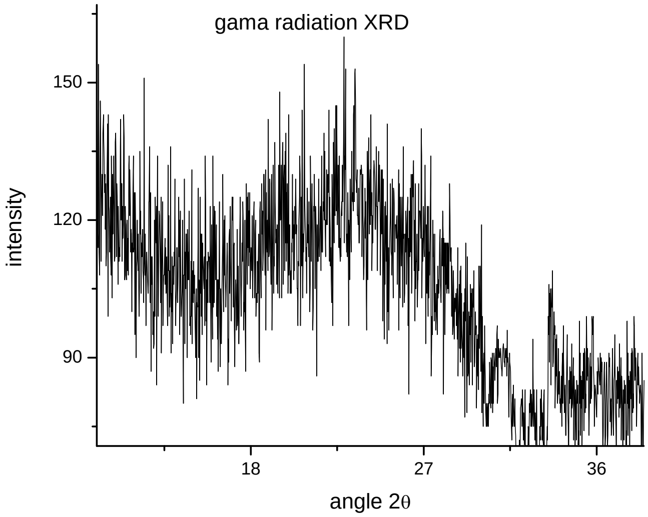

Fig. 3: XRD of Ppy prepared by γ – radiation method

Polypyrrole particles obtained had a size in the nanometer range, much less than that obtained by chemical and electrochemical polymerization techniques.

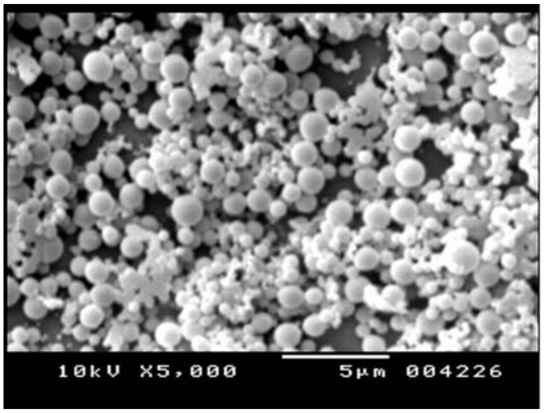

Fig. 4: SEM of Ppy prepared by γ – radiation method

Another important feature of this preparation is that the film is heavily adherent to the substrate used. In the present studies the adhesive strength of the film was calculated from the peeling strength. It was found that the films formed on glass are most heavily adherent than those formed on copper and PET sheets.

The electrical conductivity was calculated from I vs V characteristic of the film formed. The value obtained for conductivity was 0.106 X 10-3 S/cm.

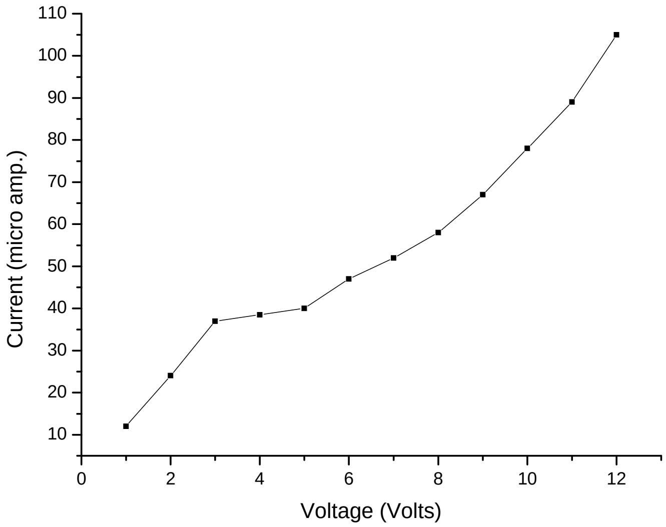

Fig. 2: Graph of current Vs Voltage Ppy prepared by γ – radiation method

Conclusion

Polymerization of pyrrole using by γ – radiation has been investigated. The FTIR spectra revealed the possibility of α – β` bonding mode on account rupture of the pyrrole ring accompanied by C=N formation. The XRD pattern shows that chains are placed at different distances from each other and do not have a unique space. This is due to inter chain interaction and cross-linking. The electrical conductivity is low as compared to the Ppy prepared by other methods like chemical oxidation, electrochemical etc. This may be due to the fact that α – β` bonding take place during Ppy formation. Secondly there was no oxidant or dopant used during synthesis of Ppy.

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