SYNTHESIS AND CHARACTERISATION OF CONJUGATED POLYMER OF 1,2 DICHLORO BENZENE AND NAPHTHALENE

B. TIWARI¹, SUDHA SHARMA² & NUTAN BALA³

¹³Chemistry, D. S. Institute of Technology and Management, Uttar Pradesh, India
²Chemistry, Mewar University, Rajasthan, India

ABSTRACT

In the present work, we tried to solve the problems of solubilization, processibility and device fabrication for the ppps. We synthesized Co-polymer of 1,2Di-ChloroBenzene with Naphthalene. The co–polymer (Poly-CIBN) has to be shifted in the PL spectra corresponding to the monomers. The property of the PPPs polymers like solubility, processibility gets quite improvised. The conjugated polymer so formed is analysed on the basis of spectroscopic method of UV, IR, and NMR spectroscopy.

KEYWORDS: NMR, IR, UV, 1, 2 Di-Chloro Benzene, Naphthalene, Conjugated Polymer, PPPs

INTRODUCTION

During the last ten years, the family of conjugated polymers has established itself as an important class of materials with interesting optical and electronic properties. The main drive for their use is the potential low cost which in the case of polymers is associated with the solution processability of such polymers. The other attribute is the coverage of the entire visible spectrum making them suitable for display applications.

Poly (p – phenylene) (PPP) is particularly interesting because it exhibits a unique combination of physical properties, namely high mechanical strengths, excellent thermal stability and chemical resistance, as well as electro luminescent and high conductivity upon doping. In particular, it is known for its exceptional thermal stability in neutral state, its resistance to environmental oxidation and irradiation, its wide conductivity range (from 10⁻¹⁸ cm⁻¹ in the pristine form to more than 10²⁶ cm⁻¹ in the doped state.) It is suitable for the realization of all plastics high energy density batteries and its applications for electro luminescent devices.

In the present work we synthesized Co-polymer of 1,2 Di-Chloro Benzene with Naphthalene. We also found out that the resulting polymer is fluorescent and show electroluminescence property. We have characterized the polymer using Fourier transform infrared spectroscopy, UV–vis absorption spectroscopy and NMR.

THEORITICAL DETAILS

Naphthalene

![Resonance Structure of Naphthalene](image)

Figure 1
Substitution occurs at the “alpha” position in naphthalene and other similar structures.

**Rationalization**: Regioselectivity in electrophilic aromatic substitution depends on the stability of the cationic intermediate. If we compare the two competing pathways, we notice that we can write several resonance structures for each of the two cationic intermediates. However, the action resulting from alpha addition (top) has one contributing structure that retains the unbroken benzene-like structure whereas the action from beta addition (bottom) does not have any benzenoid contributing structures.

Because the benzenoid bonding pattern is associated with aromatic stabilization, we conclude that the preferred pathway of addition will be the one that retains the greatest number of intact benzene-like rings among its resonance structures.

A Naphthalene molecule is composed of two fused benzene rings (rings are fused if they share two or more atoms). Accordingly naphthalene is classified as a benzenoid polycyclic aromatic hydrocarbon (PAH).

There are two sets of equivalent hydrogens-

- **Alpha Hydrogen** - The alpha positions are 1, 4, 5 and 8
- **Beta Hydrogen** - Beta positions are 2, 3, 6 and 7

The Carbon- Carbon bonds in naphthalene are not of the same length. The bonds C1-C2, C3-C4, C5-C6 and C7-C8 are about 1.6 Å (136 pm) in length whereas the other Carbon-Carbon bonds are about 1.42 Å (142 pm) long.

This has been verified by X-ray diffraction, and is consistent with the valence bond model of bonding in naphthalene which involves three resonance structures (as shown above); while the bonds C1-C2, C3-C4, C5-C6 and C7-C8 are double in two of the three structures, the others are double in only one. Naphthalene can undergo electrophilic aromatic substitution. Naphthalene can be alkylated using Friedel-Crafts reactions, naphthalene can also be alkylated by reactions with alkenes or alcohols, with sulphuric or phosphoric acid as the catalyst. Two isomers are possible for mono-substituted naphthalene, corresponding to substitution at an alpha or beta position. Usually, electrophiles attack at the alpha position. The selectivity for alpha over beta substitution can be rationalized in terms of the resonance structures of the intermediate: for the alpha substitution intermediate, seven resonance structures can be drawn, of which four preserve an aromatic ring. For beta substitution, the intermediate has only six resonance structures, and only two of these are aromatic. Sulfonation, however, gives a mixture of the “alpha” product 1-napthalenesulfonic acid and the “beta” product 2-napthalenesulfonic acid, with the ratio dependent on reaction conditions.

Naphthalene can be hydrogenated under high pressure with metal catalysts to give 1, 2, 3, 4-tetrahydronaphthalene or tetralin (C_{10}H_{14}). Further hydrogenation yields decahydronaphthalene or decalin (C_{10}H_{18}). Oxidation with chromate or permanganate, or catalytic oxidation with Oz and a vanadium catalyst, gives phthalic acid.
Physical Properties

- Chemical formula: C₁₀H₈
- Molecular weight: 130 g/mol
- Melting point: 80.2 °C
- Boiling point: 218°C
- Resonance energy: 2.651 eV
- Density: 1.14 g/cm³

1, 2 Di-Chloro Benzene

1,2 Dichlorobenzene, or orthodichlorobenzene (ODCB), is an organic compound with the formula C₆H₄Cl₂. This colourless liquid is poorly soluble in water but miscible with most organic solvents. It is a derivative of benzene, consisting of two adjacent chlorine enters.

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<th>Physical Properties</th>
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<tr>
<td>Molecular formula</td>
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<tr>
<td>Molar mass</td>
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<tr>
<td>Melting point</td>
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<tr>
<td>Boiling point</td>
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Solubility: soluble in most organic solvents

According to the structure proposed by Kekulé, there should be two isomers of 1,2-dichlorobenzene. In one structure, the chlorine atoms are separated by a single bond, and in the other, they are separated by a double bond. However, these isomers have never been isolated or detected.
EXPERIMENTAL DATA

The synthesis of the co-polymer of naphthalene and 1,2 Di-chlorobenzene (poly-CIBN) has been carried out by the conventional Kovacic method using a FeCl₃ as catalyst. The heterogeneous reaction mixture consisting of the catalyst 1,2 Dichlorobenzene and naphthalene is stirred for 4–6 hrs. at 35-40°C. After the completion of the reaction, the reaction mixture is washed with distilled water in order to remove the impurities. The orange brown polymer obtained is dried under vacuum. The characterization of the resultant polymer has been carried out by spectroscopic techniques.

**Drying:** The polymer was then dried at a temperature of about 40°C in a desiccator. After drying it became orange brown in colour.

**Solubility:** The polymer was soluble in all the common organic solvents like chloroform, carbon tetrachloride, toluene, tetrahydrofuran (THF), Chlorobenzene, NMP, Xylene etc.

CHARACTERIZATION OF CO-POLYMER OF 1,2DICHLOROBENZENE AND NAPHTHALENE

UV-VIS Absorption Spectra of the Co-Polymer of 1,2Di Chlorobenzene and Naphthalene

UV-VIS Spectra of the co-polymer of 1,2Di-Chloro benzene and naphthalene was recorded on a shimadzu UV-2401 Spectrophotometer. The absorption spectrum of the co-polymer in Chloroform exhibit absorption bands in UV regions, which are identical to the absorption spectrum of poly para phenylene (PPP). The absorption band appears to be vibronic spectra of naphthalene molecules shift owing to its attachments on poly p-phenylene chain.

![FTIR Spectra of Copolymer of 1,2Di-Chloro Benzene and Naphthalene](image)

**FTIR Spectra of Copolymer of 1,2Di-Chloro Benzene and Naphthalene**

The sample of the polymer for FTIR was prepared in freshly cleaned dry KBr and the pellet of the sample was prepared by the hydraulic process. The FTIR spectrum was recorded. The peak at 3065 cm⁻¹ due C-H stretching of dichlorobenzene ring in polymer while the peaks at 2925 cm⁻¹ and 2855 cm⁻¹ was due to C-H stretching vibrations of naphthalene ring in the polymer. The band occurs in 1745 cm⁻¹ aromatic region. The peaks at 1652 cm⁻¹ and 1379 cm⁻¹ were due to quadrant and semi-circle stretching vibrations of rings. The C-C in plane stretching of aromatic ring present at 1164, 1093 cm⁻¹ and 972 cm⁻¹. The peak at 720 cm⁻¹ shows the Para substitution of the polymer. The C-H out of plane bending present at 582 CM⁻¹.
Table 2

<table>
<thead>
<tr>
<th>Prominent Group Frequencies (CM⁻¹)</th>
<th>Functional Group</th>
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<tbody>
<tr>
<td>3065 (CM⁻¹)</td>
<td>Sp2C-H stretching (aromatic) 1,2 dichlorobenzene</td>
</tr>
<tr>
<td>2925-2855 (CM⁻¹)</td>
<td>C-H stretching stretch of naphthalene ring</td>
</tr>
<tr>
<td>1745 (CM⁻¹)</td>
<td>aromatic region</td>
</tr>
<tr>
<td>1632-1379 (CM⁻¹)</td>
<td>Quadrant and semi-circle stretching vibrations of rings.</td>
</tr>
<tr>
<td>1164, 1093, 972 (CM⁻¹)</td>
<td>The C-C in plane stretching of aromatic ring</td>
</tr>
<tr>
<td>720 (CM⁻¹)</td>
<td>Para substitution of the polymer</td>
</tr>
<tr>
<td>582 (CM⁻¹)</td>
<td>C-H out of plane bending</td>
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</tbody>
</table>

Figure 6

FTIR spectra of copolymer of 1,2-Di-chloro benzene and Naphthalene

NmrSpectra of Copolymer of 1,2di-Chloro Benzene and Naphthalene

Table 3

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<tr>
<th>Types of Proton</th>
<th>Chemical Shift S(PPM) Conc of the Product: 0.5M (V)</th>
</tr>
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<tbody>
<tr>
<td>Aromatic protons</td>
<td>7.767</td>
</tr>
<tr>
<td>Aromatic protons</td>
<td>7.395</td>
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</tbody>
</table>

Figure 7
NMR spectra of copolymer of 1,2-Di-Chloro Benzene and Naphthalene

RESULTS & DISCUSSIONS

Co-polymer of 1,2 Dichlorobenzene and naphthalene has been prepared as a soluble poly-phenylenederivative. The polymer obtained is orange brown and soluble inorganic solvents like chloroform, toluene and N-methylpyrrolidone. The reaction can be represented as:

![Poly-CIBN](image)

Figure 8

The (Poly-CIBN) conjugated polymer is synthesized and characterized by using various techniques such as UV, FTIR and NMR which are discussed as above.

CONCLUSIONS

In conclusion, we have synthesized a new co-polymer incorporating 1,2-Dichloro benzene and naphthalene using Kovacic technique, which has practical utility in the fabrication of OLEDs. The new polymer is soluble in common organic solvents and can be thermally evaporated to make thin films. Therefore, the synthesized materials have good prospects for the industrial applications as electroluminescent materials in coming days.

REFERENCES