# *Poly(azomethine)s Derived from Ether Based Aromatic Dialdehydes: Synthesis and Physicochemical Studies*

A dissertation submitted to the Department of Chemistry,
Quaid-i-Azam University, Islamabad, in partial fulfillment
of requirements for the degree of

**Master of Philosophy**

in

**Inorganic/Analytical Chemistry**

by

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**Islamabad**
**2015**

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بسم الله الرحمن الرحيم

*IN THE NAME OF ALLAH, THE MOST GRACIOUS, THE MOST MERCIFUL*

فَبِأَيِّ آلَاءِ رَبِّكُمَا تُكَذِّبَانِ

*THEN WHICH OF THE FAVORS OF YOUR LORD WILL YOU DENY?*

***Dedicated to my family***

# DECLARATION

This is to certify that this dissertation entitled ***"Poly(azomethine)s derived from ether based aromatic dialdehydes: synthesis and physicochemical studies"*** submitted by ***Mr. Abdul Hafeez,*** is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, as satisfying the dissertation requirements for the degree of ***Master of Philosophy in Analytical/Inorganic Chemistry.***

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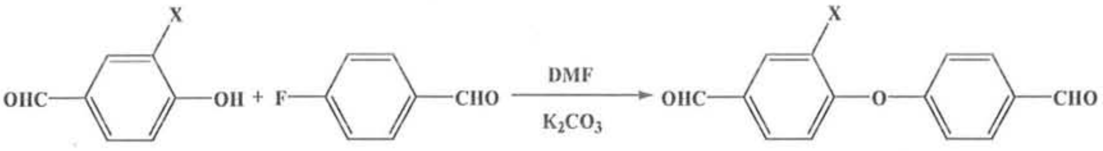
# ABSTRACT

Aromatic poly(azomethine)s are high performace materials being used in large area displays, resistive switching, and memory chips etc. Structural modification of reacting monomers leads to drastic changes in the physicochemical properties of macromolecules. Therefore, in the present study a series of nine ether-based wholly aromatic dialdehydes with different substituents ($-OCH_3$, $-OC_2H_5$, $-CH_3$, $-CF_3$) have been synthesized via etherification reaction between 4-fluorobenzenecarboxaldehyde and different phenols (i.e. di-hydroxyphenols or 4-hydroxybenzenecarboxaldehydes) in inert atmosphere. These bisaldehydes have been polymerized with two diamines (*p*-phenylenediamine, and 4,4′-diaminodiphenyl ether) using *p*-toluene sulfonic acid catalyst in *N,N*-dimethylformamide. Both the monomers and the polymers were synthesized in the presence of dry nitrogen atmosphere. The structural characterization was done with different spectroscopic techniques. Moreover, different physicochemical properties of synthesized polyazomethines have been studied using various techniques of spectroscopy, viscometry, thermal analysis, and solubility. The polyazomethines applicability in optoelectronics/semiconductors was checked by photoluminescence and conductivity techniques.

# Plan of Work

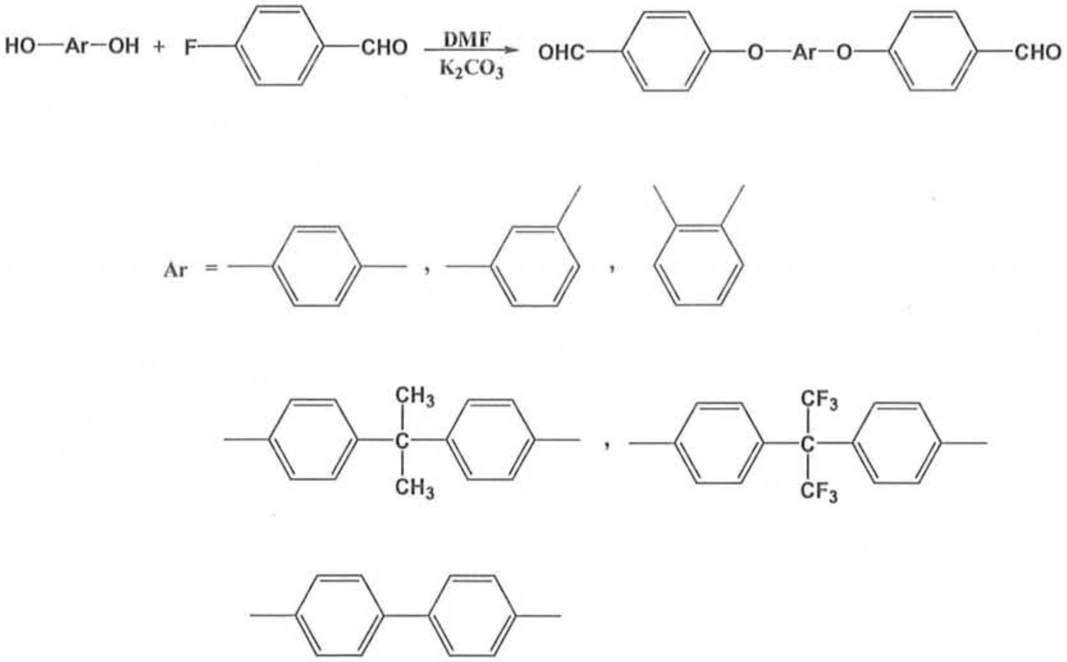
## Scheme No.1:



Where X= H
= $-OCH_3$
= $-OC_2H_5$

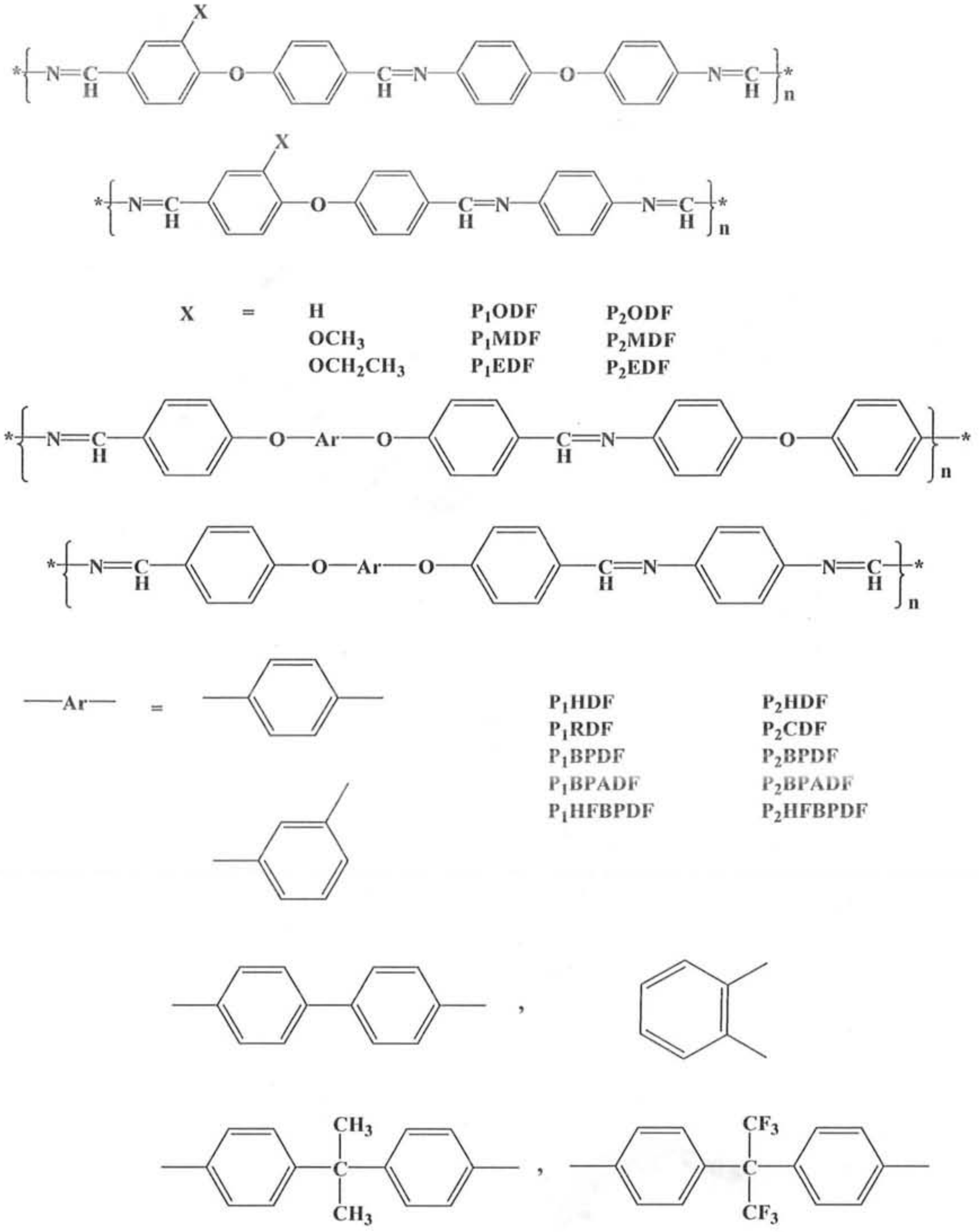
Syntheses of Mono-ether Based Aromatic Dialdehydes

## Scheme No.2:



Synthesis of Di-ether Based Aromatic Dialdehydes

**Scheme No.3:**



| | | | | |
|---|---|---|---|---|
| X | = | H | $P_1ODF$ | $P_2ODF$ |
| | | $OCH_3$ | $P_1MDF$ | $P_2MDF$ |
| | | $OCH_2CH_3$ | $P_1EDF$ | $P_2EDF$ |

—Ar— =

| | |
|---|---|
| $P_1HDF$ | $P_2HDF$ |
| $P_1RDF$ | $P_2CDF$ |
| $P_1BPDF$ | $P_2BPDF$ |
| $P_1BPADF$ | $P_2BPADF$ |
| $P_1HFBPDF$ | $P_2HFBPDF$ |

**Synthesis of Poly(azomethine)s**

## Chapter 1 Introduction

## Chapter 2 Experimental

## Chapter 3 Results and Discussions

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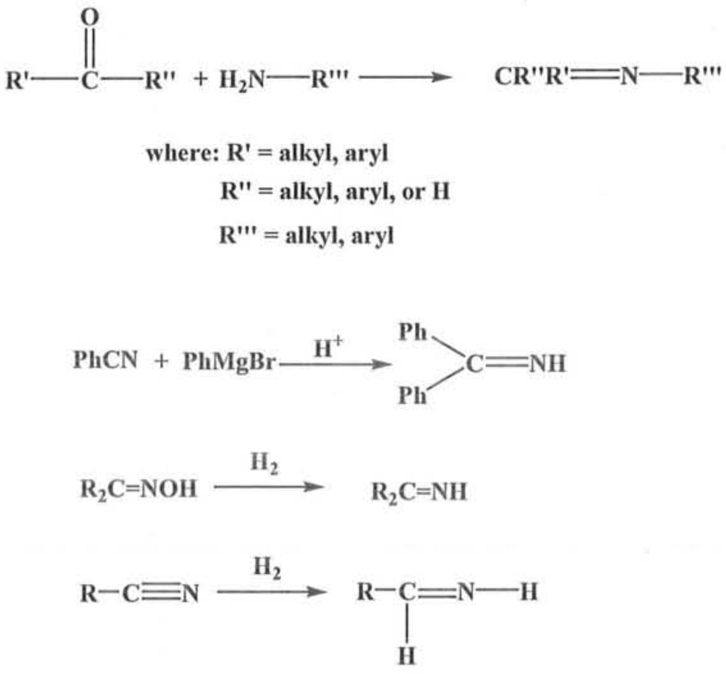
## List of Abbreviations

| | |
|---|---|
| PAM | Polyazomethine |
| PAZs | Polyazines |
| Tg | Glass transition temperature |
| SCE | Saturated calomel electrode |
| DMAc | Dimethyl acetamide |
| DMF | N,N-dimethylformamide |
| DMSO | Dimethylsulfoxide |
| $LiClO_4$ | Lithium perchlorate |
| $AgNO_3$ | Silver nitrate |
| CVD | Chemical vapor deposition |
| ITO | Indium-Tin-Oxide |
| DCM | dichloromethane |
| HMPA | hexamethylphosphoramide |
| $S_{Ar}N$ | nucleophilic aromatic substitution |
| $CH_3NO_2$ | nitromethane |
| $Ph\text{-}NO_2$ | nitrobenzene |
| DMSO-$d_6$ | deuterated dimethylsulfoxide |
| PLEDs | Polymer light emitting diodes |
| PSCs | Polymer solar cells |
| OPV | organic photovoltaics |
| BHC | bulk hyperconjugation |
| LC | liquid crystalline |
| MC-LC | main chain LC |
| SC-LC | side chain LC |

| | |
|---|---|
| DSC | differential Scanning calorimetry |
| TGA | thermogravimetric analysis |
| OPM | optical microscopy |
| PVC | polyvinyl chloride |
| ISEs | ion selective electrodes |
| TPA | triphenylamine |
| OLEDs | organic light emitting diodes |
| TBAP | tetrabutylammonium perchlorate |
| $D_2SO_4$ | deutrerated sulfuric acid |
| $CDCl_3$ | deuterated chloroform |
| WAXRD | wide angle X-ray diffraction |
| XRD | X-ray diffraction |
| NMP | N-methyl-2-pyrolidone |
| PL | Photoluminescence |
| RBF | round bottom flask |
| $N_2$ | nitrogen |
| TLC | thin layer chromatography |
| TsOH | *p*-toluenesulfonic acid |

## 1.1 Introduction:

The condensation product of carbonyl compound with an amine generates carbon-nitrogen double bond (C=N) with concomitant removal of water molecule. If an aldehyde is a reacting moiety with an amine then the condensation product is called an azomethine or aldimine. Alternatively, if a ketonic moiety is reacting with the amine then the condensing product is called ketanil or ketimine. The azomethine linkage may be generated from hydroxylamine, and alkyl nitrile using Grignard reagent or hydrogen as depicted in figure 1.1.



**where: R' = alkyl, aryl**
**R'' = alkyl, aryl, or H**
**R''' = alkyl, aryl**

**Figure 1.1: General imine formation reactions**

## 1.2 Historical Perspective:

Adams and his co-workers in 1923 generated a new class of conjugated polymers having –CH=N– linkages originating from dicarbonylic compounds (either dialdehydes or diketones) and di-amines. Since the carbon nitrogen double bond (-C=N-) is called Schiff base or azomethine or imine bond, these polymers are called poly(Schiff base)s, polyazomethines or polyimines. The polymeric C=N linked macrochains synthesized from dialdehydes are referred to as polymeric aldimines while those being originating from diketones are called polyketanils.

Adams *et al.* [1] synthesized insoluble and infusible polymeric imines by reacting 4,4′-diaminobiphenyl and ortho-dianisidine with 1,4-diformylbenzene. In 1938, Steinkopf *et al.* [2] synthesized such polymers by reacting hydrazine ($H_2N$-$NH_2$) with isophthalaldehyde and benzene-1,4-dicarboxaldehyde. In 1950s Marvel *et al.* [3] attempted solution phase polymeric imine formation of aromatic dicarboxaldehydes with hydrazine or 1,2-diaminobenzene, owing to insolubility of precipitated product this polymerization wasn't winning. The intriguing properties of polyazomethines led to the synthesis of wholly aromatic polyimines by Marvel *et al.* in 1950. During 1950s Marvel and co-workers [4] examined the properties of a number of polyimines and polyazines synthesized from 1,2-diaminobenzene and hydrazine for chelate formation study.

The interest in late 1960s as well as in early 1970s for thermally stable macromolecules led to a comprehensive study on aromatic polyaldimine by D'Alelio *et al* [5, 6]. In a review they discussed [7] the research work done on an ample selection of polyaldimines and generalized the effect of monomer's structure on the thermal stability in both air as well as nitrogen. To make melt proccessible and soluble adimines Morgan *et al* and Suematsu *et al* continued their work to get processible and soluble aldimines using different modifications in monomers. They showed that the poly(Schiff base)s can form liquid crystalline melts–whose spinning give fibers [8] of high tenacity and excellent modulus. They showed that the methyl substituent on aromatic ring as well as ethylene spacers in *p*-phenylene units give less softening temperatures to polyaldimines [9].

## 1.3 Azomethine or Schiff Base:

The imine (C=N) formed via condensation of aldehyde with amine accompanied by removal of $H_2O$ is of considerable interest to a synthetic chemist. Imine have very interesting properties ranging from anticancer [10], antimicrobial [11], insecticidal [12], antitumor [13], anti-bacterial agent [14], anti-inflammatory agents [15], antituberculosis [16], and anti-convulsant [17] activity [18]. Imines behave as versatile agents in organometallic [19], and cycloaddition reactions [20].

## 1.4 Mechanism of Azomethine Formation:

The acid catalyzed polymerization technique is generally used for the syntheses of polyimines that involves the reaction of aldehydic or ketonic carbonyl groups with bisamines. The figure 1.2 shows that the mechanism of conversion of amine and aldehyde to aldimine involves the attack of nucleophilic amine on electrophilic carbonylic carbon to give tetrahedral –OH intermediate whose dehydration affords aldimine. Since the reaction is reversible, the rate of reaction depends upon the removal of water entity which can be achieved through either azeotropic distillation [2] using Dean-Stark apparatus [21], dehydrating solvents like trimethyl orthoformate [22], tetramethyl orthosilicate [23], or using Lewis acids. The later act as not only catalysts which assist nucleophilic attack on carbonyl group but also serve as dehydrating agents from tetrahedral intermediate.

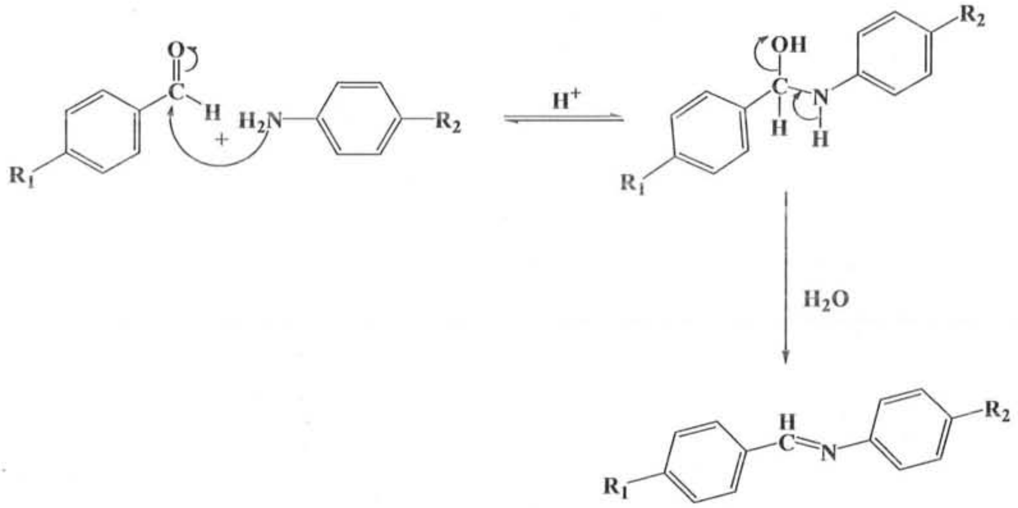


Figure 1.2: Mechanism of Azomethine Formation [24]

## 1.5 Catalysts for Azomethine:

Typically imine linkage is formed effortlessly without using catalyst but various modifications are available in literature such as Lewis acid catalysts $ZnCl_2$, $FeCl_3$ [25]; amphoteric oxide, $Al_2O_3$; $TiCl_4$ [26]; acidic and dehydrating oxide, $P_2O_5$; and hydrotalcite materials [27]. Using principles of green chemistry aldimines have been synthesized by Maeimi *et al* [28] with $P_2O_5$-$SiO_2$ to afford quantitative yields. Montmorillonite K-10 have been utilized by Verma [27] for microwave assisted solventless aldimine synthesis. Solvent free aldimine have been synthesized by Gopalakrishnan *et al* [29] with CaO catalyst using microwaves. Ravishankara, L., et al, silimarly, reported $Ce^{+3}$ catalyzed [30] preparation of aldimines. Bendale *et al* [31] have synthesized aldimines under UV chamber, sonicating conditions and employing grinding method [32]. Even one group, Suresh Patil *et al* [33] used green natural citrus fruit catalyst obtained from lemon juice.

## 1.6 Synthetic Strategies:

There are mainly two approaches to introduce C=N imine linkage in the macrochain of azomethine polymers.

i. The first approach is based on the reaction of monomeric dicarbonyl groups (i.e. dialdehydes and diketones) with diamines.
ii. The second approach involves the reaction of monomers having functional groups capable of polymerization with built in imine structure.

The C=N of polyaldimines is isoelectronic with C=C double bond, therefore this class of polymer is closely related to other classes of conjugated polymers, for example, poly(*p*-phenylene), poly(acetylene) [34, 35], poly(thiophene) [36] or poly(*p*-phenylene-vinylene) [37].

## 1.7 Solubility:

The key problem in wholly aromatic PAMs is their high softening (glass transition) temperatures ($T_g$) which makes them unsuitable for melt spinning [38] and injection molding techniques. Aromatic PAMs start to decompose before reaching their melting temperature [39]. Moreover, their insolubility and intractability [40] in common organic solvent being used for polymerization led to the development and design of architecture to modify the properties of macrochains by using different approaches. The most important approaches involve the use of symmetrically and unsymmetrically multisubstituted aromatics, incorporation of aliphatic spacers, flexible ether linkages, and substitution with alkyl as well as alkoxy side chains. Another approach to perk up the processability of PAMs is the reversible interaction or complexation with Lewis acids [41]. The figure 1.2 shows proposed H-bonding interactions responsible for PAMs solubility in acidic or weakly acidic solvents.

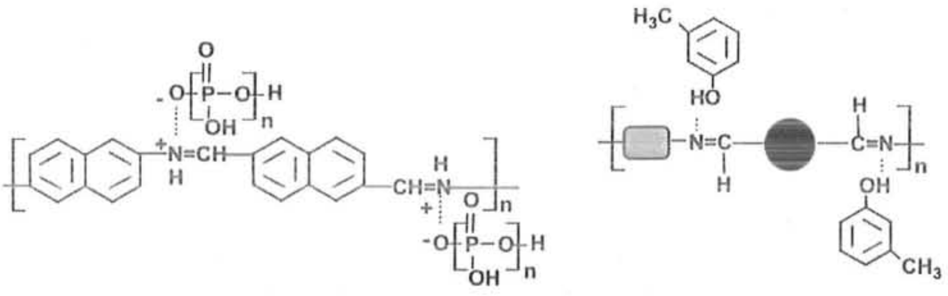


Figure 1.3: Proposed H-bonding Interaction with Acids

In most of the cases fully aromatic polyimines are insoluble. Modifying the π-conjugated chain by adding solubilizing entities disturb the delocalization of electron and results in disruption of intriguing properties of this class of conducting polymer. In recent years, the concept of utilizing cyclodextrin cavity for polymerization has been introduced [42] and this strategy has also been applied to PAMs for obtaining easily soluble rotaxanes [43]. Dhriti Nepal *et al* attempted to solublize PAMs obtained from 1,4-phenylenediamine and 1,4-diformylbenzene in β-cyclodextrin cavities but failed. They noticed that incorporation of C60 end capping and 3M excess of β-cyclodextrin afforded high molecular weight soluble rotaxane [44-47]. The effect of heteroaromatic rings, for example, triazine [48], thiazole, oxadialzole [49], fluorene, carbazole [50, 51] on solubility, electrochromic and electroluminescent properties of polymeric aldimines have been studied by different groups.

## 1.8 Synthetic Routes to Polyazomethines

### 1.8.1 Oxidative Polymerization:

Facile oxidative polymerization is usually carried out with sodium oxychloride (NaOCl) 30% solution as an oxidant in KOH or NaOH alkaline media. This polymerization technique is used for those monomers that have hydroxyl functional groups and built-in imine linkages within monomers as shown in figure 1.4. In this polymerization process 15% aqueous KOH of hydroxylated Schiff base monomers is heated at 90°C for 6 hours followed by dropwise addition of catalytic amount of NaOCl oxidant in 30 min and heating the mixture for further 6 hours [52].

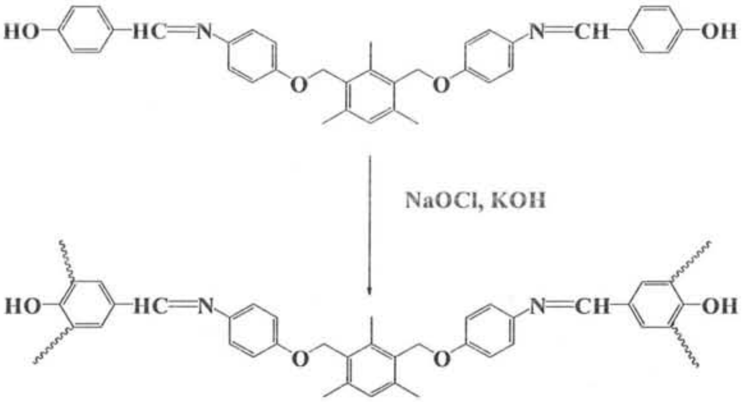


Figure 1.4: NaOCl oxidative coupling

Different oxidants ($FeCl_3$, ammonium persulfate, $H_2O_2$, and $O_2$) may be used for oxidative coupling reaction to yield polyazomethines. Figure 1.5 shows the coupling reaction carried out by $FeCl_3$ [53, 54].

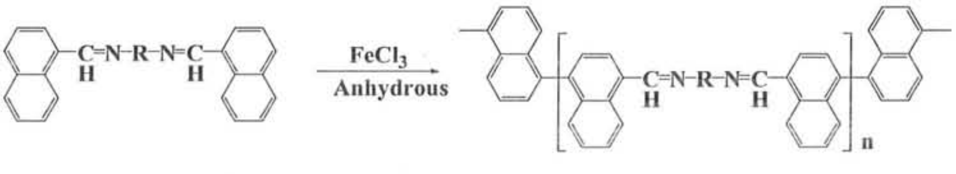


Figure 1.5: $FeCl_3$ oxidative coupling

## 1.8.2 Electropolymerization:

In a typical electrosynthetic polymerization method the two monomers are dissolved in freshly distilled DMAc. The electropolymerization is carried out using mercury pool as a cathode (working electrode), a reference saturated calomel electrode (SCE) with magnesium cylinder as an auxiliary electrode. The measurement is made in potentiostatic mode using $LiClO_4$ as an electrolyte and $NiBr_2$(bipy) as a catalyst. The precipitated polymer is worked out in dilute aqueous sulfuric acid solution and subsequently dried in vacuum oven at about 80°C. The bromide liberated in electrosynthesis is estimated with $AgNO_3$ to probe the electropolymerization [55]. This polymerization technique usually gives low molecular weight soluble polyaldimines.

### 1.8.3 Solvothermal Polymerization:

In a relatively new solvothermal polymerization process equimolar ratios of diamine and dialdehyde in a mixture of dioxane and mesitylene solvents are sonicated for ~30 min, then the sonicated mixture is transferred into autoclave along with catalytic glacial $CH_3COOH$. The heat treatment at desired temperature for specific time gives the polymeric aldimine. The resulting anisotropic, yolk-shell like, hollow sphere, or microtube polyaldimines are filtered [56].

### 1.8.4 Chemical Vapor Deposition:

Difficulty in finding appropriate organic solvent for uniform polymer film preparation accompanied with dust particles interference during electrical properties and non-uniform emission characteristics makes the chemical vapor deposition (CVD) a method of choice for the preparation of thin films of polymeric Schiff bases having uniformity [57] at centimeter level as well as linear and non-linear optical properties [58]. CVD is used to copolymerize the two monomers placed in separate cells in an effective and efficient way by evaporating the two monomers under reduced pressure. Therefore, CVD is also called vacuum deposition polymerization (VDP). The two monomers are heated to an appropriate temperature. The solvent free condensation of –CHO and $-NH_2$ groups results in the formation of high conjugation length –CH=N– linkages on top of various substrates such as fused $SiO_2$, Indium–Tin–Oxide (ITO) coated glass, and F–doped ITO etc [59].

Electric–Field–Assisted–CVD method can also be used for controlling the macroscopic characteristics of polymers. The limitation of Electric–Field–Assisted–CVD is that it has application restricted to only those monomers which have net dipole moment so that monomers can be aligned with external magnetic field [59].

### 1.8.5 Melt Polycondensation:

This method is seldom used because in most cases the polyaldimine formed do not melt before decomposition starts. Therefore, this method is not suitable for aromatic polyazomethines. In melt polycondensation reaction the two monomers (diamine and dialdehyde) are grounded in mortar–pestle and heated in micro–distillation tube under inert atmosphere until they melt. At the melting point the temperature of the melt is maintained for one hour [38].

## 1.8.6 Aza-Wittig Polymerization:

The aza-Wittig reaction is a reaction of phosphazenes with carbonylic compounds. Phosphazenes are prepared *in–situ* in the reaction mixture by reacting azide group with phosphorus (III) reagents [60] such as $PPh_3$ and $PMePh_2$ etc. The chemo-selectivity, high reactivity, and irreversibility [61] of this reaction make it a good choice for high molecular weight polymeric imine formation while other polycondensation reactions usually proceed reversibly. Therefore, Aza-Wittig Polymerization [62] is used for the synthesis of highly ordered regioregular polymeric $A_2B_2$-type or AB-type aldimine from monomer having either diazide and dicarbonyl groups or self-condensing azide and aldehyde group [63]. Figures 1.6 (a) and 1.6 (b) show the reagents, reaction conditions for AB-type, and $A_2B_2$-type aza-Wittig polymerization.

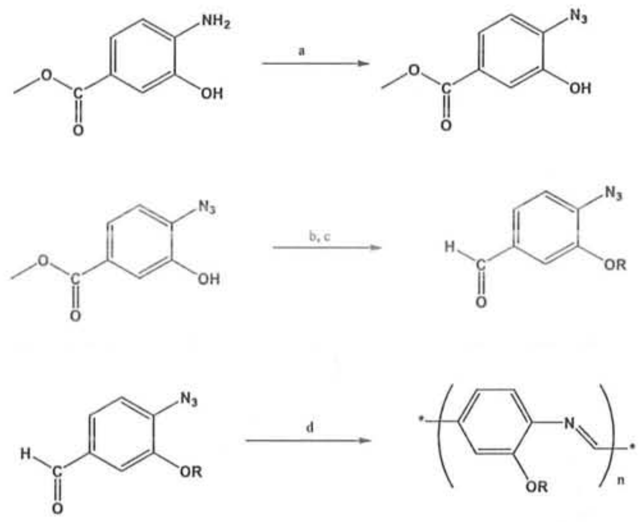


**Figure 1.6 (a): Synthesis of AB-type Polyaldimines; (a) $HNO_2$, $NaN_3$; (b) R–X, $K_2CO_3$; (c) DIBAL-H, $CH_2Cl_2$, -78°C, DMP, rt; (d) $PPh_3$, toluene, 80°C.**

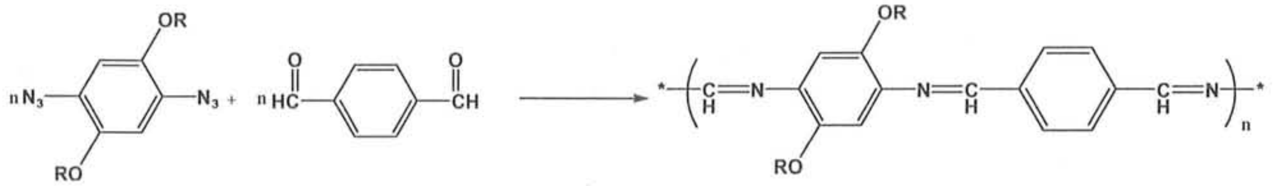


**Figure 1.6 (b): Synthesis of $A_2B_2$-type Polyaldimines; $PPh_3$, toluene, 80°C.**

### 1.8.7 Solution Polycondensation:

Polyazomethines begin to precipitate during polymerization process which obstructs their processability. The two most common approaches to tackle this problem are; (i) either introduce substituent groups on the monomers (ii) or use solvents that increase the solubility of the polymer by replacing the chain-chain intractions with solvent-chain intractions. The highly polar solvents are most suitable for that purpose and the weakly acidic solvents such as *m*-cresol are the best choice because they increase the solubility of macromolecule by forming hydrogen bonds with the lone pair of nitrogen atom of C=N imine linkage.

Different water free solvents, for example, benzene, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dichloromethane (DCM), *m*-cresol, hexamethylphosphoramide (HMPA), dimethylsulfoxide (DMSO), and polyphosphoric acid are used for polycondensation reaction of diamines and dialdehydes. The reaction between the dialdehydes and the diamines start with appreciable condensation occurring at room temperature that continues slowly as the polymer begins to precipitate or reaction mixture becomes thick paste like. The polyimine formation in high polarity solvent give high molecular weight macrochains of polyazomethines. However, high molecular weight imparts insolubility to polyazomethines in mostly used organic solvents which precludes their potential applications. It is worth mentioning that the polymer formation in polyphosphoric acid as a solvent increases the molecular weight of polyazomethines that is reflected by the 2-5 fold increase in their reduced viscosities. The azeotropic removal of water with toluene from condensation flask expedites the condensation process.

## 1.9 Types of Poly(azomethine)s:

### 1.9.1 Polyazines:

Polyazines (PAZs) is also a class of polymeric Schiff-bases family. Just like polyaldimines this family of imine polymers have –CH=N- and a direct N-N bond. PAZs are synthesized from different aliphatic or aromatic dicarbonylic molecules (dialdehydes or diketones) and hydrazine ($H_2N-NH_2$) using acid catalyzed condensation conditions. Research group led by Destri has synthesized a number of PAMs and PAZs containing thiophene units for optical waveguide materials [64].

Figure 1.7: Schematic reaction of PAZs

### 1.9.2 Poly(azomethine-siloxane)s:

Mirela-Fernanda Zaltariov *et al* (2014) used William-sons type reaction between 4-hydroxybezaldehyde and bis(chloromethyl)-dimethylsilane in DMF and potassium carbonate to form respective silicon containing bis-aldehyde. The condensation reaction of bisaldehyde with 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole produced the corresponding PAM [65, 66].

P. Budrugeac *et al* (2008) studied the thermal stability and thermo-oxidative reactivity of polyimines synthesized from bis(formyl-4-phenoxymethyl)-tetramethyldisiloxane and different bisamines. They showed that the thermal stability of poly(siloxane-imine)s depend upon the number of aromatic rings, and aliphatic chain lengths [67, 68].

### 1.9.3 Poly(azomethine-ether)s:

Poly(azomethine-ether)s are prepared from either ether containing monomeric bisaldehydes or bisdiamines as shown by different research groups [69-72] or they may be synthesized by the nucleophlic aromatic substitution ($S_{Ar}N$) of halide (-X = F, Cl etc.) from monomer having built-in aldimine linkage [73].

### 1.9.4 Poly(azomethine-ester)s:

Poly(azomethine-ester)s are usually prepared from the reaction of imine mesogen containing diols with dicarboxylic acids or dicarboxylic acid chlorides [74-77]. They have also been shown to have LC properties. E-Joon Choi in 2010 reported that the bent core mesogens in poly(imine-ester)s derived from different 1,2-substitued phenols show V-shaped mesogens that give chiral smectic phase LC [78].

### 1.9.5 Poly(azomethine-ether sulfone)s:

Synthesis of poly(azomethine-ether sulfone) involves the treatment of bis–(4–chlorophenyl) –sulfone with bis–hydroxy monomer having azomethine link using DMSO solvent and potassium carbonate anhydrous [79, 80].

### 1.9.6 Poly(azomethine–urethane)s:

The synthetic strategy for this class of carbamate poly(azomethine)s is based on the reaction of diols monomer (having azomethine linkage) with di–isocyanate to yield poly(azomethine–urethane)s [81, 82].

### 1.9.7 Polyazomethine – Dopant Interaction:

The interaction of lone pair of electron on nitrogen atom of imine (C=N) renders polyimines doped with different metal salts and acids i.e. complexation with metals or Bronsted acids and Lewis acids. Nitrogen's electron pair interaction with dopant gives flexibility to polymer films, shift in glass transition temperatures, and emission band shifting in photoluminescence spectrum. The doping with Bronsted acids give bathochromic shift to polyimine spectra. The interaction with Bronsted acids is reversible. The exposure of polyimine films with HCl vapors give a bathochromic shift while the exposure of same film with ammonia vapors shows a reversible effect [83].

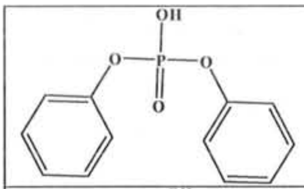
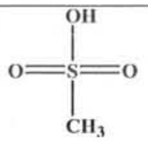
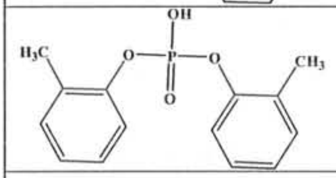
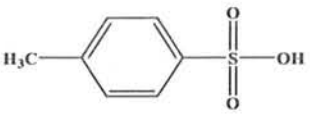
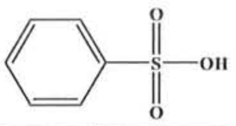
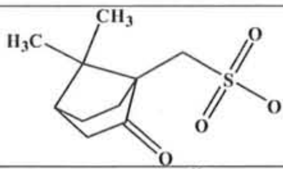
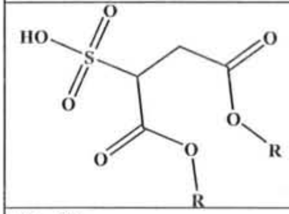
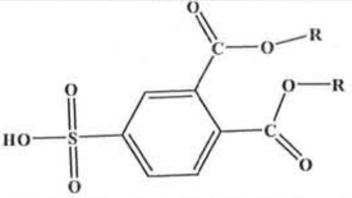
Usually insoluble in most common organic solvents polyazomethines can be made soluble in nitrobenzene or nitromethane by complexing with Lewis acid i.e. $AlCl_3$, $GaCl_3$. The solublization of polyazomethines helps in detailed investigation and characterization i.e. UV-visible, NMR, photoluminescence etc.

Different dopants (iodine, $FeCl_3$, UV, $AgNO_3$, HCl, Lewis acids, $Cl_2$, $Br_2$, polyaniline, $GaCl_3$, $AlCl_3$, $SnCl_2$, methanesulfonic acid, 10-camphorsulfonic acid, benzenesulfonic acid, *p*-toluenesulfonic acid and other organic acids) [84] have been utilized for doping of polyaldimines. To see the structural changes in polyazomethines after doping [85] with different oxidants FT-IR, and UV-visible spectral analyses are the best option. For example, the FT-IR spectra of polyazomethines doped with hydrochloric acid and $I_2$ can be compared. The spectral changes in doped PAMs showed that the mechanism of doping with HCl and $I_2$ is different. The peaks at ~1565 and ~1157 $cm^{-1}$ are assigned to PAM's complex with $I_2$ whereas the spectra of HCl doped PAMs give same peaks as undoped polymer [86]. This infers that oxidation process play pivotal role in $I_2$ doping while $-CH=NH^+$ iminium entity do not appreciably change major IR peaks of pristine polyaldimine. Moreover, iodine binds firmly with PAM and hence is difficult to escape while HCl vaporizes [87].

Similarly, doping mechanism is also studied by UV-visible spectroscopy. Protonation of polymeric aldimines by diverse dopants like sulfonic acid derivatives, alchohols, phenol, and halogenated hydrocarbons can be studied by FT-IR which demonstrates the electron-withdrawing or electron-donating characteristics. The conjugational changes upon protonation are based on the fact that delocalization of lone pair of nitrogen causes reduction in C=N bond order, hence lowering the force constant of –CH=N– group. Consequently, the stretching vibrations of these groups in polymer are observed at lower frequencies. The non-conjugated polyimines show stretching C=N vibrations at ~1675 to 1665 $cm^{-1}$ whereas conjugation with aryl moiety causes a shift of C=N stretchings to ~1630 $cm^{-1}$ [88].

Since many polyaldimines are insoluble in representative organic solvents leading to their refusal as potential candidates for quite a few applications. Co-ordination complexes of aromatic polyaldimines with $AlCl_3$ or $GaCl_3$ can be solublized in $CH_3NO_2$ and $Ph\text{-}NO_2$. Yang *et al.* [89] used di-3-cresyl-phosphate and diphenylphosphate for protonation of aldimines in *m*–cresol or HCOOH. A few of sulphonic acid based dopants and metal chlorides are listed in table 1.1.

**Table 1.1: List of Acidic Dopants for Polyazomethine**

| | |
|---|---|
|  |  |
|  |  |
|  |  |
|  |  |
| $SnCl_2$ | $AlCl_3$, $GaCl_3$ |

## 1.10 Applications of Polyazomethines:

Polyazomethines are conjugated class of organic polymers that are well known for their admirable properties such as good mechanical strength, high thermal stability, electrochromism [71], optoelectronics, electroluminescence, photoluminescence [90], electrical conductivity [91], and fiber forming applications. Their properties have been investigated for the development of large-area display organic polymer light emitting diodes (PLEDs) [92]. They are being tuned for use in organic photovoltaic devices [93], polymer solar cells (PSCs) [94] and other future energy applications. An interesting application in this regard is the production of hydrogen ($H_2$) from water using 4,4′-diaminotriphenylamine [95] based monomer. PAMs have applications in liquid crystals [96], non–linear optics [97], resistive switching [98], information storage [99], thin film formation, and laminates that are chemically resistant [100]. Conjugated poly(Schiff base)s have been synthesized by chemical vapor deposition [58] method using low pressure evaporation. PAMs have been extensively studied for their application as an active layer and/or hole-transport materials [101] in electroluminescent devices. Novel polyimines based on 4,4′-diaminotriphenylamine prepared by Niu have been tested as electron-hole transport materials [102] in electroluminescent devices. Currently, polyazomethines employing triphenylamine moiety are being tested for thin film formation [57], organic photovoltaics [93], solar cells [103], carbon nanosphere formation, and a variety of other applications ranging from electronics to photo- and optoelectronics [104].

### 1.10.1 Polymer Solar Cells (PSCs):

For the performance of PSCs the molecular energy levels and band gap are of critical importance. Tuning the band gap and molecular energy levels of conjugated polyimines are effective for organic photovoltaic (OPV) device efficiency. The major reason for low efficiency of PSCs is the disparity between solar irradiance spectrum and absorption spectrum. The PSC based on polymer that provides a better overlap of absorption spectrum with solar irradiance spectrum is superior for device fabrication. Another important reason for low efficiency of PSCs is that the molecular energy levels are not ideal yet, and a great deal of energy is lost during photon-electron conversion [105, 106].

Atsushi Kimoto and his coworker [107] synthesized low band gap polymer based on bulk hyperconjugation (BHC) strategy with phenylazomethine moiety as appending group for OPV device fabrication. One of the most effective methods for increased photoconversion efficiency is to broaden the absorption wavelength range of active layer and perk up short-circuit current. Intramolecular charge transfer between electron-donor and electron-acceptor species broaden the light absorption range. They reported that the open circuit voltage of OPV device clearly increased upon complexation of imine nitrogen with $SnCl_2$. This showed that the electronic state of active polymer layer changed upon complexation with phenylazomethine behaving as metal ion collector and preventer of $SnCl_2$ aggregates formation under large polarity.

Longbin Qiu [2014] synthesized carbon cactus-like nano-structures having high surface area from chemical decomposition of polyazomethines and used them as counter electrode prepared by solution casting on F-doped ITO glass for photovoltaic cells. The cell prepared from these carbon nano-spheres showed a considerably high conversion efficiency upto 7.5% [108].

### 1.10.2Liquid Crystalline (LC) Polymers:

The long rod like rigid structures in a macromolecule having aromatic moieties bonded directly or indirectly with a variety of linkages, is well known to induce a property called liquid crystalline (LC) behavior on thermal scanning or alternatively in highly concentrated solution.

Amid different linkages present in LC the C=N aldimine bond is a prototype. These aldimine linkages built into macromolecular chain will either induce or promote the formation of phases called mesophase formation upon changes in temperature. This is called thermotropic LC. And if mesophase formation occur at different suitable concentrations in an appropriate solvent then this is called lyotropic LC [109].

Dimer based [110] and low weight molecular LC as well as polymeric LC have variety of technological uses owing to their ability of self-assembling into mesophase. However, the investigations for newer materials that exhibit LC characteristics is still an active research area of polymeric aldimines. The synthesis of thermotropic polyimines with reasonable softeneing temperatures (called glass transition temperature, $T_g$) has been the main objective of various research groups. Pioneering work done at DuPont chemical industry revealed that $T_g$ can be favorably lowered either by introducing flexible spacers or lateral substituents in the macromolecular chain, and hence effectively form mesophases.

LC polymers combine the physico-chemical texture of polymers with those of liquids. Depending upon the mesogenic units present in polymeric macrochains, polymers have been classified as main-chain LC (MC-LC) and side-chain LC (SC-LC). MC-LC are characterized by rigid, rod like stiff regions whereas SC-LC have three different structural elements; the mesogen, the backbone, and the spacer. The poly(azomethine-ether)s form a class of thermotropic LC that form ordered alignment on heating.

The liquid crystals based on polymeric aldimines was first reported by Skoulios and Guillon from 4,4′-diformyl-α,ω-diphenoxydecane and benzidine [111]. They also used 4,4′-diamino-α,ω-diphenoxyalkanes with benzene-1,4-dicarboxaldehyde for the synthesis of liquid crystals polyimine. Similarly 4,4′-diamino-α,ω-diphenoxyalkanes were used with 1,4-phenylenediamine by Li Chang [70] for the synthesis of azomethine-ethers. The liquid crystalline properties of macromolecular imines were observed with diphenoxyalkane spacers as a function of chain length. Nematic mesophases were found to exist in ether based polyazoimines (as shown in figure 1.8) over an ample range of temperature as observed in DSC and optical microscopy (OPM).

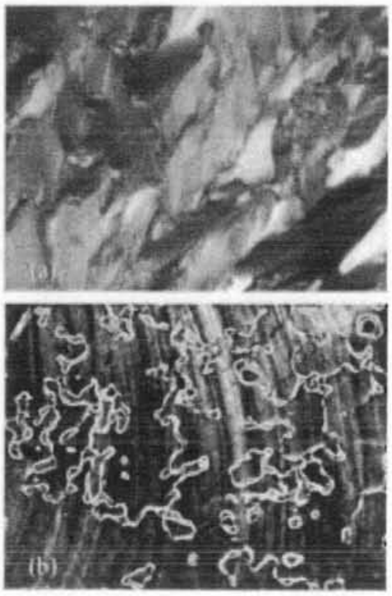


**Figure 1.8: (a) Broken conic texture, (b) thread like texture [112]**

Aly *et al* synthesized dibenzylidine based LC [113], while Jiayanthi and Kishore [114] prepared hydroxyl functionalized LC. Similarly, metal containing LC showing nematic mesophase have been attempted from hydroxyl group containing polyazoimines. Hamman and Aly synthesized a new series of LC with cyclopentanone and cyclohexanone [115, 116] using different bisaldehydes in EtOH and potassium hydroxide. Choi *et al* [117] in 2004 synthesized banana shaped mesogenic polyaldimines from different bisamines plus dialdehydes that showed nematic LC texture on heating from $T_m$ = 120-224°C.

### 1.10.2.1 LC-PAMs –Main Chain Imine Bond:

Adell and coworkers [118] reported a series of semi-flexible homo- as well as co-polymeric aldimines based on hydroxyl group containing mesogenic cores and or aliphatic spacers. They explored mesomorphic behavior and thermal characteristics by OPM and DSC. During heating of polyaldimines, exclusive homopolmers prepared from 4-methyl-*m*-phenylenediamine showed nematic mesophase while poly(Schiff base)s having aliphatic two methylene carbons and *p*-phenylene units instead of showing mesophase destruction of chains close to their melting temperature (at 333°C) occurred. The exhibition of mesophases is more favorable, on the other hand, with increasing spacer length that results in decrease of $T_g$.

### 1.10.2.2 LC-PAMs –Side Chain Imine Bond:

Mesogenic LC polazomethines may be prepared from mesogen entities bonded to main chains. Sometimes, these type of macromolecules are called comb like LC. Cano and his co-workers have reported photoinitiation and thermal polymerization of imine monomers having terminal vinyl ether or methacrylate groups. Corresponding metal complexes of these monomers and polymers showed smectic mesophases.

## 1.11 Polyazomethines Chelates:

The complexation capability of azomethine groups with diverse metal ions gives an ample diversity of possible applications [119]. The embeded transition metals in polyaldimine not only influences its chemical activity but also its physical features. For instance, Kaliyappan *et al.* [120] used polyimine matrix for complexation of diverse metal ions ($Mn^{+2}$, $Co^{+2}$, $Cu^{+2}$, $Ni^{+2}$, and $In^{+2}$) [121]. He proposed the use of polyacrylic acid's matrix functionalized with azomethine linkages for removal of waste water metal content.

Likewise, a probable application of chelating azomethines is in selective removal of costly metal ions from sea water and or waste water. Hashemi *et al.* [122] used S-containg azomethine for pre-concentration and selective separation of $Pb^{+2}$ traces from other ions ($Na^{+1}$, $K^{+1}$, $Co^{+2}$, $Cd^{+2}$, $Cu^{+2}$, $Ca^{+2}$, $Zn^{+2}$, $Hg^{+2}$) [123, 124]. Noticeably, the likelihood of removing of $Pb^{+2}$ metal traces is extremely significant in environmental safety owing to its toxicity effect. Similarly, polyvinylchloride (PVC) matrix having dispersed azomethine compounds can be employed as ion-selective electrodes (ISEs) [125]. Potentiometric sensors functionalized with azomethine groups as an ion carrier has been reported to show exceptional selectivity [121] for metal ions. The host-guest cavity and geometric control by azomethine unit provides modeling of membrane lipophilicity and complexation, thus leading to (for a specific ion) exceptional stability, sensitivity plus selectivity [126]. For instance, Jeong *et al.* [127] designed membrane electrodes for $Pb^{+2}$ ions from a PVC and azomethine mixture using tetra-(4-chlorophenyl)borate ionophore in the presence of additives and plasticizers. Ionophore affects the selectivity of ISE while plasticizer influence the lipophilicity for metal complex and ionophore mobility. The ionophore having built in pyridine and bis(salicylidene) show incomparable selectivity for $Pb^{+2}$ ions against other interfering ions ($Ba^{+2}$, $Cu^{+2}$, $Sr^{+2}$, $Zn^{+2}$, $Cd^{+2}$, $Ce^{+2}$, $Mn^{+2}$, $Co^{+2}$, $Mg^{+2}$, $K^{+1}$, $Na^{+1}$, $Ag^{+1}$, $Rb^{+1}$,$Cs^{+1}$) [128-131]. All the miscellaneous ions tested showed selectivity coefficient $10^{-3}$ or smaller (with exception of $Cu^{+2}$). This indicates that other ions wouldn't perturb to any appreciable extent the working of $Pb^{+2}$ ion electrodes [132].

## 1.12 Opto(electronic) Properties of PAMs:

Polymeric azomethine macromolecules are thermostable polymers with appealing properties for opto(electronic) applications . The modulation of polyimines' optical absorption by chemical environment or exertion of potential contributes a pivotal role in their application in optoelectronics. Opto(electronic) properties of polyaldimines include thermochromism, electrochromism [133], acidichromism, solvatochromism, electrochromism [134], thermoluminescence [135] non-linear optics [136], and photoluminescence. Amid the massive family of polyaldimines, the macrochains with triphenylamine units (either derived from diformyl or diamine) are incredibly striking materials for hole-transport candidates used in opto(electrical) applications. The isoelectronic C=N with C=C is also planar, that shows optical behavior. Ability to capture $H^+$, and coordinate with metals makes them apposite to conjugated polymers (polyacetylene, polyflurenes, PPV and polythiophene etc.) for number of opto(electronic) applications including pH and ion sensors [137, 138], organic light emitting diodes, polymer based photovoltaics, molecular wires [139], and non-linear optical devices. It is expedient to synthesize polyaldimines by polycondensation of amine and carboxaldehyde. Moreover, their purification is relatively easier. They can be purified with Soxhlet extraction and reduced pressure drying. Other π-extended conjugation polymers syntheses necessitate expensive monomer, stern conditions, and noble catalysts. High thermal stability, and purposeful end capping is advantageous to other conductive macromolecules. Niu *et al.* [140], for example, studied polyaldimines created from 4,4′-bisaminotriphenylamine and 1,4-benzenedicarboxaldehyde or ethanedial. The easy oxidation of triphenylamine (TPA) moiety at central nitrogen makes them exceptional charge transport carriers through the cation radical species ($N^{+\cdot}$). Therefore TPA based azomethines have been studied and applied in numerous materials, for example, OLEDs [92], organic field–effect transistors [141], sensors [26], dye sensitized solar cells, and large area displays. The investigations of Lio *et al* since 2005 are focused on TPA based polymeric amides, imines and imides series for striking electrochromic properties.

It is established that the macromolecules with TPA units show steady electrochromic features, and the inclusion of electron-donating lateral substituents at the para–positions of TPA give stable cationic radicals. The imine's nitrogen lone pair in the backbone of polyaldimine can form intra– or inter–molecular bondings, undergo protonation as well as complexation with metal cations, $I_2$ and acids. Therefore, polyazomethines show distinguished optical properties.

Polycondensation of mono- and di-ether based aromatic bisaldehydes with aromatic bisamines require inert atmospheric conditions since the azomethine linkage is moisture sensitive. The purity of chemicals used, solvents, and monomers is especially important for obtaining polyazomethines of desired purity. This chapter illustrates the chemicals used, purification of solvents, methods employed for synthesis of mono-ether linked and di-ether linked aromatic bisaldehyde, synthesis of aromatic polyazomethines as well as the techniques and instrumentations used for characterization of monomeric/polymeric materials.

## 2.1 Reagents and Chemicals:

The reagents and chemicals used in the synthesis of monomers and poly(azomethine)s were of high purity. Hydroquinone (1,4-dihydroxybenzene), resorcinol (1,3-dihydroxybenzene), pyro-catechol (1,2-dihydroxybenzene) were obtained from Merk (Germany) whereas 4-fluorobenzaldehyde, 4,4′-dihydroxybiphenyl, Bisphenol A, (1,1,1,3,3,3-hexafluoro)–bisphenol propane, 4–hydroxy–3–methoxybenzaldehyde, 4–hydroxy–3–ethoxybenzaldehyde, and 4-hydroxybenzaldehyde were obtained from Fluka (Switzerland). The chemicals $K_2CO_3$ anhydrous, 1,4-phenylenediamine, 4,4′-diaminodiphenyl ether, tetrabutylammonium perchlorate (TBAP), benzophenone, $P_2O_5$, calcium chloride, magnesium turnings, calcium hydride, *p*-touene sulfonic acid and iodine crystals were purchased from Aldrich company (Germany). The solvents *n*-hexane, dimethylsulfoxide, and diethyl ether were Merk's company (Germany) while chloroform, ethylacetate, toluene and dichloromethane were obtained from Panreac (Spain). The ethanol, methanol, and *N,N*-dimethylformamide were purchased from Deijing (Korea) whereas hydrochloric acid, chloroform, sulfuric acid and ethyl acetate were obtained from Riedel-de-Haen (Germany).

## 2.2 Drying of Solvents:

Solvents were dried by distillation of solvents either under reduced pressure or at atmospheric pressure using distillation assemblies. Water content of solvents was minimized by employing standard procedures [1].

**2.2.1 Chloroform ($CHCl_3$),** (b.p. 61.2°C/760 mmHg) was pre-dried on $CaCl_2$ and then refluxed over $P_2O_5$.

**2.2.2 Dichloromethane ($CH_2Cl_2$),** (b.p. 40°C/760 mmHg) was dried by refluxing with $MgSO_4$ anhydrous for 3-4 hours before collecting the distillate.

**2.2.3 Ethyl acetate (EtOAc),** (b.p. 77.1°C/760 mmHg) was pre-dried over $MgSO_4$ before reflux with $P_2O_5$.

**2.2.4 Absolute Ethanol,** (b.p. 78°C/760mmHg) was dried by refluxing in the presence of Mg turning using $I_2$ crystals as indicator. The dried ethanol was collected on $I_2$ color discharge.

**2.2.5 Methanol,** (b.p. 64-65°C/760 mmHg) was pre-dried over $CaH_2$ for overnight by stirring followed by refluxing with Mg turnings using $I_2$ crystal as an indicator.

**2.2.6 Diethyl ether,** (b.p.64.5°C/760 mmHg) was distilled with sodium metal wires employing benzophenone as an indicator [1]. Stored the dried diethylether over molecular sieves.

**2.2.7 *n*-Hexane,** (b.p. 68.7°C/760 mmHg) was predried overnight over $CaH_2$ followed by distillation with sodium metal wires in the presence of benzophenone indicator.

**2.2.8 *N,N*-Dimethylformamide (DMF),** (b.p. 153-154°C/760 mmHg), $CaH_2$ was used for drying of DMF. It was stirred for 12 hours in the presence of $CaH_2$. Then vacuum distillation was performed.

## 2.3 Instrumentation and Analytical Techniques:

### 2.3.1 Melting Point Determination:

Melting points of monomers were examined with Mel-temp, (Mitamura Riken kogyo, Inc Tokyo, Japan) apparatus with capillary tube method. The m.p. of reactants were also determined to confirm/check the purity/decomposition.

### 2.3.2 FT-IR Spectroscopic Measurements:

Direct sampling by ATR technique on Perkin Elmer Spectrum One (Ver. B) was used to obtain solid state Fourier Transform Infrared (FT-IR) spectra.

### 2.3.3 NMR Spectroscopic Measurements:

$^1H$- and $^{13}C$-NMR spectra of bisaldehydes and polyazomethines were measured on Bruker 300 MHz & 75 MHz Ultrashield Spectrophotometer using deuterated solvents ($CDCl_3$, DMSO-$d_6$, and $D_2SO_4$).

### 2.3.4 UV-visible Spectroscopic Measurements:

The UV-visible spectra of monomers and polyimines were measured on Schimadzu-1700 UV using $CHCl_3$, DMF and sulfuric acid.

### 2.3.5 Fluorescence Spectroscopic Measurements:

Fluorescence spectra of the polyazomethines were measured on Perkin Elmer Ls 55 bu instrument using single glass cell.

### 2.3.6 Viscometric Measurements:

The viscosities of polyazomethines were determined at room temperature employing U-tube Ubbelhode viscometer with 20 mL solutions.

### 2.3.7 Thermogravimetric Analysis:

Thermo gravimetric analysis was run on Perkin Elmer TGA-7 instrument at heating rate of 10°C/min upto a maximum 650-700°C.

### 2.3.8 Differential Scanning Calorimetry (DSC):

DSC studies were performed employing Mettler Toledo DSC 823e instrument at heating rate of 10°C per min in $N_2$ atmosphere.

### 2.3.9 WAXRD Analysis:

Wide-angle X-ray diffraction measurements of powdered polymers were done on Philips 3040/60 X'Pert Pro diffractometer having Cu anode with-K$\alpha$ radiation source.

### 2.3.10 Electrical Conductivity Measurements:

The electrical conductivity ($\sigma$) of polyazomethines was measured with Keithley source meter 2400.

## 2.4 Synthesis of Monomers:

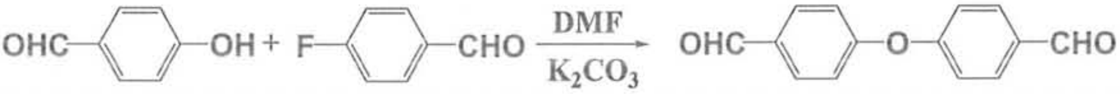
### 2.4.1 General Synthesis of Mono-ether Based Aromatic Dialdehydes:

In a typical mono-ether based monomer synthesis; phenol (1 equivalent) and anhydrous potassium carbonate ($K_2CO_3$) (1.1 equivalent) in an appropriate amount of *N,N*-dimethylformamide (DMF) solvent were added to 250 mL prebaked round bottom flask (RBF). Heated the reaction contents for about 1-2 hours at 80-90°C under inert atmosphere followed by cooling to about 40°C. Then 1 equivalent of 4-fluorobenzaldehyde was added. Continued the stirring for 45 min, followed by refluxing the mixture for 25 hours at 154°C. Different ratios of ethylacetate (EtOAc) and *n*-hexane were used to monitor the reaction via thin layer chromatography. Upon completion of reaction, poured the contents of reaction flask into 300 mL ice cold water and neutralized the base with 10% hydrochloric acid (HCl) solution. The precipitated monomers were filtered through filter paper. Then, recrystallized the collected precipitates with ethanol/ethyl ethanoate/$CHCl_3$ mixtures in appropriate ratios. After re-crystalization monomers were dried in vacuum oven and saved for polymerization.

#### 2.4.1.1 Synthesis of 4,4'-diformyldiphenyl ether (ODF):

The 250 mL prebaked round bottom flask was equipped with magnetic stirrer and charged with 3.05 g (0.025 moles) of 4-hydroxybenzaldehyde and 4.0 g (0.029 moles) anhydrous potassium carbonate ($K_2CO_3$) in 45 mL dried *N,N*-dimethylformamide (DMF). Gently heated the mixture for 1.5 hour at 80-90°C under dry nitrogen ($N_2$) atmosphere. Then cooled the mixture flask to about 40°C followed by the addition of 4-fluorobenzaldehyde (2.68 mL, 0.025 moles). After addition of 4-fluorobenzaldehyde continued the stirring under nitrogen atmosphere. Heated the mixture to reflux in paraffin oil bath for 25 hours with regular monitoring of product formation via TLC using ethyl ethanoate & *n*-hexane mixtures. When the reaction completed, cooled down the flask to room temperature followed by pouring in 300 mL ice cold water. Excess base was neutralized by adding 10% HCl dilute solution. Filtering through filter paper, washing with $H_2O$, drying in oven and then recrystalization followed by drying afforded the mono-ether based aromatic dialdehyde named as 4,4'-diformyldiphenyl ether. FT-IR ($\upsilon$= $cm^{-1}$): 3065 $cm^{-1}$ (aromatic C-H str.); 2819, 2731 $cm^{-1}$ (aldehydic C-H str.); 1675 $cm^{-1}$ (carbonyl str.); 1581, 1494 $cm^{-1}$ (aromatic C=C);

1236 cm$^{-1}$ (C-O-C ether): $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta$ = 9.99 ppm (s, 1H, -CHO), 7.95 ppm (d, 2H, $J$ = 8.4 Hz), 7.20 ppm (d, 2H, $J$ = 8.4 Hz).

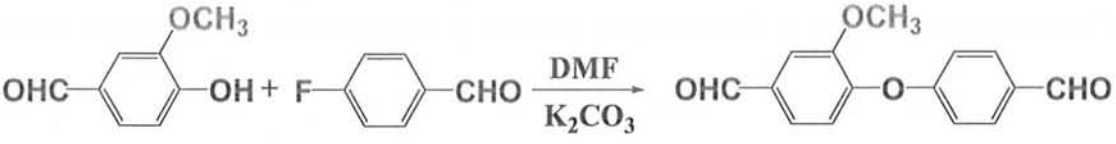


**4,4'-diformyldiphenyl ether**

**(ODF)**

**2.4.1.2 Synthesis of 2-methoxy-4,4'-diformyldiphenyl ether (MDF):**

The two necked round bottom flask 250 mL equipped with magnetic stirrer was charged with 2.5 g (0.016 moles) of 3-methoxy-4-hydroxybenzenecarboxaldehyde (or vanillin) and 2.5 g (0.018 moles) anhydrous potassium carbonate ($K_2CO_3$) in 45 mL dried *N,N*-dimethylformamide (DMF). Heated the mixture for 1.5 hour at 80-90°C on hot plate under dry nitrogen atmosphere. Then low downed the mixture temperature to about 40°C followed by the addition of 4-flourobenzenecarboxaldehyde (1.77 mL, 0.016 moles). The remaining procedure was same as mentioned in ODF synthesis. FT-IR ($\upsilon$= cm$^{-1}$): 3066 cm$^{-1}$ (aromatic C-H str.); 2978, 2928 cm$^{-1}$ (aliphatic C-H str.); 2860, 2759 cm$^{-1}$ (aldehydic C-H str.); 1680 cm$^{-1}$ (carbonyl str.); 1581, 1497 cm$^{-1}$ (aromatic C=C); 1235, 1208 cm$^{-1}$ (C-O-C ether): $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta$ = 9.97 (s, 1H, -CHO), 9.95 (s, 1H, -CHO), 7.89 (d, 2H $J$ = 8.4 Hz), 7.58 (s, 1H), 7.53 (d, 1H, $J$ = 8.1 Hz), 7.08 (d, 2H, $J$ = 8.4 Hz), 7.21 (d, 1H, $J$ = 8.1 Hz).

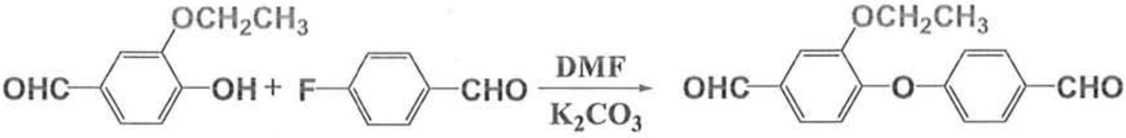


**2-methoxy-4,4'-diformyldiphenyl ether**

**(MDF)**

**2.4.1.3 Synthesis of 2-ethoxy-4,4'-diformyldiphenyl ether (EDF):**

A prebaked 250 mL round bottom flask equipped with magnetic stirrer was charged with 2.75g (0.016 moles) of 3-ethoxy-4-hydroxybenzenecarboxaldehyde and 2.5g (0.018 moles) anhydrous potassium carbonate ($K_2CO_3$) in 45 mL dried *N,N*-dimethylformamide (DMF). Heating was maintained for 1.5 hour at 80-90°C under dry nitrogen ($N_2$) atmosphere. Then cooled the mixture flask to about 40°C followed by the addition of 4-flourobenzaldehyde (1.77 mL, 0.016 moles). The rest of the procedure was same as mentioned for ODF monomer. FT-IR ($\upsilon$= $cm^{-1}$): 3063 $cm^{-1}$ (aromatic C-H str.); 2973, 2930 $cm^{-1}$ (aliphatic C-H str.); 2828, 2736 $cm^{-1}$ (aldehydic C-H str.); 1687 $cm^{-1}$ (carbonyl str.); 1577, 1497 $cm^{-1}$ (aromatic C=C); 1268, 1227 $cm^{-1}$ (C-O-C ether): $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta$ = 9.96 (s, 1H, -CHO), 9.94 (s, 1H, -CHO), 7.88 (d, 2H, $J$ = 8.7 Hz), 7.52 (d, $J$ = 8.1 Hz), 7.54 (s), 7.23 (d, 1H, $J$ = 8.1 Hz), 7.07 (d, 2H, $J$ = 8.7 Hz).



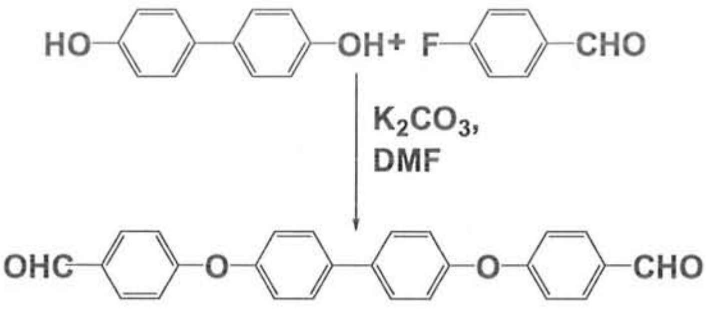
**2-ethoxy-4,4'-diformyldiphenyl ether (EDF)**

### 2.4.2 General Synthesis of Di-ether Based Aromatic Dialdehydes:

In a typical monomer synthesis; dihydroxyphenol (1 equivalent) and anhydrous potassium carbonate ($K_2CO_3$) (2 equivalents) in appropriate *N,N*-dimethylformamide (DMF) were added in 250 mL prebaked round bottom flask. Heated the reaction contents for about 1-2 hours at 80-90°C under inert atmosphere followed by cooling to about 40°C. Then 2 equivalents of 4-fluorobenzenecarboxaldehyde were added. Continued the stirring for 45 min, followed by heating the mixture for 50 hours at 154°C. TLC was run in ethylacetate (EtOAc) and *n*-hexane in different ratios to observe the reaction progress. Upon completion of reaction poured the contents of reaction flask into 350 mL ice cold water. After neutralizing the base with 10% hydrochloric acid solution collected the precipitates. Filtering through filter paper, washing with $H_2O$, drying in oven and then recrystalization with ethanol/ethylacetate/chloroform mixture followed by drying afforded the di-ether based aromatic bisaldehydes.

### 2.4.2.1 Synthesis of 4,4′-di[(4-formylphenyl)oxy]biphenyl (BPDF):

To a 250 mL prebaked round bottom flask transferred magnetic stirrer, 2.3 g (0.013 moles) biphenyl-4,4′-diol and 4.0 g (0.029 moles) and anhydrous potassium carbonate ($K_2CO_3$) in 50 mL dried *N,N*-dimethylformamide. Heated the mixture for 50 min at 80-90°C under dry nitrogen, $N_2$, atmosphere to form potassium salt of diol. Then cooled the mixture flask to about 40°C followed by the addition of *p*-flourobenzaldehyde (3.0 mL, 0.026 moles). Continued the stirring for 45 min, followed by heating the mixture for 50 hours at 154°C under refluxing conditions. TLC in ethylacetate and *n*-hexane in 1:1 ratio was utilized for monitoring the reaction. Upon completion of reaction poured the contents of reaction flask into 350 mL ice cold water and neutralized the base with 10% HCl solution. Filtered the precipitates of BPDF monomer. Recrystallized the precipitates with ethanol/ethyl ethanoate mixture. Yield, 84%, m.p. 160°C. FT-IR ($\upsilon$= $cm^{-1}$): 3062 $cm^{-1}$ (aromatic C-H str.); 2812, 2712 $cm^{-1}$ (aldehydic C-H str.); 1688 $cm^{-1}$ (carbonyl str.); 1592, 1487 $cm^{-1}$ (aromatic C=C); 1250, 1207 $cm^{-1}$ (C-O-C ether): $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta$ = 9.94 (s, 1H, -CHO), 7.98 (d, 2H, $J$ = 8.7 Hz), 7.80 (d, 2H, $J$ = 8.7 Hz), 7.27-7.21 (dd, 4H, $J$ = 8.7 Hz).

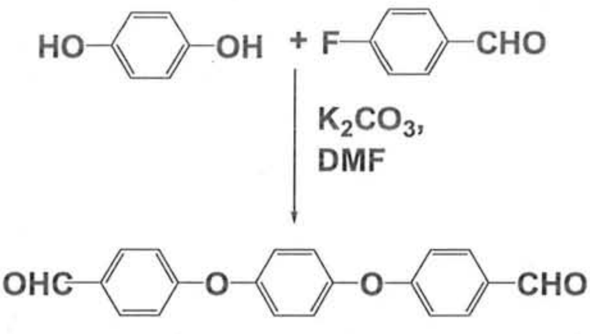


4,4′-di[(4-formylphenyl)oxy]biphenyl (BPDF)

### 2.4.2.2 Synthesis of 4,4'-[1,4-phenylene-*bis*-oxy]*bis*-benzenecarboxaldehyde (HDF):

The same procedure was followed for HDF. In a 250 mL two necked round bottom flask equipped with magnetic stirrer added 2.75 g (0.025 moles) hydroquinone and 8.0 g (0.06 moles) anhydrous potassium carbonate with 60 mL dried DMF. The mixture was heated for 1 hour at 80-90 °C under inert atmosphere. Then cooled the mixture flask to about 40°C followed by the addition of 4-flourobenzaldehyde (6.0

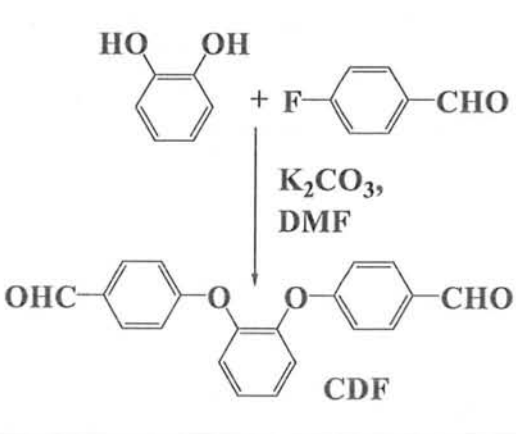
mL, 0.06 moles). The rest of the procedure is same as mentioned in general procedure for di-ether based dialdehydes. Yield, 91%, m.p. 153-155°C. FT-IR (υ= $cm^{-1}$): 3029 $cm^{-1}$ (aromatic C-H str.); 2727 $cm^{-1}$ (aldehydic C-H str.); 1692 $cm^{-1}$ (carbonyl str.); 1599, 1489 $cm^{-1}$ (aromatic C=C); 1225, 1187 $cm^{-1}$ (C-O-C ether): $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta$ = 9.95 (s, 1H, -CHO), 7.90 (d, 2H, $J$ = 8.7 Hz), 7.15 (dd, 4H, $J$ = 8.4 Hz).



**HDF**

### 2.4.2.3 Synthesis of 4,4'-[1,2-phenylene-*bis*-oxy]*bis*-benzenecarboxaldehyde (CDF):

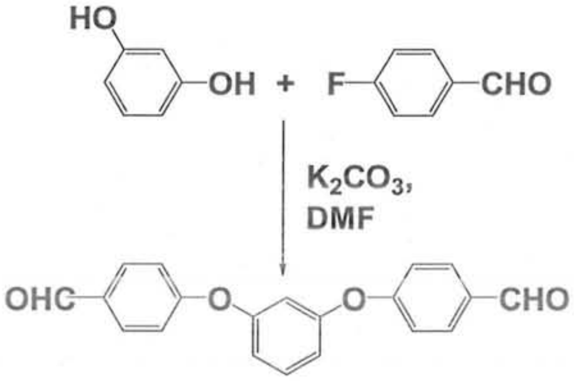
The same procedure was followed for CDF. In a 250 mL prebaked round bottom flask (RBF) equipped with magnetic stirrer added 2.75g (0.025 moles) pyrocatechol and 8.0g (0.06 moles) anhydrous potassium carbonate ($K_2CO_3$) in 60 mL dried *N,N*-dimethylformamide (DMF). The mixture was heated for 1 hour at 80-90 °C under dry nitrogen atmosphere. Then cool the mixture flask to about 40°C followed by the addition of 4-flourobenzenecarboxaldehyde (6.0mL, 0.06 moles). The rest of the procedure was same as mentioned in general procedure for di-ether based dialdehydes. Yield, 77%. $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta$ = 9.86 (s, 1H, -CHO), 6.89 (d, 2H, $J$ = 8.7 Hz), 7.32-7.21 (m, 2H), 7.77 (d, 2H, $J$ = 8.4 Hz).



**CDF**

### 2.4.2.4 Synthesis of 4,4'-[1,3-phenylene-*bis*-oxy]*bis*-benzenecarboxyaldehyde (RDF):

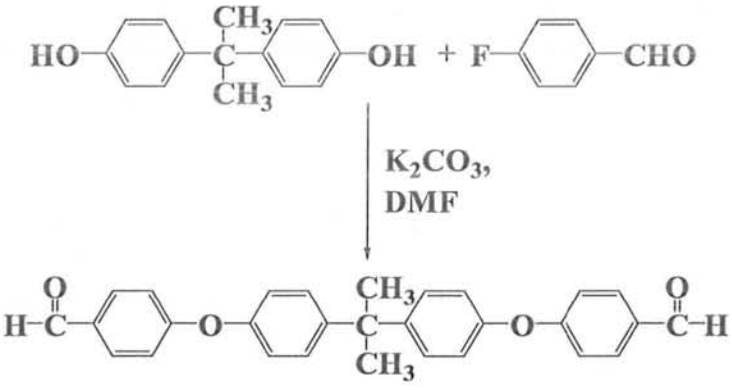
The same procedure was followed for RDF. In a 250 mL prebaked round bottom flask (RBF) equipped with magnetic stirrer added 5.5 g (0.05 moles) resorcinol and 16.0 g (0.11 moles) anhydrous potassium carbonate ($K_2CO_3$) in 60 mL dried *N,N*-dimethylformamide (DMF). Gently the mixture was heated for 1 hour at 80-90 °C under dry nitrogen ($N_2$) atmosphere. Then cooled the mixture flask to about 40°C followed by the addition of 4-flourobenzaldehyde (12.0 mL, 0.11 moles). The rest of the procedure was same as mentioned in general procedure for di-ether based dialdehydes. Yield, 82%, m.p. 108-110°C. $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta = 9.93$ (s, 1H, -CHO), 6.9-7.95 (m, 8H).



RDF

### 2.4.2.5 Synthesis of 2,2-di [4-(4′-formylphenyloxy)phenyl] propane (BPADF):

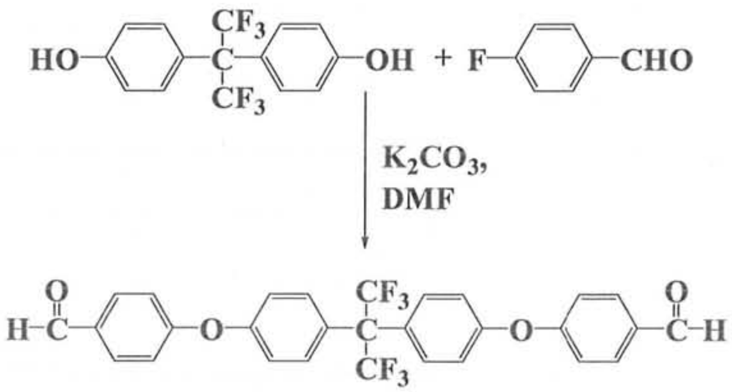
The same procedure was followed for BPADF. In a 250 mL prebaked round bottom flask (RBF) equipped with magnetic stirrer added 2.62 g (0.012 moles) 4,4'-(propane-2,2-diyl)diphenol (bisphenol-A) and 3.85 g (0.028 moles) anhydrous potassium carbonate ($K_2CO_3$) in 50 mL dried *N,N*-dimethylformamide (DMF). The mixture was heated for 2 hours at 80-90 °C employing nitrogen atmosphere. Then cooled the mixture flask to about 40°C followed by the addition of 4-flourobenzaldehyde (2.5 mL, 0.023 moles). The rest of the procedure is same as mentioned in general procedure for di-ether based dialdehydes. $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta = 9.92$ (s, 1H, -CHO), 7.09 (dd, 4H, $J = 8.7$ Hz), 7.32 (d, 2H, $J = 8.7$ Hz), 7.87 (d, 2H, $J = 8.7$ Hz), 1.74 (s, 3H).



**BPADF**

### 2.4.2.6 Synthesis of 2,2-di [4-(4′-formylphenyloxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (HFBPDF):

The same procedure was followed for HFBPDF. In a 250 mL prebaked round bottom flask (RBF) equipped with magnetic stirrer added 3.86 g (0.012 moles) 4,4'-(Hexafluoroisopropyliden)-diphenol and 4.0 g (0.029 moles) anhydrous potassium carbonate ($K_2CO_3$) in 50 mL dried *N,N*-dimethylformamide (DMF). The mixture was heated for 2 hours at 80-90 °C under nitrogen conditions. Then cooled the mixture flask to about 40°C followed by the addition of 4-flourobenzenecarboxaldehyde (2.5 mL, 0.023 moles). The rest of the procedure was same as mentioned in general procedure for di-ether based dialdehydes. FT-IR ($\upsilon$= cm$^{-1}$): 3090 cm$^{-1}$ (aromatic C-H str.); 2850, 2750 cm$^{-1}$ (aldehydic C-H str.); 1686 cm$^{-1}$ (carbonyl str.); 1588, 1494 cm$^{-1}$ (aromatic C=C); 1232, 1205 cm$^{-1}$ (C-O-C ether): $^1$H–NMR, ($CDCl_3$, 300 MHz, 25°C, ppm); $\delta$ = 9.96 (s, 1H, -CHO), 7.17 (dd, 4H, $J$ = 8.7 Hz), 7.92 (d, 2H, $J$ = 8.7 Hz), 7.47 (d, 2H, $J$ = 8.7 Hz).



**HFBPDF**

## 2.5 General Synthesis of Poly(azomethine)s:

All polyazomethines derived from mono-ether and di-ether based aromatic dialdehydes were synthesized under $N_2$ atmosphere by solution polycondensation. A typical procedure is as follows: all the dialdehydic monomers (1 equivalent) were dissolved in 20 mL DMF and 10 mL toluene. And *p*-toluenesulfonic acid (TsOH) monohydrate was added in catalytic amount. Then the equimolar diamine (1equivalent) solution in 10 mL was added drop wise with continuous stirring. The reaction was distilled for azeotropic water removal with toluene using Dean-Stark trapper. After 6 hours reflux, check the TLC for any residual monomers if present, using $CHCl_3$ eluent. If the product was directly precipitated in reaction mixture, it was poured onto 300mL ice cold water. Filtered, washed with methanol and dried at 40°C for 6 hours. On the other hand, if polymers were soluble in DMF then upon reaction completion excess DMF was reduced to half through rotary evaporation followed by precipitation in ice cold $H_2O$. Then the product was filtered, water washed, recrystallized from ethanol/chloroform, and subsequently dried at 40°C for 6 hours.

| Sr. No. | Polymer code | Aromatic Diamine | Aromatic Dialdehyde |
|---|---|---|---|
| 1 | $P_1$ODF | 4,4′-diaminodiphenyl ether | ODF |
| 2 | $P_2$ODF | 1,4-phenylenediamine | ODF |
| 3 | $P_1$MDF | 4,4′-diaminodiphenyl ether | MDF |
| 4 | $P_2$MDF | 1,4-phenylenediamine | MDF |
| 5 | $P_1$EDF | 4,4′-diaminodiphenyl ether | EDF |
| 6 | $P_2$EDF | 1,4-phenylenediamine | EDF |
| 7 | $P_1$BPDF | 4,4′-diaminodiphenyl ether | BPDF |
| 8 | $P_2$BPDF | 1,4-phenylenediamine | BPDF |
| 9 | $P_1$HDF | 4,4′-diaminodiphenyl ether | HDF |
| 10 | $P_2$HDF | 1,4-phenylenediamine | HDF |
| 11 | $P_1$BPADF | 4,4′-diaminodiphenyl ether | BPADF |
| 12 | $P_2$BPADF | 1,4-phenylenediamine | BPADF |
| 13 | $P_1$HFBPDF | 4,4′-diaminodiphenyl ether | HFBPDF |
| 14 | $P_2$HFBPDF | 1,4-phenylenediamine | HFBPDF |
| 15 | $P_1$CDF | 4,4′-diaminodiphenyl ether | CDF |
| 16 | $P_2$RDF | 1,4-phenylenediamine | RDF |

Nine ether based aromatic dialdehydes have been prepared. Using these aromatic diformyl-ether monomers sixteen new polymers have been synthesized. The polyazomethines derived from mono-ether linked and di-ether linked aromatic bis-aldehydes were formed by solution polycondensation using DMF solvent in the presence of *p*-toluenesulfonic acid catalyst and toluene as azeotropic water removal agent. There are other methods that can be used to remove water from reaction such as using $MgSO_4$, or LiCl etc [1] as dehydrating agents.

The structures of synthesized aromatic bis-aldehydes were established by spectroscopic techniques (FT–IR, $^1$H– and $^{13}$C–NMR, UV–visible spectroscopy) as well as m.p. aided the purity of monomers. Polyazomethines were characterized by spectroscopic measurements (FT–IR, $^1$H– and $^{13}$C–NMR, UV–visible spectroscopy), viscometric measurements, thermogavimetric analysis (TGA), fluorescence spectroscopic technique, differential scanning calorimetry (DSC), Wide-angle XRD analysis, and conductivity measurements.

## 3.1 Characterization of Monomers:

Nine different monomers were synthesized by reacting various mono-hydroxy-benzenecarboxaldehydes or dihydroxyphenols with 4-fluorobenzenecarboxaldehyde in DMF solvent using anhydrous $K_2CO_3$. Monohydroxy phenolic aldehydes gave mono-ether based aromatic dialdehydes whereas dihydroxyphenol's etherification [2] with *p*-fluorobenzaldehyde resulted in di-ether based aromatic bis-aldehydes as depicted in Scheme No.1 and Scheme No.2.

This etherification reaction of *p*-fluorobenzaldehyde with –OH functional groups was carried out using DMF solvent. If any other aromatic halide is used for etherification, then the solvent must be changed from DMF to DMSO [3] otherwise product is not formed. This can be associated with easy nucleophilic substitution of –F from aromatic ring owing to smaller sized and being highly electronegative element it increases the electrophilic character of carbon to which it is attached on aromatic ring. As a result nucleophilic phenoxide's ($-PhO^-$) attack on electropositive carbon becomes easy. For successful etherification reaction of other aryl halides DMSO solvent can be used because it is high boiling solvent and is necessary to overcome reaction's activation energy barrier. In fact, reactions using other aryl halides in DMF solvent were tried but resulted in product failure. The table 3.1 shows the physical characteristics of monomers. All ether linked dialdehyde monomers were obtained in appreciable yield. The monomers BPADF, HFBPDF and CDF were gelatinous at the time of synthesis and were separated carefully followed by washing and drying in oven at 40 °C until completely dried. Then the product was recystallized from $CHCl_3$/ethyl acetate mixtures. The rest of monomers were directly precipitated out upon the addition of reaction mixture to ice cold water and processed as discussed in experimental section.

**Table 3.1: Physical Characteristics of Aromatic Dialdehydes**

| Code | Color | Physical Sate | m.p. | % Yield |
|---|---|---|---|---|
| ODF | Orange | Crystalline | 55-60°C | 90 |
| MDF | Orange | Crystalline | 67-68°C | 88 |
| EDF | Orange | Amorphous | 68-70°C | 85 |
| BPDF | Off-white | Amorphous | 160°C | 84 |
| HDF | Maroon | Crystalline | 153-155°C | 91 |
| RDF | Brick red | Amorphous | 108-110°C | 82 |
| CDF | Grayish red | Amorphous | - | 77 |
| BPADF | Light orange | Crystalline | 112°C | 79 |
| HFBPDF | Light yellow | Amorphous | 90-94°C | 73 |

The structures of bisaldehydes synthesized via etherification reaction were established by FT–IR, $^1$H– and $^{13}$C–NMR Spectroscopic measurements. The FT–IR spectral data (table 3.2) and NMR signals data (table 3.3 and table 3.4) are discussed below.

### 3.1.1 FT-IR Spectroscopic Analysis:

The FT-IR spectra of all the bis-aryl-carboxaldehydes (as mentioned in table 3.2) evidenced the successful synthesis of monomers. The representative IR spectrum of EDF is given in figure 3.1 and respective peaks of functional groups are labeled. The absence of –OH peaks of reactant phenol above 3200 cm$^{-1}$ confirmed the successful etherification. The aryl group moieties gave weak bands from 3029-3090 cm$^{-1}$ in the spectrum. The aldehydic carbonyl stretching (H–C=O) was observed from 1675-1692 cm$^{-1}$. The aliphatic C-H stretching bands and ether's C–O–C absorption bands also appeared in the respective regions as shown in table 3.2.

**Table 3.2: FT-IR data of Aromatic Dialdehydes**

| Code | Aromatic C-H str. | Aliphatic C-H str. | Aldehydic C-H str. | C=O str. | Aromatic C=C | C-O-C |
|---|---|---|---|---|---|---|
| ODF | 3065 | -- | 2819, 2731 | 1675 | 1581, 1494 | 1236 |
| MDF | 3066 | 2978, 2928 | 2860, 2759 | 1680 | 1581, 1497 | 1235, 1208 |
| EDF | 3063 | 2973, 2930 | 2828, 2736 | 1687 | 1577, 1497 | 1268, 1227 |
| HDF | 3029 | -- | 2727 | 1692 | 1599, 1489 | 1225, 1187 |
| BPDF | 3062 | -- | 2812, 2712 | 1688 | 1592, 1487 | 1250, 1207 |
| HFBPDF | 3090 | -- | 2850, 2750 | 1686 | 1588, 1494 | 1232, 1205 |

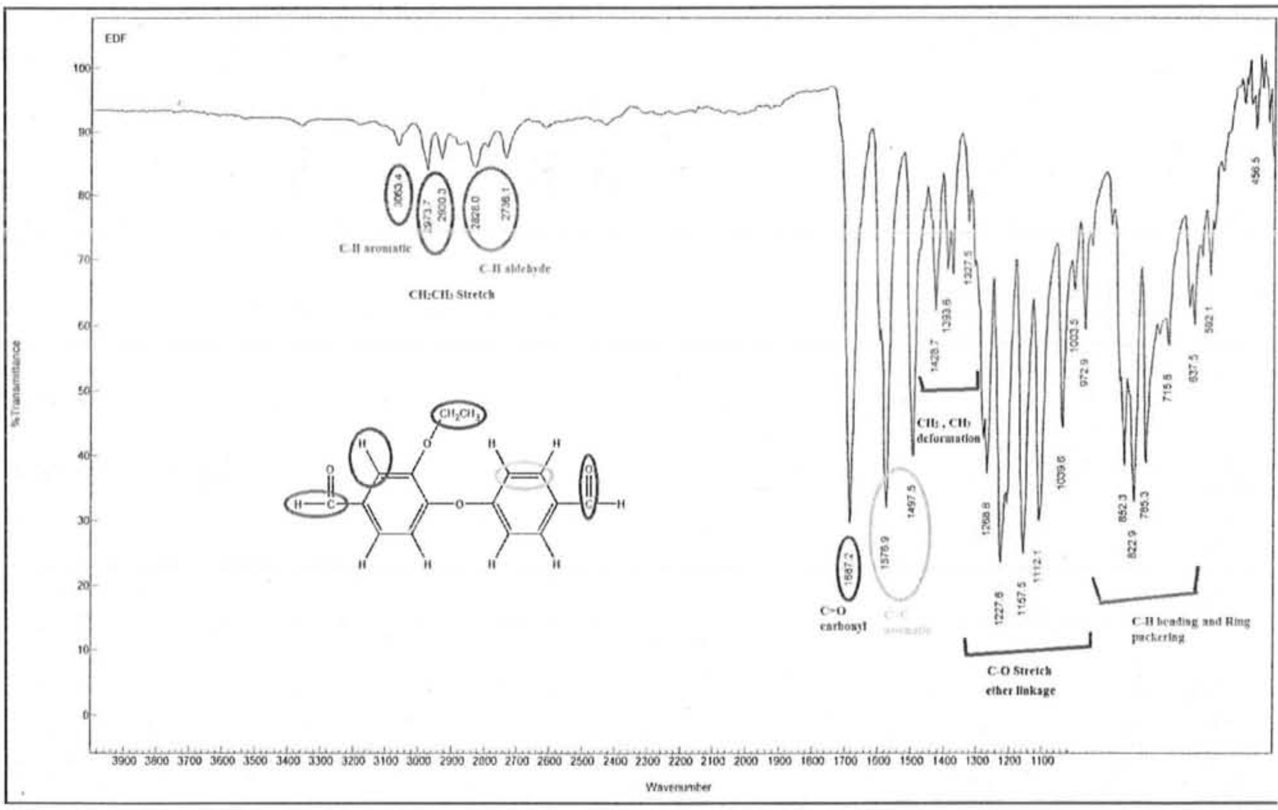


**Figure 3.1: FT–IR graph of Monomer EDF**

### 3.1.2 $^1$H– and $^{13}$C–NMR Spectroscopic Analysis:

The $^1$H–NMR and $^{13}$C–NMR spectra of all ether based bis-aldehydes were consistent with the proposed.structures. The carboxaldehydic proton (O=C–H) gave singlets appearing at $\delta = 9.90 - 9.97$ ppm. All the symmetrically substituted bisaldehydes gave one singlet peak due to O=C–H whereas the two monomers (named as MDF and EDF) having unsymmetrical aromatic rings gave two singlets (at $\delta = 9.97$, 9.95 ppm and 9.96, 9.94 ppm, respectively). Moreover, the singlets in the spectrum of MDF, and EDF due to 1H (at $\delta = 7.58$ ppm and 7.54 ppm) in aromatic region confirm the structure. The singlet at $\delta = 3.90$ ppm, triplet at $\delta = 1.27$ ppm, and quartet at $\delta = 4.12$ ppm are also confirmatory of MDF, and EDF structures, respectively. All the aromatic hydrogens gave doublets (at $\delta = 7.03 - 7.95$ ppm) with coupling constants ($J$ ) ranging from 8.4 – 8.7 Hz which clearly indicates the *p*-phenylene units are present in monomers. The monomer RDF gave multiplet signals in aromatic region (at $\delta = 6.9 - 7.75$ ppm) while the singlet of –CHO at $\delta = 9.93$ ppm confirms the proposed structure. The figure 3.2 shows the $^1$H–NMR spectra of ODF monomer. The singlet at $\delta = 9.90$ ppm due to –CHO group and two doublets at $\delta$ 7.95 (2H, d, $J = 8.4$ Hz), and $\delta$ 7.20 (2H, d, $J = 8.4$ Hz) are in consistent with the proposed.structure.

**Table 3.3: $^1$H–NMR Data of Aromatic Dialdehydes**

| Code | –CHO ($\delta$ ppm) | Ar-H ($\delta$ ppm) | $-CH_3$, $-CH_2-$ ($\delta$ ppm) |
|---|---|---|---|
| ODF | 9.90 (s) | 7.95 (d, $J = 8.4$ Hz), 7.20 (d, $J = 8.4$ Hz) | -- |
| MDF | 9.97 (s)<br>9.95 (s) | 7.08 (d, $J = 8.4$ Hz), 7.21 (d, $J = 8.1$ Hz), 7.58 (s), 7.53 (d, $J = 8.1$ Hz), 7.89 (d, $J = 8.4$ Hz) | 3.90 (s) |
| EDF | 9.96 (s)<br>9.94 (s) | 7.07 (d, $J = 8.7$ Hz), 7.23 (d, $J = 8.1$ Hz), 7.52 (d, $J = 8.1$ Hz), 7.54 (s), 7.88 (d, $J = 8.7$ Hz) | 1.27(t), 4.12 (q) |
| HDF | 9.95 (s) | 7.90 (d, $J = 8.7$ Hz), 7.15 (dd, $J = 8.4$ Hz) | -- |
| BPDF | 9.94 (s) | 7.98 (d, $J = 8.7$ Hz), 7.80 (d, $J = 8.7$ Hz), 7.27-7.21 (dd, 4H, $J = 8.7$ Hz) | -- |
| BPADF | 9.92 (s) | 7.09 (dd, 4H, $J = 8.7$ Hz), 7.32 (d, 2H, $J = 8.7$ Hz), 7.87 (d, 2H, $J = 8.7$ Hz), 1.74 (s, 3H) | 1.74 (s, 3H) |
| CDF | 9.86 (s) | 6.89 (d, 2H, $J = 8.7$ Hz), 7.32-7.21 (m, 2H), 7.77 (d, 2H, $J = 8.4$ Hz) | -- |
| RDF | 9.93 (s) | 6.9-7.95 (m) | -- |
| HFBPDF | 9.96 (s) | 7.17 (dd, 4H, $J = 8.7$ Hz), 7.92 (d, 2H, $J = 8.7$ Hz), 7.47 (d, 2H, $J = 8.7$ Hz). | -- |

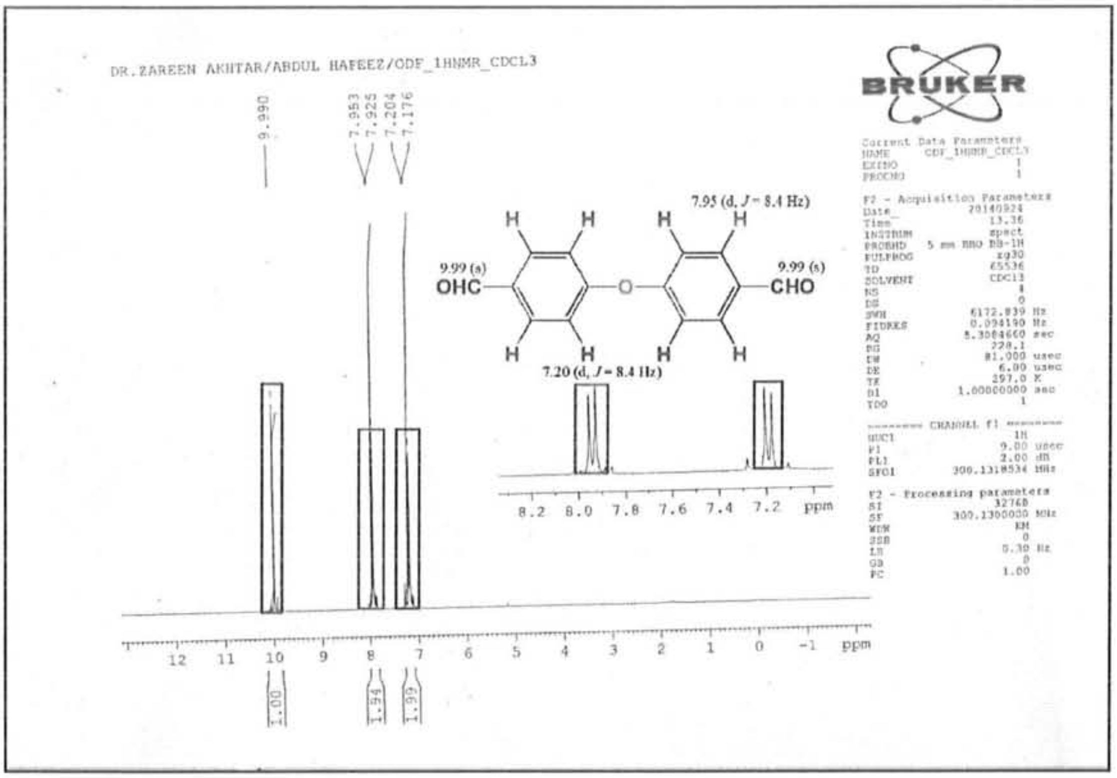


Figure 3.2: $^1$H–NMR spectra of Monomer ODF

The table 3.4 shows the $^{13}$C–NMR spectral data of ether linked bisaldehydes. The signals at $\delta = 190.6 - 192$ ppm have been assigned to –CHO carbons. The ether linked carbons gave signals at $\delta = 148 - 163$ ppm. The signals in the range of 111 – 136 ppm are assigned to aryl carbons, whereas the aliphatic carbons gave signals at $\delta = 14 - 64$ ppm. The figure 3.3 shows the $^{13}$C–NMR spectrum of monomer ODF.

**Table 3.4: $^{13}$C–NMR Data of Aromatic Dialdehydes**

| Code | –CHO ($\delta$ ppm) | C–O–C ($\delta$ ppm) | Ar ($\delta$ ppm) | Aliphatic C ($\delta$ ppm) |
|---|---|---|---|---|
| ODF | 190.6 | 161 | 119-133 | -- |
| MDF | 190.8, 190.7 | 162,152, 148 | 134-111 | 56 |
| EDF | 190.9, 190.8 | 162, 151, 149 | 134-112 | 64, 14 |
| HDF | 190.8 | 163, 151 | 132-117 | -- |
| BPDF | 192 | 162.7, 154.8 | 136-118 | -- |
| BPADF | 190.8 | 163, 152, 157 | 131-117 | 42, 31 |
| CDF | 190.7 | 162, 146 | 132-116 | -- |
| RDF | 190.85 | 162, 156 | 132-112 | -- |
| HFBPDF | 190.7 | 161, 156 | 132-115 | 64 |

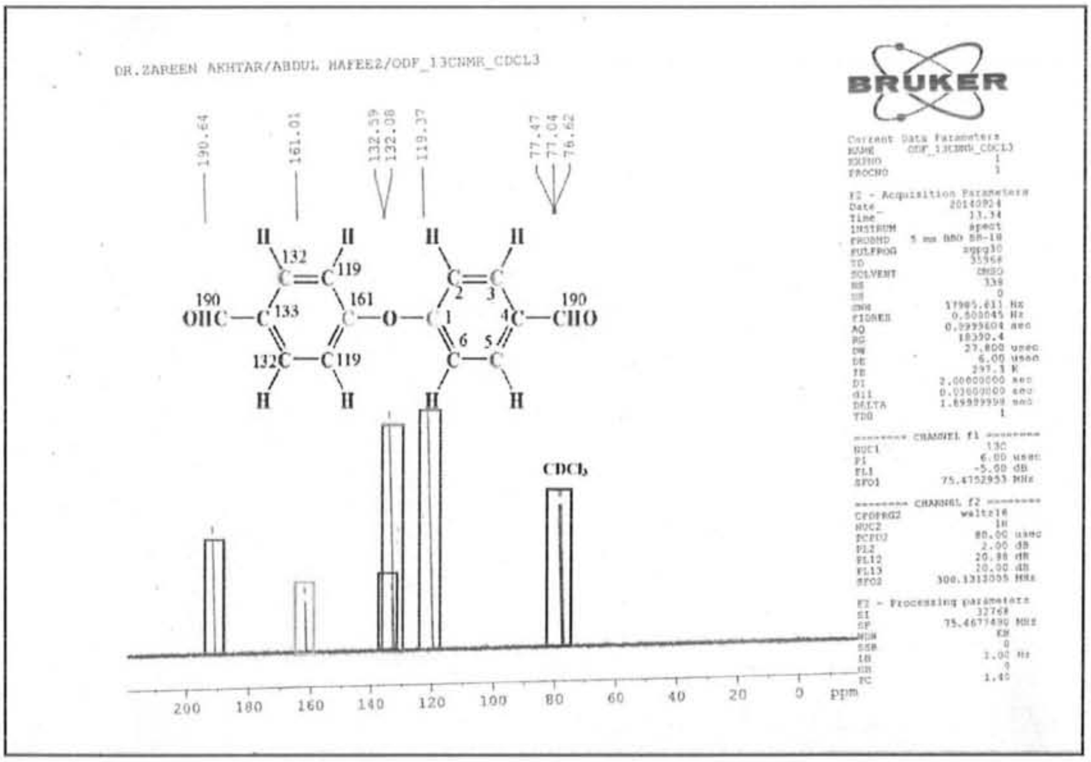


Figure 3.3: $^{13}$C–NMR spectra of Monomer ODF

### 3.1.3 UV-visible Measurements of Monomers:

The electronic spectra of bis-carboxaldehydes were recorded from 245-850 nm using conc. $1\times10^{-6}$M in chloroform. The optical properties ($\lambda_{max}$ and absorbance) are shown in table 3.5 and spectra are presented in figure 3.4. All the monomers exhibited a good agreement between $\lambda_{max}$ observed and calculated through Woodward-Fieser Rules [4]. The concurrence between the two reinforced the proposed structures. The maxima at 277-294 nm can be assigned to $\pi\rightarrow\pi^*$-transition of aryl moiety. All the bis-carboxaldehydes exhibited a single maxima while the two monomers MDF, and EDF having $-OCH_3$ and $-OC_2H_5$ lateral substituents showed shoulder peaks at 314 nm and 315 nm, respectively. The shoulder maxima (314 nm, and 315 nm) could be attributed to auxochromic effect of these –OR groups.

**Table 3.5: UV-Visible Data of Aromatic Dialdehydes**

| Code | Wavelength (Obs. $\lambda_{max}$ nm) | Wavelength (Calc. $\lambda_{max}$ nm) |
|---|---|---|
| HDF | 285 | 289 |
| MDF | 292, 314 | 295 |
| EDF | 283, 315 | 295 |
| HFBPDF | 277 | 289 |
| CDF | 280 | 289 |
| RDF | 291 | 289 |
| ODF | 292 | 289 |
| BPDF | 294 | 289 |
| BPADF | 288 | 289 |

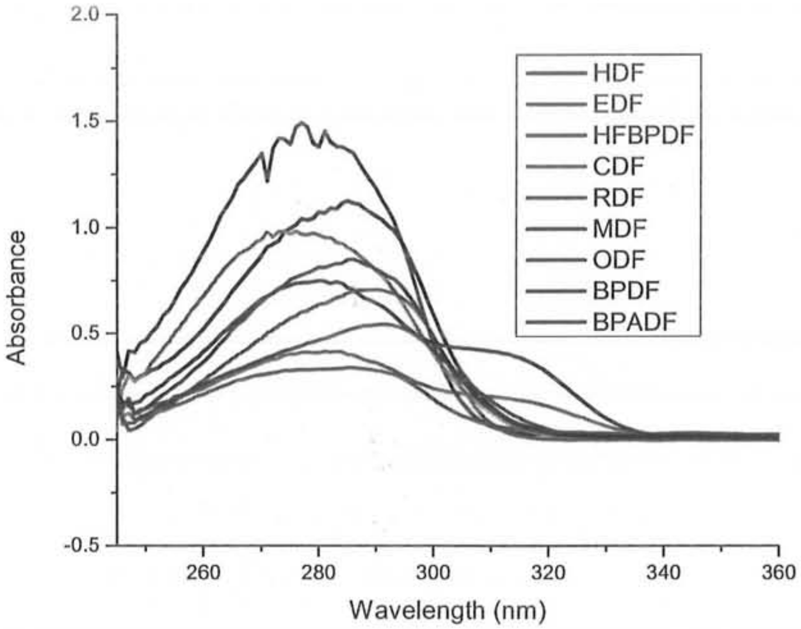


Figure 3.4: UV-Visible spectra of Monomers in $CHCl_3$

## 3.2 Characterization of Polymers:

### 3.2.1 FT-IR Spectroscopic Analysis:

The table 3.6 shows the major FT-IR characterization band for the polyaldimines i.e. –CHO, –C=N–, C=C and C–O–C while detailed peaks labeling have been shown for polymer $P_2MDF$ in representative figure 3.5 of three polymers. The graph shows respective stretching bands of aryl =C–H, aliphatic C–H, aldehydic O=C–H, aromatic C=C, ether C–O, and *p*-substituted benzene rings are well defined. The nonappearance of primary $-NH_2$ peaks in ~3300-3500cm$^{-1}$ region indicates the successful polymerization whereas the decrease in intensity of –CHO absorption infers the –CHO end group functionalized polyaldimines [5, 6]. The absorption band at 1663-1695 cm$^{-1}$ have been associated with H–C=O group while those at 1611-1628 cm$^{-1}$ attributed to azomethine (–HC=N) linkage. Moreover, the aromatic C–C vibrational bands and ether C–O–C peaks (1210-1247cm$^{-1}$) are in their respective regions.

**Table 3.6: FT-IR Data of Polymers**

| Code | C=O (cm$^{-1}$) | -C=N- (cm$^{-1}$) | C=C (cm$^{-1}$) | C-O (cm$^{-1}$) |
|---|---|---|---|---|
| $P_1MDF$ | 1690 | 1625 | 1484 | 1225 |
| $P_2MDF$ | 1695 | 1623 | 1493 | 1220 |
| $P_2EDF$ | 1670 | 1616 | 1493 | 1213 |
| $P_1HDF$ | 1692 | 1626 | 1493 | 1237 |
| $P_2ODF$ | 1685 | 1618 | 1484 | 1247 |
| $P_1BPDF$ | 1670 | 1628 | 1495 | 1240 |
| $P_2BPDF$ | 1671 | 1622 | 1493 | 1240 |
| $P_2BPADF$ | 1690 | 1622 | 1493 | 1228 |
| $P_2HFBPDF$ | 1664 | 1623 | 1497 | 1233 |
| $P_1RDF$ | 1663 | 1628 | 1498 | 1210 |
| $P_2CDF$ | 1671 | 1611 | 1477 | 1210 |

Figure 3.5 shows the representative graph of three polymers ($P_2$MDF, $P_2$BPADF and $P_2$ODF).

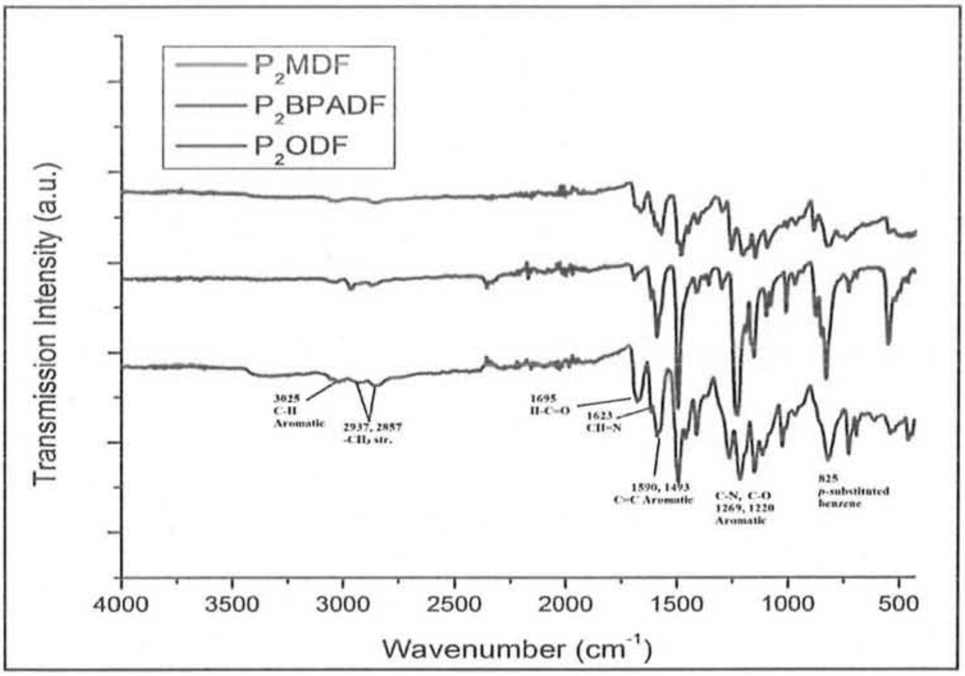


**Figure 3.5: FT-IR spectra of three polymers**

### 3.2.2 $^1$H–NMR Spectroscopic Analysis:

$^1$H–NMR spectra of polyaldimines were taken in $D_2SO_4$ because of limited solubility of these polymers in any other solvent including high polarity DMSO-$d_6$. Even the unsubstituted polyazomethine-ethers showed only partial solubility upon addition of TsOH. It is the acidic proton of TsOH that interact with basic nitrogen of aldimine to enhance solubility via lowering chain-chain interaction [7].

The $-CH_3$ aliphatic protons gave singlets (at $\delta = 3.54$, 1.75, and 2.29 ppm). The aryl protons of macrochain gave multiplets (at $\delta = 6.62 - 7.95$ ppm) owing to different aromatic moieties. The azomethinic proton (–CH=N–) signals appeared in characteristic range (at $\delta = 8.23 - 8.43$ ppm). The figure 3.6 shows the $^1$H–NMR spectrum of polymer, $P_1$MDF. The signals at $\delta = 3.54$ (s), 6.68 – 7.60 (m), and 8.33 (s) confirm successful macrochain formation of polyaldimines. The figure 3.6 shows the representative $^1$H–NMR spectrum of $P_1$MDF polymer.

Table 3.7: $^1$H–NMR Data of Polymers

| Code | $-CH_3$ (δ ppm) | Ar-H (δ ppm) | -CH=N- (δ ppm) |
|---|---|---|---|
| $P_1$MDF | 3.54 (s) | 6.68-7.60 (m) | 8.33 (s) |
| $P_1$ODF | -- | 6.62-7.82 (m) | 8.39 (s) |
| $P_1$BPADF | 1.75 (s) | 6.65-7.82 (m) | 8.23 (s) |
| $P_1$BPDF | -- | 6.73-7.92 (m) | 8.35 (s) |
| $P_1$HDF | -- | 6.71-7.95 (m) | 8.25 (s) |
| $P_2$BPADF | 2.28 (s) | 6.76-7.72 (m) | 8.23 (s) |
| $P_2$ODF | -- | 6.79-7.63 (m) | 8.42 (s) |
| $P_2$BPDF | -- | 6.73-7.61 (m) | 8.37 (s) |
| $P_2$HDF | -- | 6.77-7.66 (m) | 8.43 (s) |
| $P_2$MDF | 2.29 (s) | 7.14-7.95 (m) | 8.29 (s) |

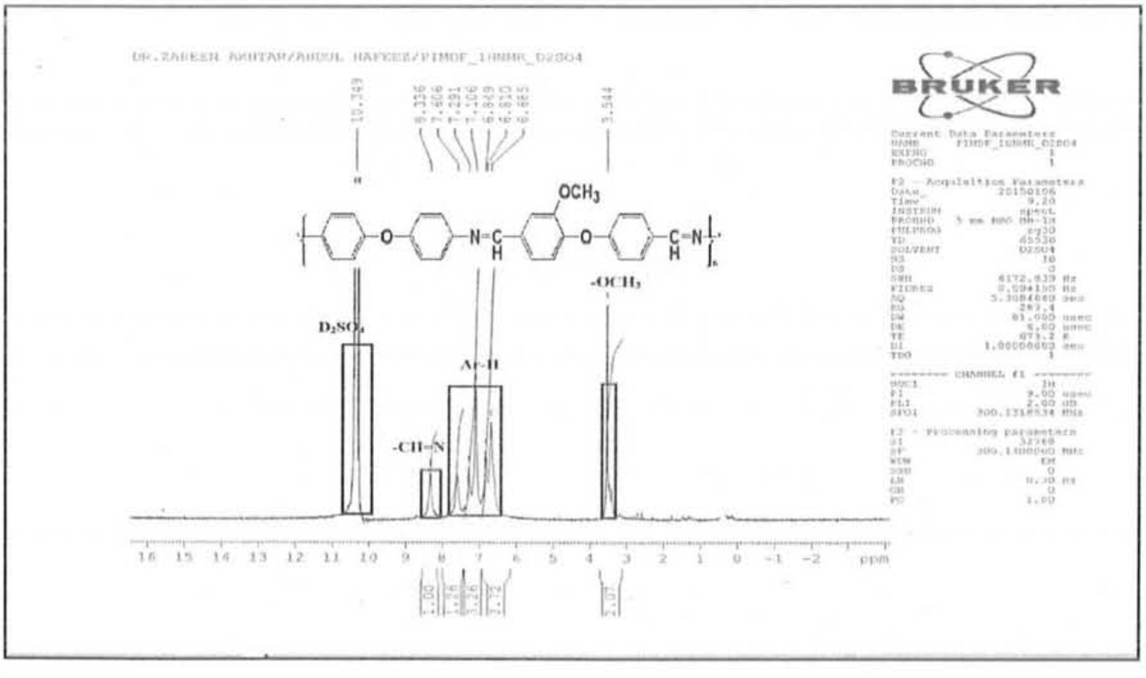


Figure 3.6: $^1$H–NMR spectrum of polymer $P_1$MDF

### 3.2.3 Solubility:

The solubility of polyaldimines was checked in different solvents (DMF, DMSO, *N*-methyl-2-pyrolidone (NMP), $CHCl_3$ and sulfuric acid). The polyaldimines derived from non-substituted aromatic bisaldehydes (named ODF, HDF, BPDF) were found to be almost insoluble in DMF, DMSO, NMP and chloroform, whereas, others (having $-OC_2H_5$, $-CF_3$ groups) were found to be showing nearly complete solubility in these solvents. The polymers (with $-OCH_3$, and $-CH_3$) were partially soluble. All polymeric azomethine's solubility in conc. $H_2SO_4$ was good even at room temperature. The table 3.8 shows the respective solubility of all polyazomethines in aforementioned solvents.

**Table 3.8: Solubility Data of Polymers**

| Polymer | DMF | DMSO | NMP | $CHCl_3$ | $H_2SO_4$ |
|---|---|---|---|---|---|
| $P_1$ODF | − − h | − − h | − − h | − − h | + + + |
| $P_2$ODF | − − h | − − h | − − h | − − h | + + + |
| $P_1$HDF | − − h | − − h | − − h | − − h | + + + |
| $P_2$HDF | + − h | + − h | + − h | − − h | + + + |
| $P_1$BPDF | − − h | − − h | − − h | − − h | + + + |
| $P_2$BPDF | + − h | + − h | + − h | − − h | + + + |
| $P_1$RDF | + − h | + − h | + − h | + − h | + + + |
| $P_2$CDF | + − h | + − h | + − h | + + + | + + + |
| $P_1$MDF | + − h | + − h | + − h | + − h | + + + |
| $P_2$MDF | + + + | + + h | + + h | + + + | + + + |
| $P_1$EDF | + + h | + + h | + − h | + + + | + + + |
| $P_2$EDF | + + + | + + + | + + + | + + + | + + + |
| $P_1$BPADF | + + + | + + h | + + h | + − h | + + + |
| $P_2$BPADF | + − h | + − h | + − h | + − h | + + + |
| $P_1$HFBPDF | + + h | + + h | + + h | + + + | + + + |
| $P_2$HFBPDF | + + + | + + + | + + + | + + + | + + + |

+ + + = soluble at room temperature, + − h = partially soluble on heating

− − h = insoluble on heating, + + h = soluble on heating

### 3.2.4 Viscometric Measurements:

The viscosity of polyaldimines is a measure of resistance to cooperative segmental movement of macrochains. It depends on flexibility of macrochain, chain entanglement, inter- and intramolecuar interactions, oxygen atoms (–O–), and side groups. At room temperature (25°C) the relative viscosities ( $= t/t_o = \eta/\eta_o = \eta_{rel}$) of polyimines were measured (using U-tube Ubbelhode viscometer) by preparing fresh solutions (0.2 g per 100 mL – called 0.2 wt% solution) in conc. sulfuric acid.

**Table 3.9: Viscometric Data of Polymers**

| Code | $\eta_{rel}$ | $\eta_{sp}$ | $\eta_{red}$ (dl/g) | $\eta_{inh}$ (dl/g) |
|---|---|---|---|---|
| $P_1$MDF | 1.45 | 0.45 | 2.25 | 1.98 |
| $P_2$MDF | 1.25 | 0.25 | 1.28 | 1.84 |
| $P_1$EDF | 1.18 | 0.18 | 0.94 | 1.78 |
| $P_2$EDF | 1.12 | 0.12 | 0.60 | 1.72 |
| $P_1$BPADF | 1.09 | 0.09 | 0.48 | 1.70 |
| $P_2$BPADF | 1.38 | 0.38 | 1.92 | 1.93 |
| $P_1$HFBPDF | 1.12 | 0.12 | 0.60 | 1.72 |
| $P_2$HFBPDF | 1.17 | 0.17 | 0.86 | 1.77 |
| $P_2$CDF | 1.37 | 0.37 | 1.87 | 1.93 |
| $P_1$ODF | 1.136 | 0.14 | 0.68 | 1.74 |
| $P_2$ODF | 1.178 | 0.18 | 0.89 | 1.77 |
| $P_1$HDF | 1.118 | 0.11 | 0.59 | 1.72 |
| $P_2$HDF | 1.159 | 0.16 | 0.80 | 1.76 |
| $P_1$BPDF | 1.121 | 0.12 | 0.60 | 1.72 |
| $P_2$BPDF | 1.044 | 0.04 | 0.22 | 1.65 |

Relative viscosity = $t/t_o = \eta/\eta_o = \eta_{rel}$

Specific viscosity = $\eta_{sp} = \eta_{rel}-1$

Reduced viscosity = $\eta_{sp}/c$

Inherent viscosity = $\ln(\eta_r/c)$

(where t = time of flow of $H_2SO_4$, $t_o$ = time of flow of polyaldimines, $\eta$ = viscosity of solution, and $\eta_o$ = viscosity of $H_2SO_4$)

### 3.2.5 UV-visible Spectroscopic Analysis:

The drift in electronic absorption spectra ($\lambda_{max}$) of polyaldimines to bathochromic region infers the extension of delocalized π-conjugated length as compared to monomeric units. The UV-vis spectra of polyaldimines (recorded by ~$10^{-6}$M solutions) gave maximum absorption at 335-363.5 nm in $CHCl_3$ while 332.5-371.5 nm in DMF. The solutions of partially soluble polyaldimines were filtered before electronic spectrum. Complelety insoluble polyimines showed no absorption peaks. The electronic absorption maxima ($\lambda_{max}$) of polyazomethines depend upon solvent polarity: dipole moment; $\mu$ = 1.01D for $CHCl_3$, and $\mu$ = 3.86D for DMF. The $\lambda_{max}$ blue shift (negative solvatochromism) has been observed in DMF for $P_1$MDF, $P_1$EDF, and $P_1$BPADF as reported by Sek [8] whereas polymers of series $P_2$: $P_2$MDF, $P_2$EDF, $P_2$BPADF, and $P_2$HFBPDF showed a red shift in DMF (positive solvatochromism) as described by Jenekhe [9] while other polymers showed no significant effect on change in solvent polarity. The blue shift in polymers derived from oxydianiline may be attributed to the more stable ground state [10] as compared to excited state and partial hindrance to electronic configuration of ether linkage The polymers derived from ODF, HDF, BPDF, and RDF being insoluble gave either no absorption or less characterized peaks. The UV-vis spectra are shown in figure 3.7 and 3.8 in $CHCl_3$ and DMF, respectively. The respective maximum wavelengths are given in tables 3.10 (a), and 3.10 (b).

**Table 3.10 (a): UV-Visible Data of Polymers**

| Code | $CHCl_3$ ($\lambda_{max}$ nm) | DMF ($\lambda_{max}$ nm) |
|---|---|---|
| $P_1$MDF | 344.5 | 344, 286 |
| $P_2$MDF | 363.5, 285 | 371.5, 281 |
| $P_1$EDF | 344, 282 | 338, 285.5 |
| $P_2$EDF | 363.5, 280 | 371.5, 283 |
| $P_1$BPADF | 335, 284 | 332.5, 285.5 |
| $P_2$BPADF | 357, 288.5 | 358, 287 |
| $P_1$HFBPDF | 335, 278 | 335, 280 |
| $P_2$HFBPDF | 360, 280 | 363, 283 |
| $P_2$CDF | 357, 278 | 357, 283 |
| $P_1$ODF | -- | -- |
| $P_2$ODF | -- | -- |
| $P_1$HDF | 284 | -- |

| | | |
|---|---|---|
| $P_2$HDF | --- | --- |
| $P_1$BPDF | --- | 294.5 |
| $P_2$BPDF | --- | --- |
| $P_1$RDF | --- | 337 |

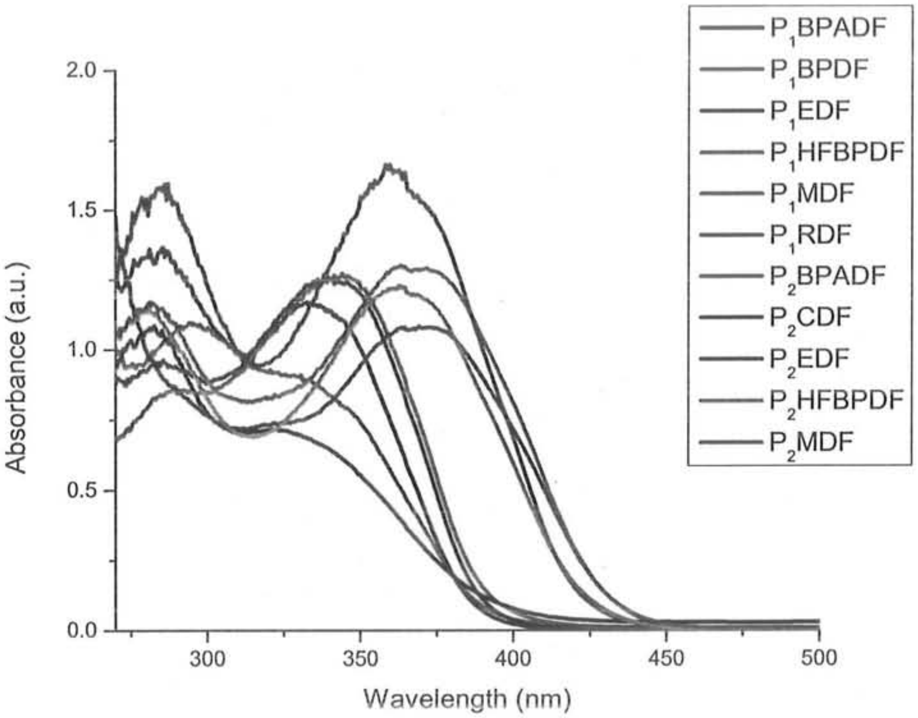


Figure 3.7: UV-visible Spectra of Polyazomethines in DMF

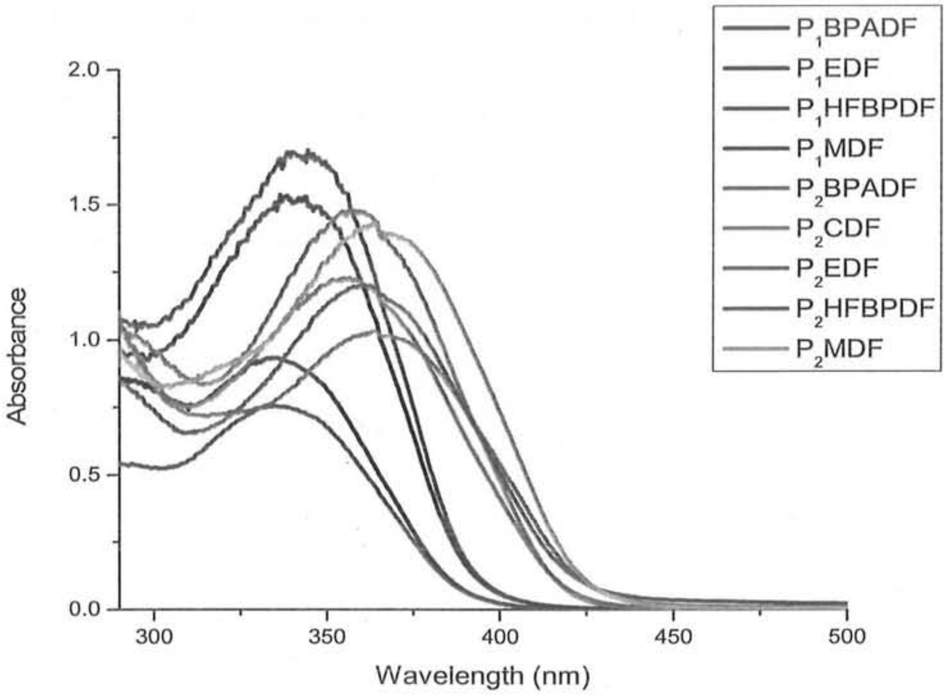


Figure 3.8: UV-visible Spectra of Polyazomethines in $CHCl_3$

**Table 3.10 (b): UV-Visible Data of Polymers**

| Code | $H_2SO_4$ ($\lambda_{max}$ nm) | $E_g$ |
|---|---|---|
| $P_1$MDF | 414 | 2.99 |
| $P_2$MDF | 402 | 3.08 |
| $P_1$EDF | 405 | 3.06 |
| $P_2$EDF | 390 | 3.18 |
| $P_1$BPADF | 385 | 3.22 |
| $P_2$BPADF | 402 | 3.08 |
| $P_1$HFBPDF | 391 | 3.17 |
| $P_2$HFBPDF | 405 | 3.06 |
| $P_2$CDF | 395 | 3.14 |
| $P_1$ODF | 410 | 3.03 |
| $P_2$ODF | 429 | 2.89 |
| $P_1$HDF | 399 | 3.12 |
| $P_2$HDF | 425 | 2.92 |
| $P_1$BPDF | 389 | 3.19 |
| $P_2$BPDF | 414 | 2.99 |
| $P_1$RDF | 423 | 2.93 |

Acidichromism behavior can be easily mirrored in UV-visible spectra of macromolecular imines (table 3.10 (b) and figure 3.9). The acidic solutions turned dark yellow or red while the corresponding neutral solutions were light colored. Electronic spectrum taken in sulfuric acid shows that the charge transfer from Bronsted acid to lone pair of electron on nitrogen in aldimine has taken place. It is believed that protonation of aldimine linkage result in coplanar backbone, thus, leading to increased π-electronic cloud delocalization. The protonated form (–CH=NH$^+$) enhances greater π-electronic charge separation (that is N$^{+\cdot}$) by forming stronger electron-acceptor centers.

The band gap ($E_g$) values were calculated [11] using this equation;

$E_g = 1240/\lambda_{max}$

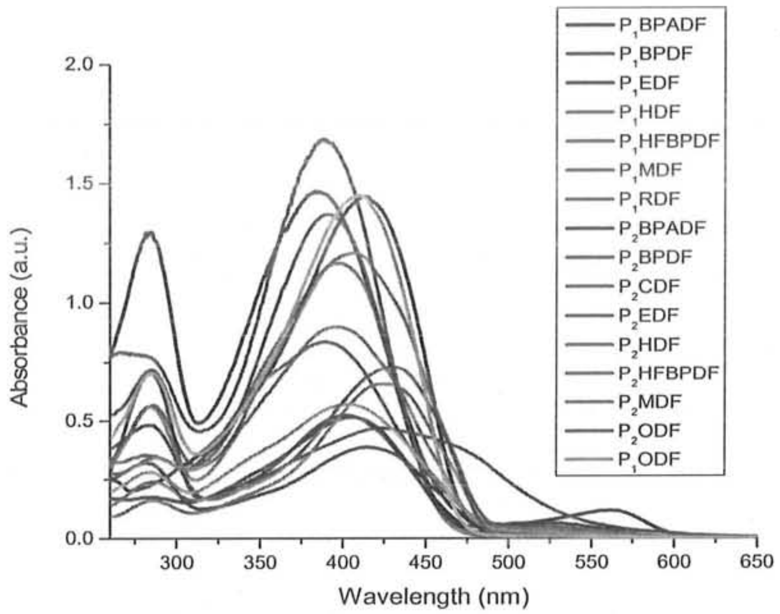


**Figure 3.9: UV-visible Spectra of Polyazomethines in $H_2SO_4$**

### 3.2.6 Photoluminescence Measurements:

The electroluminescent properties of polyaldimines are of meticulous interest because of instability of blue light (440–490 nm) emitting materials. The light emitting ability of polyaldimines have been explored on grounds of photoluminescence (PL) spectra measured in sulfuric acid (~$10^{-6}$– $10^{-8}$M solutions) using 420 nm as excitation λ that is close to $\lambda_{max}$ values, whereas, emission spectra were examined at 440 nm wavelength (with slit width 10 nm at scanning rate of 1500 per second). Almost all the poly(Schiff base)s showed emission $\lambda_{PL}$ nm ( in the range 479-493 nm) that lies in blue light region. The difference in absorption λ and emission λ maxima (called stokes shift) indicates energy decline during electronic transitions. This energy loss (~59-97 nm) can be attributed to excimer formation as evidenced by bathochromic effect and emission bands enlargement [12].

**Table 3.11: Photoluminescence Data of Polymers**

| Code | $\lambda_{max}$ nm | $\lambda_{PL}$nm | Stokes Shift (nm) |
|---|---|---|---|
| $P_1$MDF | 414 | 490 | 76 |
| $P_2$MDF | 402 | 490 | 88 |
| $P_1$EDF | 405 | 492 | 85 |
| $P_2$EDF | 390 | 483 | 93 |
| $P_1$BPADF | 385 | 482 | 97 |

| | | | |
|---|---|---|---|
| $P_2$BPADF | 402 | 482 | 80 |
| $P_1$HFBPDF | 391 | 482 | 91 |
| $P_2$HFBPDF | 405 | 483 | 78 |
| $P_2$CDF | 395 | 482 | 87 |
| $P_1$ODF | 410 | 481 | 71 |
| $P_2$ODF | 429 | 485 | 56 |
| $P_1$HDF | 399 | 493 | 94 |
| $P_2$HDF | 425 | 484 | 59 |
| $P_1$BPDF | 388 | 483 | 95 |
| $P_2$BPDF | 414 | 479 | 65 |
| $P_1$RDF | 423 | 482 | 59 |

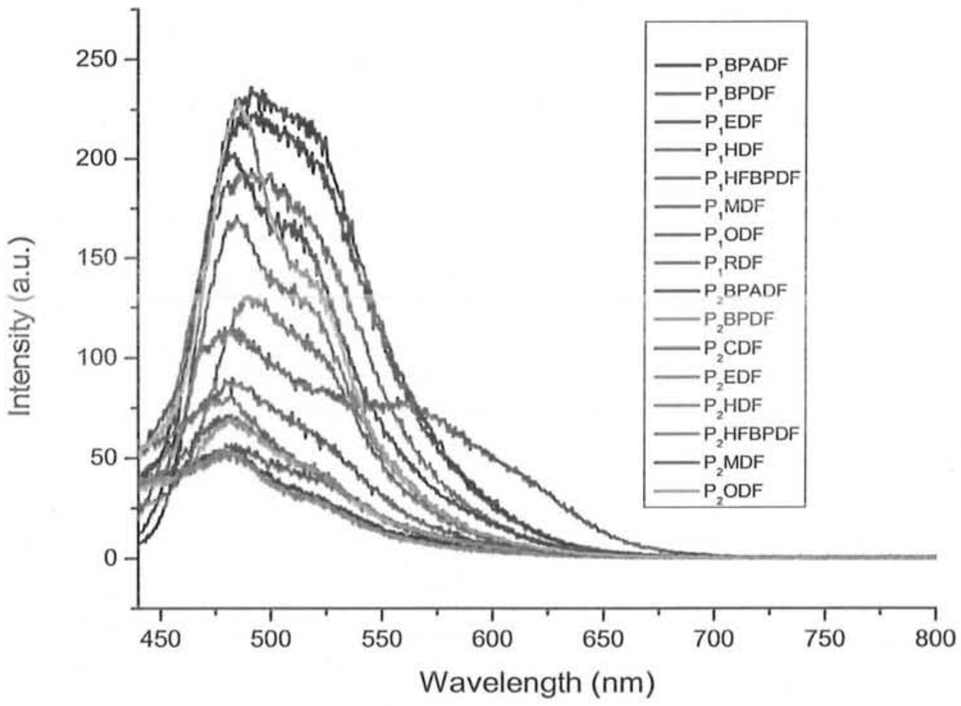


**Figure 3.10: Photoluminescence Spectra of Polyazomethines**

### 3.2.7 Thermal Measurements:

Thermal stability measurements of aromatic polyaldimines were carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal stabilities of aromatic polyaldimines were evaluated at 5% and 10% weight loss temperatures, $T_{5\%}$ and $T_{10\%}$ respectively, measurements in air atmosphere for comparison (using thermograms). The results of thermograms given in table 3.12

show that aromatic polyazomethines is a family of organic macromolecules that posses exceptional stability [13]. They did not show appreciable weight loss before 400°C (except $P_1$HFBPDF which shows $T_{5\%}$ = 175°C), accompanied by one-step decomposition behavior with more than 50% char yield residue at 600 °C. The maximum decomposition temperatures ($T_{max}$) of macromolecules situated in the temperature range 425-575 °C.

**Table 3.12: TGA Data of Polymers**

| Code | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{max}$ (°C) | Residue (%) at 600°C |
|---|---|---|---|---|
| $P_1$MDF | 390 | 410 | 475 | 58 |
| $P_1$HDF | 470 | 485 | 550 | 58 |
| $P_1$HFBPDF | 175 | 250 | 425 | 60 |
| $P_2$BPADF | 475 | 492 | 525 | 52 |
| $P_2$ODF | 500 | 520 | 575 | 59 |

### 3.2.8 Wide Angle XRD Measurements:

The wide angle X-ray diffractograms of powdered polyazomethine samples was measured using Cu as anodic material (with Kα = 1.154 Å). The polyaldimines constituted of only aromatic rings linked by azomethine or ether linkages showed semicrystalline state that is supposed to formed during high temperature polycondensation. The semicrystalline state of unsubstituted polyadimines can be assigned to high chain regularity, symmetry, and rigidity of 1,4-phenylene rings. Those polymers that have one tetrahedral carbon atom (having two $-CH_3$ or $-CF_3$ groups) in the main polymer chain showed one halos that can be attributed to polydispersity of macrochain caused by tetrahedral geometry of four coordinated carbon atom [14]. The polymers with $-OCH_3$ and $-OC_2H_5$ substituents on aryl moiety also showed amorphous behavior that can be assigned to less efficient macrochains packing. The table 3.14 shows the polymers morphology while the graph 3.11 shows the representative WAXRD graph of polymers.

**Table 3.13: WAXRD Data of Polymers**

| Polymer | Angle (2θ) | Crystallinity |
|---|---|---|
| $P_1$ODF | 19.8, 20.9, 23, 29 | Semicrystalline |
| $P_2$ODF | 19.8, 20.8, 23.3, 29.1 | Semicrystalline |
| $P_1$HDF | 19.4, 21.1, 23.1, 29.1 | Semicrystalline |
| $P_2$HDF | 16.7, 19.1, 20.8, 23.1, 29.1 | Semicrystalline |
| $P_1$BPDF | 19.7, 22.9, 29.1 | Semicrystalline |
| $P_2$BPDF | 19.8, 21.4, 23, 28.77 | Semicrystalline |
| $P_1$MDF | 19.3 | Amorphous |
| $P_2$MDF | -- | Amorphous |
| $P_1$EDF | -- | Amorphous |
| $P_2$EDF | -- | Amorphous |
| $P_1$BPADF | 18.6 | Amorphous |
| $P_2$BPADF | 14.84, 20.37 | Semicrystalline |
| $P_1$HFBPDF | -- | Amorphous |
| $P_2$HFBPDF | -- | Amorphous |

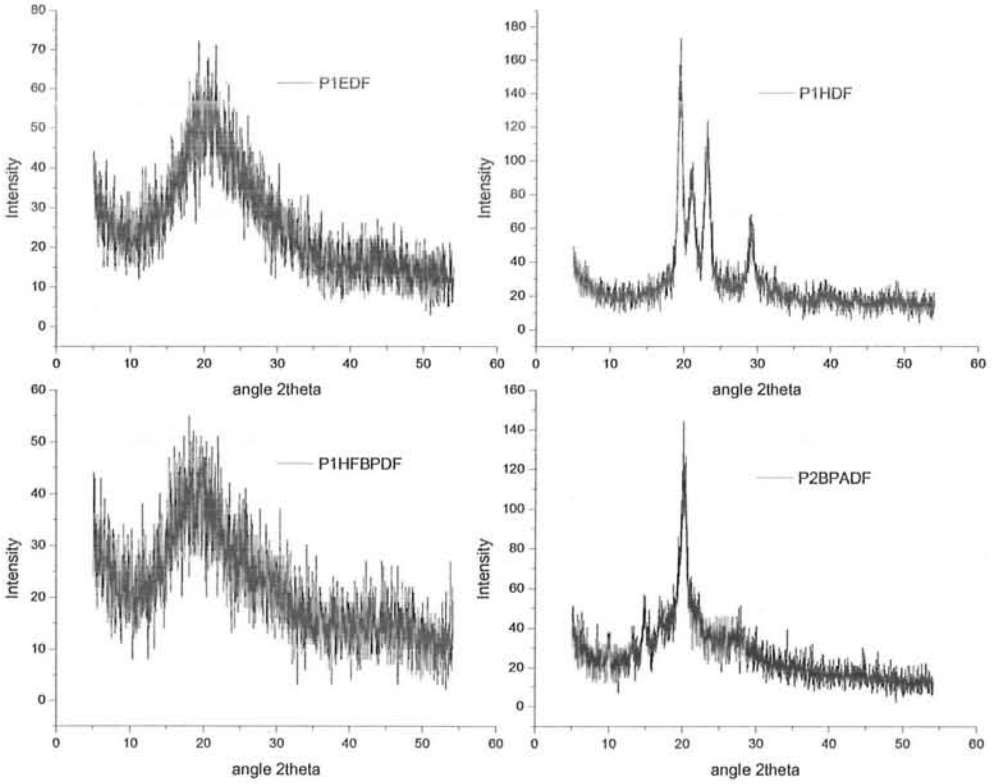


Figure 3.11: WAXRD graph of four polymers

### 3.2.9 Electrical Conductivity Measurements:

The electrical characteristics of synthesized polyaldimines were determined with Keithly source meter-2100 using pelletized polymer (0.5g sample pressed at 4.9 metric ton pressure for 5 minutes) with four probe conductivity technique. The four electrical connections were made with Cu wires placed at equal distance apart on pellet. The connections were fixed with silver conducting paste. The current (from 1-3μA) was used as input while measuring the voltage (V) as output signal. Then calculated the conductivity of each polyimine (with pellet dimensions as: diameter = 1.25 cm; radius = 0.625; area = 1.22718 cm$^2$; and distance between two probes = 0.3 cm).

**Table 3.14: Conductivity Measurement of Polymers**

| **Polymer** | **Conductivity (mS cm$^{-1}$)** |
|---|---|
| $P_1$MDF | 25 |
| $P_2$MDF | 32 |
| $P_1$EDF | 27 |
| $P_1$BPADF | 29 |
| $P_2$BPADF | 29 |
| $P_1$HFBPDF | 29 |
| $P_2$HFBPDF | 23 |
| $P_2$CDF | 27 |
| $P_2$ODF | 23 |
| $P_1$HDF | 27 |
| $P_1$BPDF | 33 |
| $P_2$BPDF | 17 |

The electrical conductivities (ranging from 17–33 mScm$^{-1}$) of all the polymeric imines lie in the semiconductors region [15].

## Conclusions:

The polyazomethines derived from non–substituted aromatic bisaldehydes (named ODF, HDF, BPDF) were found to be almost insoluble in DMF, DMSO, NMP and chloroform, whereas, others (having $-OC_2H_5$, $-CF_3$ groups) were found nearly complete soluble in these solvents. The polymers (with $-OCH_3$, and $-CH_3$ substituents) were partially soluble. All polymeric azomethine's solubility in conc. $H_2SO_4$ was good even at room temperature. The results of thermograms show that aromatic polyazomethines posses exceptional stability. They did not show appreciable weight loss before 400°C (except $P_1$HFBPDF which shows $T_{5\%} = 175$), accompanied by one-step decomposition behavior with more than 50% char yield residue at 600 °C. The maximum decomposition temperatures ($T_{max}$) of macromolecules situated in the temperature range 425-575 °C. The light emitting ability of polyaldimines have been explored on grounds of photoluminescence (PL) spectra measured in sulfuric acid ($\sim10^{-6}$– $10^{-8}$ M solutions) using 420 nm as excitation $\lambda$ that is close to $\lambda_{max}$ values, whereas, emission spectra were examined at 440 nm wavelength (with slit width 10 nm at scanning rate of 1500 per second). Almost all the poly(Schiff base)s showed emission $\lambda_{PL}$ nm ( in the range 479 – 493 nm) that lies in blue light region.

The reasonable solubility accompanied by photoluminescence and electrical conductivity measurements show that all the polyazomethines are blue light emitters having conductivity in the semiconductors range, therefore, they may be explored for their ability of being used in optoelectronic application for solar cell devices.

## Future Plans

The synthesized ether based dialdehydes with be polymerized with polydimethylsiloxane (PDMS) for their thermo-oxidative stability and opto(electronic) properties exploration. Moreover, the synthesized poly(azomethine)s will be doped with different dopants (10-camphorsulfonic acid, Ag+, I2, quinine sulfate, p-toluene sulfonic acid, FeCl3 etc) and their effect on opto(electronic), and electroluminescent properties will be studied. After doping, these poly(azomethine)s will be studied for their electrical properties (impedance, resistivity, and conductivity) and the mechanism of conduction will be derived based on cyclic voltammetric measurements, density functional computational calculations, as well as FT-IR spectroscopic analysis. The polyazomethines prepared by polycondensation and chemical vapor deposition methods will be compared based on better performance in solar cell device fabrication. The physicochemical properties will be investigated by incorporation of ferrocene and other heterocyclic aromatics (oxadiazole, flurene, thiadiazdole rings) as main chain or as pendent groups. The synthesized aromatic dialdehydes will be polymerized with different aliphatic or aromatic diamines and their liquid crystalline properties will be examined. The metal (Eu+3, La+3, Cu+2, Zn+2, Al+3 etc) complexes of polyazomethines will be studied for their liquid crystalline phases. The carbon nanoparticles will be synthesized from polyazomethine's calcinations in inert atmosphere and these particles will be explored for catalytic activity as well as electrode materials in solar cell device.

# References

## Introduction

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**Results and Discussions**

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