Chapter-9

FTIR Spectra of Electronically Doped Polypyridines
1. INTRODUCTION

Approaches to bridged planar Polypyridine derivatives for maximization of extended $\pi$-conjugation are known (1). Self-assembled, aligned and cleaved supramolecules of poly(2,5-pyridinediyl) have also been studied (2). Synthesis of highly functionalized pyridines for planar polymers has been carried out and maximized $\pi$-conjugation in electron-deficient macromolecules has been studied (3).

In the present work, FTIR spectra of linear polymers such as poly(2,5-pyridine) and poly(3,5-pyridine) having different symmetry structures have been studied. They are also characterized with UV-visible-near-IR spectroscopy. Further, the linear polymers are heavily doped with organic acceptors such as TCNE, TCNQ, DDQ, Chloranil and KI-I$_2$ and their FTIR spectra are obtained. Some of the doped polymers show two-band transport.

2. EXPERIMENTAL

Poly(2,5-pyridine) and poly (3,5-pyridine) were obtained from Aldrich chemical company and were doped with TCNE(tetracyano-p-ethylene), TCNQ (7,7,8,8-tetracyano-p-quinodimethane), DDQ (2,3-dichloranil-5,6-dicyano-p-benzo-quinone), Chloranil and KI-I$_2$ which were also highly pure reagent grades. These electronic acceptors were mixed in 60% with two linear polymers and were grinded in an agate mortar with an agate pastle. Fine homogeneous powders prepared in this manner were compressed in a die with the help of a manually operated
compressing machine. Circular discs prepared in this way were placed in a dark chamber of standard spectrophotometer and FTIR spectra were recorded.

The spectra in the range 400-4000 cm\(^{-1}\) were recorded using a GXFTIR spectrophotometer manufactured by Perkin-Elmer company, USA having resolution of 0.15 cm\(^{-1}\), a scan range of 15,600-30 cm\(^{-1}\), a scan time 20 scan/sec, an OPD velocity of 0.20 cm/sec and MIRTGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode.

3. RESULTS AND DISCUSSION

The molecular structures of polypyridine is shown (Figure 1). Poly (3,5-pyridine) is somewhat asymmetric with respect to polymeric chain while poly(2,5-pyridine) is symmetric with respect to linear chains. Rigid bends or kinks present in poly (3,5-pyridine) are absent in poly (2,5-pyridine). As a result poly (3,5-pyridine) is less conducting than poly (2,5-pyridine).

The UV-visible-near-IR spectra of poly (3,5-pyridine) and poly (2,5-pyridine) are shown (Figure 2a and 2b). The ultraviolet range in both spectra contain \(\sigma \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions. The spectra in the near IR range above 1500 nm contain five bands corresponding to
intermolecular vibration or LO and TO modes of phonons in solid states. One of the band around 2300 nm is a doublet in poly (3,5-pyridine) while the same is a single band in poly (2,5-pyridine). This is due to asymmetry present in poly (3,5-pyridine). There are two bands between 1000 nm and 1500 nm which are oscillator models in semiconducting poly (3,5-pyridine) but these are broadened to show almost gaussian bands marked with G’s in the spectrum of poly (2,5-pyridine). This reveals that poly (2,5-pyridine) is highly conducting due to electronic delocalization shown by the gaussian bands. There is a colour band at 500 nm in poly (2,5-pyridine) which is absent in poly (3,5-pyridine).

Figure 2 : UV-visible-near IR spectra of (a) poly (3,5-pyridine) and (b) poly(2,5-pyridine)
The FTIR spectra of poly (2,5-pyridine) and poly(3,5-pyridine) are shown (Figure 3a and 3b). There is a range of nature of transition above 1800 cm\(^{-1}\) in poly (2,5-pyridine) and above 2000 cm\(^{-1}\) in poly (3,5-pyridine). These nature of transitions are fitted to be allowed indirect transitions in both the linear polymers (Figure 4a and 4b). Although the nature of transition is same, the band gap of poly(2,5-pyridine) is found to be 0.225 eV while the band gap of poly (3,5-pyridine) is found to be somewhat higher, i.e. 0.24 eV. The band gap is due to peierls transition along symmetric and uniform chain of poly (2,5-pyridine) while the band gap corresponds to a non-universal Hubbard gap in poly (3,5-pyridine). One of gaussian band in the range around 600 cm\(^{-1}\) in fitted (Fig. 4c) for poly (2,5-pyridine) while there is no gaussian band in poly (3,5-pyridine) in the same range (Fig.-3).
Figure 3: FTIR spectra of (a) poly (2,5-pyridine) and (b) poly(3,5-pyridine)

\[
\frac{(Ah_v)^{1/2}}{} \text{ vs } h_v
\]

4(a)
After the above comparison of both the linear polymers, the effect of electronic doping with electron acceptors such as TCNE, TCNQ, DDQ, Chloranil and KI-I$_2$ on FTIR spectra of both the polymers are studied in the present work. The FTIR spectra of doped poly (2, 5-pyridine) are shown (Figure 5a-e). The similar spectra of doped poly (3, 5-pyridine) are separately shown (Figure 6a-e).
Figure 5: FTIR spectra of poly (2,5-pyridine) doped with (a) TCNE (b) TCNQ (c) DDQ (d) Chloranil and (e) KI-I₂
Figure 6: FTIR spectra of poly (3,5-pyridine) doped with (a) TCNE (b) TCNQ (c) DDQ (d) Chloranil and (e) KI-I2

The forbidden indirect transitions obeying $A_h\nu = B (h\nu - E_g \pm E_p)^3$ are found in poly (2,5-pyridine) complexes (Fig. 7a-e) and low-frequency gaussians are also fitted (Fig. 8a-e). Similar plots of nature of transitions (Fig. 9a-e) and gaussian bands of poly (3,5-pyridine) complexes (Fig. 10a-e) are also shown.

![Graph showing $(A_h\nu)^{1/3}$ vs $h\nu$]

7(a1)
\((Ah\nu)^{1/3} \text{ vs } h\nu\)

7(a)

\((Ah\nu)^{1/3} \text{ vs } h\nu\)

7(b)

\((Ah\nu)^{1/3} \text{ vs } h\nu\)

7(c)
Figure 7 : Forbidden indirect transitions in poly (2,5-pyridine) doped with

(a) TCNE (b) TCNQ (c) DDQ (d) Chloranil and (e) KI-I$_2$
\[ \ln A \text{ Vs } (\lambda - \lambda_0)^2 \]

8(a)

\[ \ln A \text{ Vs } (\lambda - \lambda_0)^2 \]

8(b)

\[ \ln A \text{ Vs } (\lambda - \lambda_0)^2 \]

8(c)
Figure 8: Low-frequency gaussian bands fitted for poly (2,5-pyridine) doped with (a) TCNE (b) TCNQ (c) DDQ (d) Chloranil and (e) KI-I₂
\[(Au)^{1/3} \text{ vs } h\nu\]

9(a₁)

\[(Au)^{1/3} \text{ vs } h\nu\]

9(a₂)

\[(Au)^{1/3} \text{ vs } h\nu\]

9(b₁)
(\text{Ah}\nu^{1/3} \text{ vs } \nu)

9(b_2)

(\text{Ah}\nu^{1/3} \text{ vs } \nu)

9(c)

(\text{Ah}\nu^{1/3} \text{ vs } \nu)

9(d)
Figure 9: Forbidden indirect transitions in poly (3,5-pyridine) doped with (a) TCNE (b) TCNQ (c) DDQ (d) Chloranil and (e) KI-I₂
\[ \ln A \text{ Vs } (\lambda - \lambda_0)^2 \]

10(b)

\[ \ln A \text{ Vs } (\lambda - \lambda_0)^2 \]

10(c)

\[ \ln A \text{ Vs } (\lambda - \lambda_0)^2 \]

10(d)
The nature of transition changes from allowed indirect to forbidden indirect upon complexation with electronic acceptors in both polymers probably because of stretching of bonds among the monomer units. Ring–ring distance increases in both polymers because of stretching induced by electronic acceptors. Low-frequency gaussian band around 600 cm\(^{-1}\) broadens in doped polymers for poly (2,5-pyridine) while the gaussian bands are appearing in doped polymers of poly (3,5-pyridine) which is absent in pure poly (3,5-pyridine). Only TCNE complex of poly (2,5-pyridine) show two band transport while both TCNE and TCNQ complexes of poly (3,5-pyridine) show two band transport. There are two conduction bands in these complexes.

In the region of nature of transitions (1700-2800 cm\(^{-1}\)) of both the polymers as well as in all of their complexes there are number of phonon bands poking out of background featureless absorption are found. The
spectrum is similar to that of gallium phosphide (4) which has got bands due to excitons-phonon coupling. Here also in all of the FTIR spectra, the threshold energies of formation of excitons are found with phonon emissions.

The complexes of poly (2,5-pyridine) all show a Peierls gap except TCNE complex which also shows a Hubbard gap of 0.29 eV as well. Similarly poly (3,5-pyridine) complexes show Peierls gap of 0.225 eV except TCNE and TCNQ complexes which also show Hubbard gap of about 0.30 eV. Thus whenever there is two band transport the higher gap is a Hubbard gap while the lower gap is a Peierls gap. There is only a Hubbard gap in pure poly (3,5-pyridine) while its complexes also show a Peierls gap. Thus in the cases of two band transport both donor and acceptor chains seem to be conducting. The Peierls gap is along the acceptor chains.

4. CONCLUSIONS

Poly (2,5-pyridine) is a Peierls semiconductor at room temperature and ambient pressure while poly (3,5-pyridine) is a Hubbard semiconductor in similar condition. However, the polymeric complexes or electronically doped Peierls semiconducting nature with also a Hubbard gap when there is two band transport.
REFERENCES