Synthesis, Development and Characterization of Some Advance Matrix Materials

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by

Amir Badshah

Department of Chemistry
Quaid-i-Azam University
Islamabad, Pakistan
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This dissertation entitled “Synthesis, development and Characterization of advance matrix materials” submitted by Mr. Amir Badshah, Department of Chemistry, Quaid-i-Azam University, Islamabad, for the degree of Doctor of Philosophy in Organic Chemistry has been evaluated by the following panel of Foreign Referees.

1. **Prof. Dr. Bob Hill**  
   School of Chemistry, Joseph Black Building, University of Glasgow, G128QQ, Uk.  
   E-mail: bob.hill@glasgow.ac.uk

2. **Prof. Dr. Jurgen Martens**  
   Laboratory of Organic Chemistry, Institute of pure and applied Chemistry Carl von Ossietzky University Oldenburg w3 2-301  
   Carl Von-von-Ossietzky-Strass 9-11 D-26129 Oldenburg i.o./ Germany  
   E-mail: juergen.martens@uni-oldenburg.de

3. **Prof. Dr. Thomas Wirth**  
   School of Chemistry Cardiff University, Main Building Park Place  
   Cardiff CF10 3AT, United Kingdom.  
   E-mail: wirth@cf.ac.uk
Dedicated
to
My Parents
Who make me pursue my dreams
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Phthalonitrile resins are high temperature thermosetting polymers, which are considered ideal materials for marine, aerospace, and electronic applications. The synthesis of phthalonitrile monomers with self-catalyzing nature and with large processing window – defined as the temperature between the melting temperature of the monomer and the gelation temperature of the polymer network – are gaining much more importance because of ease in processability and high thermal stability.

In the present study, some novel phthalonitrile resins were synthesized using ortho-linked phthalonitrile monomers and self-catalyzing phthalonitrile monomers with different linkages such as: ether, imide-ether, and amide-ether between the reactive ends. All the synthesized monomers were characterized by spectroscopic techniques such as FT-IR, 1H-NMR and 13C-NMR. FT-IR indicated absorption peaks around 1522 and 1355 cm\(^{-1}\) and around 1010 cm\(^{-1}\) indicated the formation of triazine and phthalocynine rings (heterocyclic rings formed as a result polymerization) respectively after post curing. The thermal analyses were carried using DSC, TGA, DMA, and Rheometry. DSC and rheometric studies showed that the monomers with ortho linkages have low melting point and high crosslinking temperature. In self-catalyzed monomers, the monomers having amino group at ortho position or 1,2-linked (ortho) monomers have broad processing window. The complex viscosity (\(\eta^*\)) was very low (<1 Pa.s) in between melting and the crosslinking temperature, which is highly suitable for resin transfer molding, resin infusion molding, and filament winding. TGA studies revealed that the resin synthesized from the monomer with heterocyclic ring shows high thermal stability and residual mass (char yield). The thermal stability of the polymer having ether or imide-ether linkages are nearly the same but more than the polymer having amide-ether linkage, indicating the effect of crosslinking density and structural changes. DMA measurements showed that storage moduli (\(E'\)) and glass transition temperature (\(T_g\)) enhance with the increase of curing temperature. These measurements also indicated that the polymers having imide-ether and amide-ether linkages have higher storage moduli than the polymers have only ether linkages.
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<tr>
<td>$m$-APB</td>
<td>1,3-bis(3-aminophenoxy)benzene</td>
<td></td>
</tr>
<tr>
<td>$m$-BAPS</td>
<td>Bis[4-(3-aminophenoxy)phenyl]sulfone</td>
<td></td>
</tr>
<tr>
<td>$p$-BAPS</td>
<td>Bis[4-(4-aminophenoxy)phenyl]sulfone</td>
<td></td>
</tr>
<tr>
<td>3-BDS</td>
<td>3,3'-bismaleimidodiphenylsulphone</td>
<td></td>
</tr>
<tr>
<td>6FPh</td>
<td>2,2-bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane</td>
<td></td>
</tr>
<tr>
<td>$\eta^*$</td>
<td>Complex viscosity</td>
<td></td>
</tr>
</tbody>
</table>
Chapter - 1
INTRODUCTION

1.1 Composite Materials

Composite materials have been known to mankind for several hundred years, for example in the form of straw-reinforced mud bricks and steel-reinforced concrete. Due to their high specific strength and stiffness of composites, modern composite materials have grown significantly in applications ranging from sporting equipment to aerospace structures. These rapid increases in the utilization of composites, suggest the demand for composites and their innovation will continue to increase steadily. The demands made by industries for the materials that are both light and strong remain the main driving force in the development of composites. These materials are used in a large number of products with the discovery of their benefits. However, these materials will never totally replace traditional materials like steel as well as the cost associated with the raw material used for their synthesis.

The word composite has been derived from a Latin word ‘‘componere’’ which means put together. In the field of materials, a composite is a mixture of two or more constituents having a distinct interface between them. It is a compatible combination of materials, which produces synergistic and bulk properties, significantly higher and different from those of its constituents. Composite materials mainly consist of a continuous phase (matrix) and a discontinuous phase (reinforcement). The matrix plays two important roles i.e. holding the reinforcement in an orderly pattern and to transfer load among the reinforcements under applied force. On the other hand, the reinforcement provides extra strength to the matrix phase. Fig. 1.1, indicates the constituents of composite.

The form of the reinforcements can be classified into three categories: fibers, particles and whiskers. Fiber reinforcement has a much higher length compared to its cross-section. Particles have approximately equal dimensions in all directions, and have no prefer orientation and shape. Discontinuous fibers of different cross sections are called whiskers or chopped fibers.
1.2 Matrix Materials

The strength of composites is derived mostly from the high strength reinforcement, but the matrix materials play an important role in supporting the fibres and in equal distribution of load among them. A resin starved composite is weaker due to free space among the reinforcements. The selection of a matrix mainly depends on compatibility with the reinforcement and the purpose of use of composite. Matrices are classified into three classes on the bases of their nature. They are given here.

i Metal matrix materials
ii Ceramic matrix materials
iii Polymer matrix materials

1.3 Polymer Matrix Materials

A lot of work has been done in the field of polymeric materials for the last few decades. They are highly attractive due to the unique properties of polymeric materials such as low cost, lightweight, easy processing, resistance to chemicals, and in obtaining desirable
properties\textsuperscript{4-8}. However, the low modulus and low strength of polymer matrices produce obstacles in their use\textsuperscript{9}. A number of polymers are available as a matrix for the formation of composite, but two main kinds i.e. thermoplastic and thermosets are used commonly.

1.3.1 Thermoplastics
Thermoplastics are high molecular weight polymers, which can be reshaped easily by heat and pressure. They are mostly non-reactive compared to thermosets. Thermoplastic-based composites are developed from the polymeric form. Due to the high viscosities of these high molecular weight polymers, the processing of thermoplastic composites is difficult. In addition, these materials mostly needed high pressures and temperatures. Some common thermoplastic used as matrices are polypropylenes (PP), polyamides (PA) polyethersulphones (PES), and polyetheretherketones (PEEK).

1.3.2 Thermosets
Thermosets are polymers which form three-dimensional (3D) net works by curing. Curing or cross-linking is a chemical reaction carried out by heat, pressure or by adding some curing agent along with heating. These resins undergo irreversible reaction on heating and changed into insoluble and infusible materials. The resulting product, which is called a thermoset resin, is very tough, hard and infusible. These materials cannot be reversed back, otherwise they will decompose. Some common examples of thermosetting polymers are phenolics, polyesters, epoxies, and polyimides etc.

1.3.2.1 Phenolics
Phenolic resins are well known for their applications in the field of electronics and construction. Their wide range of applications are due to low cost, resistance to heat, ability to remain as a prepolymer (B-stage) for a long time, good dielectric properties, and high resistance to chemicals, moisture, and solvents. They are fire resistant and emit very low smoke on burning. On the basis of these remarkable properties, the composites of phenolic resins have found a proper position in the market\textsuperscript{10-12}.

Phenolic prepolymer are of two types, i.e. resoles and novolacs\textsuperscript{13}. Resoles are prepared under basic conditions by the reaction of phenol with an excess of formaldehyde up to 1:3. The mechanism is base catalyzed electrophilic aromatic substitution reaction to form mono, di or trihydroxymethylphenols, which are then reacted further to form prepolymer. The prepolymer are formed under two pathways depend on \(pH\) and temperature. If the medium is weakly acidic or neutral and the temperature is less than
130 °C, then dihydroxydibenzyl ether prepolymer is the main product, which lead to dihydroxydiphenylmethane prepolymer by heating. If the medium is alkaline and the temperature is in between 130-150 °C, then dihydroxydiphenylmethane prepolymer is major product as shown in Fig. 1.2.

![Diagram of Resole prepolymer formation](image1)

Figure 1.2: Resole prepolymer formation

Novolacs are synthesized by the reaction of excess of phenol or its derivatives with formaldehyde under acidic conditions. In the initial stage methylol-phenol is formed through an electrophilic substitution reaction, followed by reaction with another phenol molecule to form dihydroxydiphenylmethane as shown in Fig. 1.3.

![Diagram of Novolac prepolymer formation](image2)

Figure 1.3: Novolac prepolymer formation

Resoles are cured only by heating without any curing agent, while novolacs are cured by the use of curing agents such as hexamethylenetetramine to produce nitrogen containing network\textsuperscript{13,14}. However, some volatile products are released during curing of novolacs such as ammonia and formaldehyde, which can cause voids formation in the cross-linked
product. To overcome this problem, novolacs can be converted into epoxy resins which are crosslinked by using amines.

**1.3.2.2 Polyesters**

Polyester resins are used for the formation of composites, widely used in building boats. Glass fiber reinforced polyesters are used for the fabrication of main body of leisure boats due to their resistance to deterioration in marine environments. Unsaturated polyesters are used as liquid molding resins\textsuperscript{15}. They are widely used in various industries. Due to their low cost and high strength, one can find their uses in the tanks, pipes and electronic equipments. The unsaturated polyesters, reinforced with fiber glass or some other inert filler for improving their mechanical properties and decreasing their cost, are used for house-wares, bathtubs, furniture and many other daily usable items\textsuperscript{16-18}.

Polyesters are stable polymers, which are prepared by the esterification of di or polyelectrolyte acids and anhydride with di- or poly-hydric alcohols. They are classified into saturated polyesters and unsaturated polyesters\textsuperscript{19}. Unsaturated polyesters are used in composite materials, which are formed in three steps. In the first step a condensation reaction take place between a di-hydric-alcohol and an anhydride or a di-basic acid to form a prepolymer, followed by addition of a monomer such as styrene. In the third step, they are cured in the presence of peroxide, following a free radical mechanism as shown in Fig. 1.4. Different types of monomers are added as diluents, but styrene is preferred due to its low cost and low viscosity. Unsaturated polyesters are preferred due to their crosslinking ability to form a three dimensional network structures. These cross-links do not allow them to be remelted or reshaped by applying pressure or heat\textsuperscript{18}.

![Figure 1.4: Synthesis of polyester](image-url)
Polyester resins are inexpensive compared to other thermosetting resins but, on the other hand, they are more prone to degradation by water due to hydrolysable ester groups in the main chain. As a result, they may lose their inherent strength after immersion in water.

1.3.2.3 Epoxies

Epoxies are widely used in industry due to their unique characteristics such as excellent moisture resistance, good adhesion, resistance to chemicals, low shrinkage on curing, minimum pressure for fabrication, and excellent electrical insulating properties. They are used as adhesives, paints, varnishes, dyes, encapsulating materials, and for structural applications. For conventional composites, difunctional epoxy-based resins are often used as the matrix, but for high performance composites multifunctional epoxies are used.

Epoxies comprise more than one epoxide groups within the molecule. The epoxide (oxirane) group is a three membered ring, comprising two carbon atoms and one oxygen atom, which are introduced by either epichlorohydrin or by the epoxidation of double bond with peracids. The nature of the backbone of these polymers depends upon the nature of diol used, which may be aliphatic or aromatic. They are synthesized in two steps. In the first step a diol reacts with an excess amount of epichlorohydrin in basic medium to form an oligomeric monomer, followed by curing with diamines to form a three-dimensional network as shown in Fig. 1.5. Other curing agents used include carboxylic acids, anhydrides, and phenols.

![Synthesis of epoxy resin](image)

Figure 1.5: Synthesis of epoxy resin
Modification in epoxy resin, for convenience in processing, increases the demand of these resins. However, advanced applications require materials which can be used at high temperatures and have excellent mechanical properties. Epoxy resins have some limitations in these fields. Some other properties, like inherent brittleness due to high crosslinking density, limit their uses in composite formation by the formation of microcracks. Epoxy resins often need to be stored at low temperatures, have relatively low upper service temperatures (less than 200 °C), have high cost, and burn with a high degree of smoke emission. In order to overcome these problems, some alternative materials are needed which have high service temperature and better dielectric properties.

1.3.2.4 Polyimides

Polyimides (PIs) are well known for their many excellent properties such as resistance to heat and chemicals, very high thermal stability, exceptional optical properties, and outstanding mechanical and insulating properties. They have many uses requiring high temperature, which include aerospace, marine, electronics, adhesives, coatings, advanced composites, semiconductors, and automotive applications.

Polyimides have a heterocyclic imide linkage in the polymer skeleton. The synthesis involves a two step condensation reaction between dianhydrides and diamines in aprotic solvent. In the first step a processable poly-(amic acid) is formed, followed by cyclodehydration to form an insoluble imidized product as shown in Fig. 1.6.
Polyimides have some limitation in their uses. They have poor solubility, high melting temperature, and poor processability. The reason behind their insolubility and high melting temperature are lack of flexibility and strong interactions between chains due to highly polar groups and symmetry. In order to overcome these problems, these resins are processed in their soluble precursor poly-(amic acid) form, followed by imidization to obtain polyimide. However, melt processing is economical and more desirable from an environmental point of view. The product obtained through melt processing is comparatively suitable and of excellent qualities. The most serious problem is that the imidization is carried out at very high temperature to carry out the cyclodehydration. As a result, the generated water condensate can cause voids to form in the final product, which has very adverse effects on their mechanical properties of the polymers.

### 1.3.2.5 High Temperature Functional Group Polymers

In order to overcome the problems concerned with polyimides, pre-imidized oligomeric monomers terminated by reactive end groups were introduced, which are polymerize by addition mechanism without producing any by-products such as water and produce void-free products. Generally, these oligomeric monomers with unsaturated end caps are capable of thermal crosslinking with low viscosity, near the region where curing take place. Sometimes, these potential reactive end-groups are found as pendant in the oligomeric monomers. A wide range of end-groups have been used, whose name and chemical structure are shown in the Table. 1.1.

**Table 1.1: Potential end groups for high temperature polymers**

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Structure</th>
<th>Name</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethynyl</td>
<td>CH</td>
<td>Phenylethynyl</td>
<td>CH-Ph</td>
</tr>
<tr>
<td>Maleimide</td>
<td>N=O=N</td>
<td>Nadimide</td>
<td>N=O=O</td>
</tr>
<tr>
<td>Biphenylene</td>
<td></td>
<td>Phenylmaleimide</td>
<td>N=O=O</td>
</tr>
<tr>
<td>Benzocyclobutene</td>
<td></td>
<td>Phthalonitrile</td>
<td>C=C=O</td>
</tr>
</tbody>
</table>

The driving force behind the development of these potential end-group polymers is not only to cover the shortcomings of polyimides but also an alternative for other high
performance polymers such as phenolics and epoxies. The selection of these potential end-group polymers depends on the thermal stability requirements of the system.

1.3.2.5.1 Phenylethynyl End Group Polymers
Considerable effort has been made to develop such end-group polymers that can be crosslinked to a greater extent, develop a high glass transition temperature, and be used over a wide processing window. The phenylethynyl end group polymers are capable of producing thermally stable networks with resins which are easy processed. Besides these advantages, they undergo curing at about 370 °C without producing by-products; provide a material with an outstanding mechanical strength processed over a broad processing window.

McGrath et al. have performed considerable work in enhancing the stability of polyimide by using \( m \)-aminophenyl acetylene. They were successful in producing a highly stable net-work but their resins had a very narrow processing window. By using phenylethynyl aniline the processing window was enhanced by shafting the curing temperature up to 380-450 °C. However, these amine containing end-caps are toxic. Therefore, much attention was given to phenylethynyl end-capping groups having low toxicity, yet being capable of producing high level of crosslinking, and a broad processing window. In this connection, a series of polyimide oligomers end-capped with phenylethynyl were synthesized with molecular weights between 3000 and 15000 g mol\(^{-1}\). Upon curing these oligomers for a certain period of time at certain temperature, the glass transition temperature increased. The 5 % weight loss temperature for the fully cross-linked product was in the range of 537-555 °C. Meyer et al. synthesized a series of poly(arylene ether phosphine oxide) copolymers with pendant phenylethynyl groups having molecular weights between 7000-10000 g mol\(^{-1}\). Upon curing, these copolymers formed a highly cross-linked network with \( T_g \) values in the range of 200-220 °C.

In a similar study, a series of oligomeric polyimide end-capped with phenylethynyl were synthesized of 3200 g mol\(^{-1}\), 4200 g mol\(^{-1}\), and 7000 g mol\(^{-1}\) with different substituents attached to the phenyl ring of phenylethynyl end group as shown in Fig. 1. In this study, the effect of various substituents on their stability and cross-linked density was investigated. It was found that the 3200 and 7000 g mole\(^{-1}\) oligomers with electron-withdrawing groups decreased the onest cure temperature. Additionally, by curing the oligomers at high temperature the \( T_g \) increased. The oligomers with nitrile and fluoro
groups showed the fastest rate of increase in $T_g$. However no substantial difference was observed in the 5 % weight loss temperature compared to unsubstituted oligomers 43.

Figure 1.7: Substituted phenylethynyl end-capped polyimides

Similar approach has been used for other kinds of polymers 44 in addition to polyimides, end-capped with acetylene end-groups as shown in Fig. 1.8. Their thermal behavior was measured using different analytical techniques. The cure behavior, evaluated by differential scanning calorimetry under air and nitrogen indicated crosslinking peak in the range of 212-261 °C and 220-276 °C respectively. This similarity indicated that the oxygen has little role in curing, contrasting the results of other studies 45,46 which had indicated that the rate is retarded in an oxygen atmosphere. The 5 % weight loss temperature for the cure product obtained from the monomers BEBB and BEBN was between 500 and 630 °C, while for the cured product obtained from monomer BEPP was higher by 15 to 30 °C due to its different chemical structure. The 5 % weight loss temperature increases with post curing. Their shear moduli decrease with increase of temperature in air.

Figure 1.8: p-Ethynyl-terminated monomers
These oligomeric monomers polymerize without producing any by-products. They have good thermal resistance and low uptake of water. However, the major disadvantage is the cost of the starting chemicals and the catalysts required for them. The presence of minute amount of catalyst in the product also affects their properties. The acetylenic terminated oligomides have also narrow processing window.

1.3.2.4.2 Maleimide and Nadeimide End Group Polymers

Bismaleimides (BMIs) and bisnademides (BNIs) are the most commonly studied thermosetting resins which are commercially available. They are of great interest because these end-capping reins have desirable crosslinking, easy processing, and comparatively low cost\textsuperscript{47-50}.

BMIs are synthesized by the reaction of diamine with maleic anhydride via a two step process. In the first step maleamic acid is formed, followed by thermal or chemical cyclization to form maleimide, without isolation of intermediate as shown in Fig. 1.9.

\begin{center}
\includegraphics[width=0.8\textwidth]{bismaleimide.png}
\end{center}

\textbf{Figure 1.9: Synthesis of bismaleimide and polymerization}

\textsuperscript{4,4'}-bismaleimidodiphenyl methane (BDM) is commonly used for the synthesis of BMIs, because the diamine used in its synthesis is of low cost and are easily available. However BDM has poor processing, a high melting point, and requires a high curing temperature. In addition, the resulting resin from BDM is brittle as well as rigid\textsuperscript{51}. Therefore, a major research focus of the polymer community has been to improve the toughness of BMIs without compromising their thermal and thermo-oxidative stability. In this connection the role of diallylbisphenol A (DBA) and its isomers\textsuperscript{52,53} has been studied widely. Another approach for increasing the strength of cross-linked BMIs is the polymerization of bimaleimide with diamines. The reaction is a nucleophilic attack of the amino group on the double bond promoted by electron-withdrawing tendency of adjacent carbonyl groups. As a result the molecular weight increases and thus the strength improves\textsuperscript{54}. 
A main focus is on the development of highly cross-linked BIMs which show high stability\textsuperscript{55}. In this connection BMIs of $\beta,\beta'$-dichloroterephthalyl dimalonitrile were prepared and cross-linked by heating at 300 °C as shown in \textbf{Fig. 1.10}. The resulting networks were analyzed through various thermal techniques. TGA results indicated 5% weight loss temperature in the range of 355-389 °C under both nitrogen and air. The char yield generated by the cured product under nitrogen was in the range of 57-66% up to 800 °C.

Besides maleimide, its derivatives have also been used as potential end-capping groups such as phenyl maleimide. It has been reported that these end-capping reagents have superior properties over maleimides\textsuperscript{56}. The polyimides, end-capped with phenylmaleimide cured at high temperature, exhibited high thermo-oxidative resistance due to a high degree of cross-linking. Similarly, ether and imide-based oligomers end-capped with maleimide derivative were synthesized with a broad processing window\textsuperscript{57}. The resulting net-works have higher $T_g$ than the corresponding oligomeric monomers. The polymer net-work based on hexafluorinated dianhydride (FDA) showed high $T_g$ values after curing. TGA of the polymer network based on FDA displayed a 5% weight loss temperature above 550 °C. The polymer network of the oligomers obtained from bisphenol-A dianhydride and m-phenylene diamine showed $T_g$ in the range of 215 to 230 °C. TGA indicated 5 % weight loss temperature above 500 °C in air. It was concluded that the broad processing window and high stability of these oligomers make them suitable candidates for high performance polymers.

\begin{center}
\textbf{Figure 1.10: Synthesis of $\beta,\beta'$-dichloroterephthalyl dimalonitrile and imidization}
\end{center}
Much interest\textsuperscript{58,59} has been shown in the curing BMI oligomers other than homopolymerization. Many of these approaches are meaningful; however, in many cases they lower $T_g$ and thermal stability. Different types of BMIs oligomers like 4,4\textasciiacute- bismaleimidodiphenylmethane (BDM), 4,4\textasciiacute- bismaleimidodiphenylether (BDE), and 3,3\textasciiacute- bismaleimidodiphenylsulphone (3-BDS) were cured with different mole \% of allylamine. It was found that, among these combinations the resulting network from 50 mol \% BDM allylamine have higher $T_g$ and thermal stability\textsuperscript{60}.

A related system to BMIs are the Nademides end-capped resins are commonly used for the formation of composites, which are used in aircraft engines due to high thermal oxidative stability\textsuperscript{61}. These resins can be synthesized from the oligomeric monomers end-capped by nadic groups, which are in turn, cross-linked to form light and highly stable materials. A classical synthesis of bisnademides (BNIs) involve the reaction of diamine, dimethyl ester of benzophenone-3,4,3\textasciiacute,4\textasciiacute-tetracarboxylic acid, and mono methyl ester of nadic diacid via a two step process. In the first step amic acid is formed, followed by thermal imidization to form imide, and finally cross-linked through retro Diels-Alder reaction as shown in \textbf{Fig. 1.11}. However, the removal of by-products formed during imidization and low molecular weight components during the reactions create problems\textsuperscript{62}.

\begin{center}
\textbf{Figure 1.11: Synthesis of BNIs and polymerization}
\end{center}
1.3.2.4.3 Phthalonitrile End Group Polymers

In aircraft, all those structural composites are used, which are light in weight and have high fuel efficiency. With the utilization of composites in aircraft, it was needed to develop materials of low flammability and of light weight to maintain airframe loads. Polymeric materials are used both in non-structural and semi-structural applications in cabin interiors. But mostly, these materials release significant smoke when burned and do not meet the requirements for aircraft fire safety. In addition, using high temperature polymeric materials creates problems in processing. In order to overcome these problems, materials are needed which are inflammable, easily processable, and still have adequate mechanical properties.

Phthalonitrile-based polymers are highly inflammable and thermally stable up to 375 °C. Phthalonitrile monomers polymerize without releasing any volatile products, and thus they form void free composites. They are superior over other polymers in terms of excellent thermal properties and easy processing. The most striking advantage of these materials is the indefinite shelf life of the prepolymer under ambient conditions, which can be stored for later usage. The rate of polymerization of these monomers can be also controlled as a function of curing temperature and curing agents. The fully cured phthalonitrile-based polymers show glass transition temperatures higher than 450 °C and retain their mechanical properties at high temperatures. Currently polyimides can stand up to 316 °C but they have problems in processing and the formation of micro-voids in the panel products. Polyimides have a narrow processing window which makes them inadequate for fabricating composite components. In order to overcome these problems, phthalonitrile resins have a wide processing window, are inflammable, and are thermally stable. The most commonly used phthalonitrile monomer is biphenyl-based phthalonitrile monomer for formulation of composites, using carbon or glass fibres as reinforcement. Phthalonitrile monomers are processed by non-autoclavable processing techniques such as resin transfer molding, resin infusion molding and filament winding, due to their low melt viscosity (0.01-1Pa.s). Only phthalonitrile-based composites can meet the stringent requirements of navy submarines.

Marvell and Martin considered bisphthalonitriles as a precursor of thermally stable polymers. The monomer used by them was bis(3,4-dicyanophenyl)ether, believing that this monomer was less reactive due to inflexibility. Some new monomers were synthesized with long spacer groups between the phthalonitrile units to enhance their
reactivity. Transition metals and their salts were used to enhance the degree of polymerization. The degree of polymerization could also be enhanced by using small amounts of primary amines, and it was considered that the bisphthalonitriles react as difunctional monomers to form poly-isoindolenine. In addition to amine, amidine salts were also used to promote the mechanical properties along with increasing extent of curing. Phthalonitrile reagents are cured thermally in the presence of minute amounts of curing agents, through triazine ring mostly to form a stable network with good processability and high strength and stiffness. In addition, conversions of these monomers to phthalocyanine, isoindoline and dehydrophthalocyanine structures are also possible as shown in **Fig. 1.12**.

The proposed mechanism for the polymerization and formation of triazine rings is depicted in **Fig. 1.13**. The reaction proceeds through simple nucleophilic addition mechanism. In the last step, cyclization takes place to form trizine ring and eliminate the amine which is free now to initiate another reaction cycle.
Phthalonitrile based monomers are cured in the presence of minute amount of 1,3-bis(3-aminophenoxy)benzene (m-APB) as a curing agent. However, it has been found that during curing at high temperature, volatilization\(^7^4\) of (m-APB) occurs, which results in a slowdown of the curing reaction and creates problems in attaining anticipated properties. The use of (m-APB) also reduces the processing window, due to its high reactivity and low boiling temperature, by increasing the viscosities. Keller \textit{et al.}\(^7^5\) used some less reactive and high boiling temperature diamines in order to improve the processability of phthalonitrile monomers. He used three different types of diamines to find their effect on the processability of 4,4'-bis(3,4-dicyanophenoxy)biphenyl (BPh) net-work systems as shown in \textbf{Fig. 1.14}. Among the three used aromatic diamines, \textit{p}-BAPS has proven to be the most promising due to its high boiling temperature, low reactivity and production of a net-work with a high glass transition after post-curing.

Keller \textit{et al.}\(^7^6\) employed another approach to enhance the mechanical properties of the net works of phthalonitrile by using a variety of structural changes within the monomers. In addition to 4,4'-bis(3,4-dicyanophenoxy)biphenyl (BPh), two other different monomers used were 2,2-bis(4-(3,4-dicyanophenoxy)phenyl)hexafluoropropane (6FPh) and 2,2-bis(4-(3,4-dicyanophenoxy)phenyl)propane (BAPh). The curing agent used was \textit{m}-APB. The polymerization or increase in rate of viscosity was dependent on the concentration of curing agent at 260 °C and with widest processing window of BAPh compared to BPh and 6FPh. This widest processing window of BAPh is due to the electron donating effect of the –\text{C(CH\textsubscript{3})\textsubscript{2}}– linking group. The TGA studies indicated that the polymer network of all the three systems have a 5% weight loss temperature at 450 °C under nitrogen with char yields between 50 and 60%. In air, all the network polymers
have no char yield up to 800 °C with 5 % weight loss temperature in the range of 500–600 °C. The glass transition temperatures of all the three systems were enhanced with increasing curing temperature and time.

Figure 1.14: 4,4′-bis(3,4-dicyanophenoxy)biphenyl (BPh) and aromatic diamine
Keller\textsuperscript{77} reported the incorporation of imide groups in the phthalonitrile oligomeric monomer to enhance the mechanical properties by the formation of void free composites. The polymerization study of the monomer with reactive end groups was analyzed by DSC, using \textit{m}-APB as a curing agent. The time to increase in viscosity can be easily controlled as a function of concentration of \textit{m}-APB and the reaction temperature. It was observed that with the increase of extent cure the glass transition temperature increased and finally no distinct transition was observed from the glassy state to the rubbery state upon post-curing at 316 °C for 16h. TGA studies showed that thermal stability increased with increasing of extent of curing. The 5 % weight loss temperature for the post-cured sample was near about 500 °C under nitrogen with char yields near 60%. In air, the 5 % weight loss temperature is nearly the same as under nitrogen with catastrophic degradation occurring at about 550 °C. The post cured product has no char yields up to 650 °C under air.

Keller \textit{et al.}\textsuperscript{78} reported another approach to enhance the processing window, thermal stability, and mechanical properties by using resorcinol based phthalonitrile monomer. Both \textit{m}-BAPS and \textit{p}-BAPS were used as curing agents for comparative study. The polymerization reaction was studied with 2.4 and 5.8 mol % of \textit{m}-BAPS and \textit{p}-BAPS by DSC. The results showed that both curing agents with the mentioned mol % have nearly the same reaction temperature with the monomer. The processing window is about 70–100 °C between the melting transition and polymerization reaction. Thus, a large amount of the curing reagent can be used without affecting the properties of the final cured product. During fabrication of the monomer, the viscosity can be easily controlled as a function of curing temperature and the amount of curing reagent. TGA results showed that the monomer cured with 2.4 mol % of \textit{m}-BAPS and \textit{p}-BAPS exhibited char yields of 70 and 66 % under nitrogen, respectively, after heating to 1000 °C. The higher weight retention of the sample cured with \textit{m}-BAPS is due to the enhanced reactivity of \textit{m}-BAPS compared to \textit{p}-BAPS. However, the samples cured with 5.8% of \textit{m}-BAPS and \textit{p}-BAPS showed nearly the same char yields of about 74 and 73 %, respectively. This is probably due to enhancement in the curing. These results indicated that extent of curing and thermal stability is a function of curing reagents during polymerization. In air, the sample, post-cured with 2.4mol % of \textit{m}-BAPS and \textit{p}-BAPS, exhibited the same oxidative stability up to 450 °C, followed by a sudden decomposition in the range of 500–700 °C. However, the sample cured with \textit{p}-BAPS started the thermal and oxidative
decomposition at a relative higher temperature than the sample cured with $m$-BAPS. The post cured samples with both amines resulted in polymers with storage moduli about 1GPa at 40 °C, followed by a gradual decrease with the increase of temperature and increase in damping factor above 375 °C. These results indicate that the cross-linked product maintained excellent mechanical properties at high temperatures. However, the modulus of the $m$-BAPS cured sample decreased gradually and the damping factor increased slowly above 375 °C, indicating the softening and further curing of the sample. On the other hand, the modulus of $p$-BAPS cured sample remained smooth, without any rise in damping factor up to 400 °C, indicating that the sample maintained its structural properties.

Dominguez and Keller\textsuperscript{79} investigated the effect of variable length of multiple ether linkages on the phthalonitrile monomers for improving their processability without compromising their thermal stability, using $p$-BAPS and $m$-APB as curing additives.

\begin{center}
\includegraphics[width=0.5\textwidth]{ether.png}
\end{center}

$n = 2, 4, 6, 8$

DSC was carried out from 0 to 400 °C to study the polymerization of the $n = 2$ and $n = 4$ oligomeric monomers with 5 mole % $p$-BAPS and $m$-APB as a curing additives. It was observed from the thermograms for each prepolymer that they have a wide processing window (> 200 °C) due to lower melting transitions and higher cross-linking temperatures. By comparing the polymerization temperature of the $n = 2$ and $n = 4$ oligomeric monomers with the same amount of curing agent, the former has lower cross-linking temperature due to high concentration of cyano groups. The lower heat of melting of these monomers indicated that they are more amorphous than lower molecular weight monomers. However, the heat of curing is nearly similar to that of lower molecular weight monomers indicated that structural changes were not significant. TGA studies indicated that 5 % weight loss temperatures of the $n = 2$ and $n = 4$ phthalonitrile monomers cured up to 375 °C with 5 mole % $p$-BAPS and $m$-APB, were 487 and 493 °C, with char yields of 55 and 62 % at 1000 °C, respectively, under nitrogen. In air, the 5 % weight loss temperatures were 479 and 486 °C. After curing the $n = 2$ and $n = 4$ monomers at 425 °C for 8h, the 5 % weight loss temperature increased to 565 and 560 °C, respectively, under nitrogen. Char yields were increased to 72 % and 69 % at 1000
°C, respectively. In air, the 5 % weight loss temperatures increased to 558 and 552 °C, respectively. The high thermal and thermal oxidative stability at high curing temperature is due to the increased conformational freedom in the net-work system. Similarly the decomposition of n = 2 and n = 4 monomer based network is more gradual than for other polymers. DMA analyses were carried out on polymer samples from 40 to 450 °C, in order to find the effect of chain length and different heat curing on the storage modulus and damping factor. It was found that both storage moduli and damping factors increased with the increase of curing temperature from 375 to 425 °C, due to formation of a stable network which hindered the motion. The storage modulus of the n = 2 monomers is higher due to high crosslinking density and it decreases steadily with the increase of temperature due to releasing stress in the network.

Laskoski et al.\textsuperscript{80} described another approach for improving oxidative stability by incorporating phosphine oxide linking groups along with resorcinol and bisphenol A in the oligomeric monomers. The polymerization studies were carried out by DSC in the presence of 3 wt % of \textit{p}-BAPS, as a curing additive due to its high thermal stability. It was found that both resorcinol and bisphenol-A based oligomeric monomers with phosphine oxide, showed low melting temperatures and had a wide processing window. Rheometric studies showed no visible changes from the glassy to rubbery state up to 400 °C. However, the storage modulus decreased slowly and gradually with the increase of temperature due to flexibility within the polymer backbone during heating. This mobility and flexibility do not cause any catastrophic degradation. The decrease in storage modulus was not the same throughout heating, but a much slower decrease was observed from 325 to 400 °C. The curve for indicating damping factor showed some minor transitions at low temperature along the broader one around 300 °C. These minor transitions are due to the chain mobility within the backbone of cross-linked product. TGA analysis indicated 5 % weight loss temperature was around 490 °C for both resorcinol and bisphenol-A based monomers and showed char yields of 65 and 56 %, respectively, up to 1000 °C under nitrogen. In air, 5 % weight loss temperature was 490 and 495 °C, respectively. They showed catastrophic decomposition between 600 to 800 °C and with char yields of 4.3 and 8.0 % at 1000 °C. The oxidative stability was also studied at high temperature for a long period of time. It was showed that the percentage of total weight loss at various temperatures, for the polymers having phosphorus atom was lower than the polymers having no phosphorous atom in the backbone. A
cumulative weight loss for resorcinol and bisphenol A based monomers with phosphine oxide was 3.9 and 4.2 %, respectively upon heating from 250 to 375 °C, which are slightly improved over bisphenol A based oligomeric monomers without phosphorus, where 4.0 and 7.2 % weight loss, respectively, was shown. When they were heated up to 400 °C for 8h, more weight loss of 4 and 6.6 % was observed. These results indicated that the polymers without phosphorus have a 2-3 times higher weight loss than the phosphorus containing polymers.

Du et al.\textsuperscript{81} reported another approach for improving processability without any compromise on thermal stability by incorporating variable length aromatic ether nitrile linkages, using 2-6 % wt of 2,6-bis(4-aminophenoxy)benzonitrile (BAB) as a curing agent.

\begin{tikzpicture}
\draw (0,0) circle (0.5cm);
\draw (1,0) circle (0.5cm);
\draw (2,0) circle (0.5cm);
\draw (3,0) circle (0.5cm);
\draw (4,0) circle (0.5cm);
\draw (0,0.5) -- (1,0.5);
\draw (1,0.5) -- (2,0.5);
\draw (2,0.5) -- (3,0.5);
\draw (3,0.5) -- (4,0.5);
\draw (0,-0.5) -- (1,-0.5);
\draw (1,-0.5) -- (2,-0.5);
\draw (2,-0.5) -- (3,-0.5);
\draw (3,-0.5) -- (4,-0.5);
\draw (0,0.5) -- (0,-0.5);
\draw (1,0.5) -- (1,-0.5);
\draw (2,0.5) -- (2,-0.5);
\draw (3,0.5) -- (3,-0.5);
\draw (4,0.5) -- (4,-0.5);
\node at (2,0) {\textsuperscript{n} = 2, 4, 6, and 8};
\end{tikzpicture}

DSC results indicated that the all (\textsuperscript{n} = 2, 4, 6, and 8) oligomeric monomers had a wide processing window compared to biphenyl based phthalonitrile monomers\textsuperscript{82}, due to lower melting transition and high curing temperatures. The increase, in curing temperature with the increasing of ‘\textsuperscript{n}’ value from 2 to upward, is due to a decrease in the concentration of cyano groups with the increase in length. It was also reported for \textsuperscript{n} = 2 phthalonitrile monomer that with the increase of concentration of curing agent, the curing temperature decreases. Both concentration of curing agent and curing temperature affect the rheological behaviors of \textsuperscript{n} = 2 phthalonitrile monomer. With the increase of curing temperature and curing agent the rate of curing enhanced. TGA studies indicated that for \textsuperscript{n} = 2 phthalonitrile monomer, 5% weight loss temperature increased with the increase in concentration of curing additive. The thermal stability of the polymers, cured with the same amount of curing agent, decreased with the increase in chain length.

Selvakumar et al.\textsuperscript{83} described the incorporation of imide and ether units in phthalonitrile oligomeric monomers for studying the effect of structural changes on their properties, using 4,4′-diamindiphenylsulphone (DDS) as a curing agent. DSC studies indicated a reasonable processing (~ 100 °C) between the melting transitions and curing temperatures. Rheometric studies were carried out with different amounts of DDS under
isothermal conditions at 290 °C. Melt viscosity increased as a function concentration of curing agent and time. TGA measurements were reported from room temperature to 800 °C under nitrogen and air. The results showed that the 5 % weight loss temperatures of the cured product at 340 °C under nitrogen were in the range of 428–433 °C, with char yields of 73 to 76 % at 800 °C. In air, 5 % weight loss temperatures were in the range of 416–424 °C, with char yields of 43 to 48 % at 800 °C. By exposing to high curing temperature, enhancement in thermal stability was observed.

Zhou et al. reported the synthesis of a self-catalyzed oligomeric phthalonitrile monomer to overcome the problem of volatization of curing agents at high temperature during curing. DSC studies indicated both melting transition and curing temperature overlapped at a heating rate of 0.5 °C min⁻¹, due to rapid reaction in the presence of high concentration of amino groups. The curing peak was very broad indicating a very slow cure reaction. TGA results of the products cured for 15 min and 30 min indicated enhancement in thermal stability with curing time. The 5 % weight loss temperature of the 30 min cured product was 446 °C, with char yield of 73 % at 800 °C.

Zeng et al. attempted to reduce the effect of external curing agent by introducing a self-catalyzing hydroxyl group to phthalonitrile monomers. TGA results indicated that with increasing curing time at a dwell temperature of 225 °C, 5 % weight loss temperature improved remarkably, compared to uncured samples. The char yields of the cured product not only increased with increasing time for curing, but were also closely related to the structure of the monomers. Maximum char yields up to 70 % were observed for all cured monomers after curing for 60 min. Results indicated that no obvious improvement in thermal properties was observed after 60 min heat treatment due to slow progress in the rate of the polymerization reaction. DSC thermograms remain featureless for all the monomers indicating a very fast rate of polymerization due to maximum concentration of hydroxyl groups.
Phthalonitriles with different architectures, spacers, and connectivities have been synthesized in order to improve resin flow during processing without compromising thermal stability and were characterized to establish the structure-property relationships. These polymers attracted the attention of many people due to no voids formation during polymerization unlike polyimides, and a broad range of applications, especially for marine, aerospace, and electronic applications. They are divided into two classes on the base of the monomer building blocks in non-catalyzed and self-catalyzed phthalonitrile resins.

2.1 Phthalonitrile Resins Based on Non-catalyzed Monomers

In this class of phthalonitrile resin a variety of structural changes were made between the reactive end groups. Major work has been done so far in this category. Although different structural changes were made in the polymer backbone, but no attempts were made to create a catalyzing group in the structure of the phthalonitrile monomers to eliminate the need for curing additives. Typically, phthalonitrile resins reactions are cured in the presence of metals and metallic salt, strong organic acids, strong organic acid/amine salts, and thermally stable aromatic diamines. But commonly thermally stable amines are used, such as 1,3-bis(3-aminophenoxy)benzene, and 4,4'-bis(3,4-dicyanophenoxy)phenyl)sulfone. A brief description of the work done so far in this class is going to be presented here.

2.1.1 Synthesis of Bisphenol-A based Phthalonitrile Polymers

Keller synthesized a new monomer, 4,4'-bis(3,4-dicyanophenoxy)biphenyl, by the simple nucleophilic substitution reaction of dialkaline salt of 4,4'-dihydroxybiphenyl with 4-nitrophthalonitrile. The polymerization was carried out in a controlled manner as a function of 4,4'-methylenediamine (MDA), used as a curing additive, and the curing temperature. The cured product was considered as a potential candidate for advanced composites such as aircraft engine and electronic devices. Furthermore, the light weight, and resistance to corrosion are their important aspects of its uses in military and space technologies.
2.1.2 Synthesis of Multiple Aromatic Ether and Keto based Phthalonitrile Polymers

Keller\textsuperscript{71} synthesized some new oligomeric monomers by the reaction of 4,4\textsuperscript{'-}(hexafluoroisopropylidene)bisphenol or 4,4\textsuperscript{'-}dihydroxybiphenyl with 4,4\textsuperscript{'-}difluorobenzophenone in the presence of base, followed by the reaction with 4-nitrophthalonitrile. These oligomers were cured in the presence of a small amount of 1,3-bis(3-aminophenoxy)benzene (\textit{m}-APB) or \textit{p}-toluenesulfonic acid. The polymerization of these oligomers appeared to be occurred by competing reaction involve polyphthalocyanine, polytriazine, and polyimine formation.
2.1.3 Synthesis of Thermally Stable Resorcinol based Phthalonitrile Polymers

Keller et al.\textsuperscript{78} synthesized a new monomer, 1,3-bis(3,4-dicyanophenoxy)benzene, by the reaction of a nucleophilic substitution reaction in 4-nitrophthalonitrile by the dialkaline salt of resorcinol. The monomer was cured in the presence of a small amount of 1,3-bis(3-aminophenoxy)benzene (\textit{m}-APB) or bis[4-(4-aminophenoxy)phenyl]sulfone (\textit{p}-BAPS). Thermal and rheological studies indicated that the synthesized monomer was superior in many aspects than 4,4'-bis(3,4-dicyanoophenoxy)biphenyl, which was considered ideal materials for marine and aerospace applications.

\[
\begin{align*}
\text{HO-A-OH} & \quad + \quad \text{O}_2\text{N-CN-CN-CN} \quad \xrightarrow{\text{Base, DMSO}} \quad \text{NC-O-O-CN-CN} \quad 9 \\
\text{Curing additive} & \quad \xrightarrow{\Delta} \quad \text{Polym er} \quad 10
\end{align*}
\]

2.1.4 Synthesis of Aromatic Ether and Phosphine Oxide based Phthalonitrile Polymers

Laskoski et al.\textsuperscript{80} synthesized some new oligomeric monomers by the reaction of bisphenol A or resorcinol with bis(4-fluorophenyl)phenylphosphine oxide in the presence of K\textsubscript{2}CO\textsubscript{3} in \textit{N,N}-dimethylforamide/toluene solvent mixture, followed by end-capping with 4-nitrophthalonitrile. The cured resin maintained structural integrity at high temperature and a remarkable improvement in oxidative stability compared to non-phosphorus containing phthalonitrile resins.

\[
\begin{align*}
\text{HO-A-OH} & \quad + \quad F-P-F \quad \xrightarrow{\text{K}_2\text{CO}_3, \text{DMF/Toluene}} \quad \text{K-O-A-O} - \text{n} \quad 12 \\
\text{Curing Additive} & \quad \xrightarrow{\Delta} \quad \text{Polymer} \quad 10
\end{align*}
\]
2.1.5 Synthesis of Multiple Aromatic Ether-linked and Bisphenol-A based Phthalonitrile Polymers

Laskoski et al. synthesized a new oligomeric monomer with multiple aromatic ether-linkages, ended by terminal reactive phthalonitrile units. The synthesized oligomeric monomers were prepared by the reaction of an excess amount of 4,4’-bis(3,4-dicyanophenoxy)biphenyl with 4,4’-difluorobenzophenone in the presence of K$_2$CO$_3$ in an aprotic solvent such as N,N-dimethylforamide and toluene mixture, followed by reaction with 4-nitrophthalonitrile. The post-cured product showed high structural integrity at elevated temperature. They exhibited excellent thermal and long term oxidative stability. They absorbed less than 2.5% water by weight by exposing to an aqueous environment for extended period of time. The oligomeric monomer has a longer processing window compared to only 4,4’-dihydroxybiphenyl based oligomer due to lower softening temperature, without compromising the thermal and oxidative stability. The fully cured product did not exhibit a glass transition temperature ($T_g$). These notable properties made them suitable candidates for advanced uses.
2.1.6 Synthesis of Purely Multiple Aromatic Ether-based Phthalonitrile Polymers

Dominguez and Keller\(^7\) synthesized a series of oligomeric monomers of low melting point with variable ether linkages between the terminal phthalonitrile functionalities. They were synthesized by the reaction of resorcinol with 1,3-dibromobenzene to form a hydroxyl-terminated intermediate, followed by end-capping with phthalonitrile units by the reaction with 4-nitrophthalonitrile. The viscosity measurements showed the oligomeric monomers cured at moderate temperature using a small amount of bis (4-(4-aminophenoxy)phenyl)sulfone and 1,3-bis(aminophenoxy)benzene. The prepolymer showed low complex viscosity before curing. Thermogravimetric and dynamic mechanical studied indicated that these polymers are superior than the phthalonitrile polymers obtained from 4,4\(^{\prime}\)-bis(3,4-dicyanophenoxy)biphenyl and 1,3-bis(3,4-dicyanophenoxy)benzene. The overall study indicated that the synthesized polymers are the most favorable for the use in advanced composites.

\[ HO \quad OH + \quad \text{Br} \quad \text{Br} \quad \text{Cul, 1,10, phenanthroline} \quad K_2CO_3, \text{DMF/ toluene} \quad \text{K} \quad \text{O} \quad \text{K} \quad n = 2, 4, 6 \text{ or } 8 \]

\[ n = 2, 4, 6 \text{ or } 8 \quad 4\text{-nitrophthalonitrile} \]

\[ \text{Polymer} \quad \triangle \quad \text{Curing additives} \quad \text{NC} \quad \text{NC} \quad \text{CN} \quad \text{CN} \]

\[ n = 2, 4, 6 \text{ or } 8 \quad 22 \]

2.1.7 Synthesis of Imide based Phthalonitrile Polymers

Keller\(^7\) synthesized a new oligomeric monomer with imide, keto, and ether functionalities, terminated by reactive phthalonitrile units. The synthesized oligomeric monomer was prepared by the reaction of 4-(3-aminophenoxy)phthalonitrile with 3,3\(^{\prime},4,4\(^{\prime}\)-benzophenonetetracarboxylic dianhydride (BTDA) to form di(amic acid) phthalonitrile intermediate under ambient condition, followed by refluxing and heating up to 200 °C. The oligomeric monomer was cured in small amount of 1,3-bis(3-aminophenoxy)benzene (\(m\)-APB) by an addition polymerization mechanism. They
exhibited excellent thermal and oxidative stability. The synthetic route is simple, short, and high yielded. This oligomeric monomer can be fabricated without void formation, because imide ring is already formed before polymerization. The polymer obtained, showed higher stability than the polymer obtained from bisphenol-based monomers. Thermal stability enhances with high curing temperature but oxidative stability reduces at high temperature.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{OH} \\
\text{O}_2\text{N} & \quad \text{CN} \\
\text{CN} & \quad \text{CN}
\end{align*}
\]

\[ \text{NaOH} \quad \text{DMF} \]

\[
\text{24}
\]

\[
\begin{align*}
\text{BTDA} & \quad \text{DMF} \\
\end{align*}
\]

2.1.8 Synthesis of Aromatic Ether and Nitrile based Phthalonitrile Polymers

Du et al. synthesized a series of oligomeric monomers with variable ether-nitrile linkages between the terminal phthalonitrile functionalities. They were synthesized by the reaction of bisphenol-A (in excess) with 2,6-dichlorobenzonitrile to form a hydroxyl-terminated oligomeric intermediate, followed by end-capping with phthalonitrile. The oligomeric monomers were cured at different temperature using different amount of 2, 6-bis(4-diaminophenoxy)benzonitrile. The perpolymers showed low complex viscosity before curing. Thermogravimetric analysis indicated that the completely cured products have 5 % weight loss temperature \((T_{5\%})\) above 500 °C both under nitrogen and air. The fully cured polymer did not show a glass transition temperature upon heating to 450 °C. The overall study indicated that the synthesized polymers are the most favorable for heat resistance and high performance composites.
2.1.9 Synthesis of Oligomeric Imide based Phthalonitrile Polymers

Keller developed a new method for the synthesis of a new oligomeric monomer with different functionalities and end-capping with reactive phthalonitrile units. The oligomeric monomers were prepared by the reaction of an aromatic amine with an excess amount of dianhydride and capped with phthalonitrile reactive end groups by reacting with 4-aminophthalonitrile in one step. The size of the oligomeric monomer can be varied in a controlled manner by varying the amount of reactants. The synthesized oligomers were soluble in common solvents, which are very helpful for using in the fabrication of electronic devices and advanced composites. The synthetic route is very simple and high yielded.
2.1.10 Synthesis of Aromatic Ether and Imide based Phthalonitrile Polymers

Selvakumar et al. synthesized some new oligomeric monomers with aromatic ether and imide linkages between the terminal phthalonitrile functionalities. They were synthesized by the reaction of pyromellitic dianhydride (PMDA) with aromatic anhydride in dimethylacetamide (DMAc) and toluene solvent mixture. The resulted oligomeric anhydride intermediate was end-capped with phthalonitrile units by reacting with 4-(aminophenoxy)phthalonitrile. The oligomeric monomers were cured at different temperature using different amount of 4,4′-diaminodiphenyl sulphone (DDS) and bis(4-diaminophenoxy)benezonitrile. The prepolymer showed low complex viscosity before curing. Viscosity increased as a function of time and concentration of curing reagent. Thermogravimetric analysis indicated that the completely cured product have 10 %
weight loss temperature ($T_{10\%}$) near 500 °C under nitrogen and near 480 °C under air. The post-cured polymer indicated char yield of about 45% at 800 °C under air and around 80% at 800 °C in Nitrogen atmosphere.

2.1.11 Synthesis of Flexible Aryl Ether and Imide based Phthalonitrile Polymers

Selvakumar et al. synthesized a series of some new oligomeric monomers with aromatic ether and imide linkages between the terminal phthalonitrile functionalities. They were synthesized by a multi steps synthetic route involving the reaction of bisphenols with 4-nitrophthalonitrile to form bisphthalonitriles. The resulted oligomeric intermediates were hydrolyzed to tetracarboxylic acids, followed by refluxing in acetic anhydride/acetic acid solvent mixture to form dianhydrides. These products were treated with 4-(aminophenoxy)phthalonitrile to obtain phthalonitrile terminated monomers. They were cured at different temperature using 4,4′-diaminodiphenyl sulphone (DDS) as a curing agent. Thermogravimetric analysis indicated that the completely cured products have 5% and 10 % weight loss temperature in the range 433-499 °C under nitrogen and 424-480 °C under air, respectively. The post-cured polymer exhibited char yield of about 40-51% at 800 °C.
2.1.12 Synthesis of Aromatic Ether and Triazine based Polymers

Yu et al. synthesized a series of some new oligomeric monomers with aromatic ether between the terminal cyano functionalities. They were synthesized by the reaction of various type of diols with 4-chlorobenzonitrile to form bis(ethernitrile)s by simple nucleophilic substitution reaction. They were polymerized with or without the presence of terephthalonitrile (TPH) in the catalysis of ZnCl\textsubscript{2} under normal pressure. Differential Scanning calorimetry (DSC) did not indicate any endo peak for glass transition temperature up to 450 °C. Thermogravimetric analysis indicated that the completely cured products have 5 % weight loss temperature in the range of 493-540 °C under nitrogen.

Yu et al. synthesized a series of some new oligomeric monomers with aromatic ether between the terminal cyano functionalities. They were synthesized by the reaction of various type of diols with 4-chlorobenzonitrile to form bis(ethernitrile)s by simple nucleophilic substitution reaction. They were polymerized with or without the presence of terephthalonitrile (TPH) in the catalysis of ZnCl\textsubscript{2} under normal pressure. Differential Scanning calorimetry (DSC) did not indicate any endo peak for glass transition temperature up to 450 °C. Thermogravimetric analysis indicated that the completely cured products have 5 % weight loss temperature in the range of 493-540 °C under nitrogen.
2.1.13 Synthesis of Ether based Phthalonitrile Polymers Under Microwave Irradiation

Selvakumar et al. synthesized a new oligomeric monomer with aromatic ether and imide linkages between the terminal phthalonitrile functionalities. They were synthesized by a multi steps reaction route involving the reaction of naphthalene 1,5-diol with 4-nitrophthalonitrile to form bisphthalonitrile. The resulted oligomeric intermediates were hydrolyzed to tetracarboxylic acids, followed by refluxing in acetic anhydride/acetic acid solvent mixture to form dianhydrides. These products were treated with 4-(3-aminophenoxy)phthalonitrile to get phthalonitrile terminated monomer. It was cured at different temperature using 4,4′-oxydianaline (ODA) as a curing agent. Thermogravimetric analysis indicated that the completely cured product exhibited excellent thermal stability with 61% char yield. The use of microwaves reduced the curing time dramatically to about 70 minutes.

\[
\begin{align*}
\text{HO} & \quad \text{O}_2\text{N} \\
\text{CN} & \quad \text{CN} \\
\text{+} & \quad \text{K}_2\text{CO}_3 \\
\text{DMF} & \quad \text{O} \\
\text{EtOH/KOH} & \quad \text{O} \\
\text{Ac}_2\text{O}/\text{CH}_3\text{CO}_2\text{H} & \quad \text{H}_2\text{N} \\
\text{DMF/Toluene} & \quad \text{OH} \\
\text{MW} & \quad \text{Polymer} \\
\end{align*}
\]
2.2 Phthalonitrile Resins Based on Self-catalyzed Monomers

Typically phthalonitrile resins are processed in the form of binary system i.e. phthalonitrile monomers and curing additives. However, in such system vigorous stirring is needed along with heating to get a uniform mixture to ensure uniform curing, which is difficult. Additionally, volatilization of the diamines is observed at elevated temperature in an open mold, which results in a slowdown of the curing reactions and creates problems in attaining anticipated properties. Therefore, it is desirable to modify the structure of phthalonitrile monomers to eliminate the need of curing additives. A simple and well known, effective method is the incorporation of auto-catalyzing groups into the reactive phthalonitrile units. Where, various hydroxyl or amino-functional phthalonitrile monomers/oligomers cross-link by self-promoted curing without the addition of curing additives. The work done so far in this class is presented here.

2.2.1 Synthesis of Ether and Keto based Self-catalyzed Phthalonitrile Polymers

Zhou et al.\textsuperscript{84} synthesized a new oligomeric phthalonitrile monomer with aromatic ether and keto linkages and was cured without the addition of catalysts due to the self-catalyzing nature of monomer’s amino group. The monomer was synthesized by a multi-steps reaction route involving the reaction of 3,5-dinitrobenzoyl chloride with ethoxybenzene in the presence of aluminum chloride to form 4′-ethoxyphenyl-3,5-dinitrophenyl methanone, followed by dealkylation to form 4′-hydroxyphenyl-3,5-dinitrophenyl methanone. The compound 49 was treated with 4-nitrophthalonitrile to form phthalonitrile derivative 50, followed by selective reduction with SnCl\textsubscript{2} to obtain 4-[4-(3,5-diaminobenzoyl)phenoxy]phthalonitrile. The monomer building blocks for the polymers were cured without the addition of catalysts due to the self-catalyzing nature of the monomer’s amino group at 230 °C for various intervals of time under nitrogen. Thermogravimetric analysis indicated that the completely cured product exhibited 5% and 10% weight loss temperatures in the range of 442-446 °C and 504-505 °C, respectively, at 800 °C. The post-cured polymer exhibited char yield of about 69-72.71% at 800 °C.
2.2.2 Synthesis of Ether-based Self-catalyzed Phthalonitrile Polymers

Zeng et al.\textsuperscript{95} synthesized a new amino containing oligomeric monomer with aromatic ether linkages between the terminal phthalonitrile functionalities. It was synthesized by a simple nucleophilic displacement reaction of 5-aminoresorcinol hydrochloride with 4-nitrophthalonitrile to form 3,5-bis(3,4-dicyanophenoxy)aniline. The oligomeric monomer was cured without adding any curing agent due to self-promoting curing behavior. Thermogravimetric analysis indicated that the completely cured polymers showed excellent thermal stability with a char yield of 70.6% under nitrogen.
2.2.3 Synthesis of Ether based and Hydroxy containing Self-catalyzed Phthalonitrile Polymers

Zeng et al. synthesized some new hydroxy containing oligomeric phthalonitrile monomers. They were synthesized by a simple nucleophilic displacement reaction of bisphenols with 4-nitrophthalonitrile in 1:1 to form hydroxy containing phthalonitrile derivatives. The oligomeric monomer was cured without adding any curing agent due to self-promoting curing behavior of hydroxyl group. Thermogravimetric analysis of the cured polymers showed excellent thermal stability. The 5% and 10% weight loss temperatures were in the range of 320-420 °C and 360-490 °C, respectively. They exhibited a char yield of 50-73 % under nitrogen at 800 °C.

2.3 Plan of Work

Phthalonitrile resins have been studied thoroughly for the last three decades. They are being studied for use in recent technologies for the development of heat resistance, moisture resistance, flame resistance, and for the creation of void free materials. However, the reported synthetic routes for the preparation of these materials are mostly complex and of low yielding. On the other hand, they also offered problems in flow during processing, thermal stability, and of low processing window – defined as the temperature difference between the melting temperature of the monomer and the gelation temperature of the polymer network. For practical purposes, such material must have improved flow during processing, higher thermal stability, widest processing window, and high glass transition temperature. Therefore, it was planned to synthesize the target materials with anticipated properties through an easy and high yielding schemes.
2.3.1 Synthesis of Oligomeric Monomers

The functional groups used to interlink the aromatic rings in the oligomeric monomers play important role in getting the anticipated properties. The flexible ether group, which helps us in lowering the melting point, is highly needed to achieve a broad processing window without compromising thermal stability. The ortho-linkages in the molecular structures create kinks and disrupt the close packing; which is very helpful in lowering the melting point.

2.3.1.1 Synthesis of Oligomeric Phthalonitrile Monomers with Ortho-linkages

Different type of diols may be used to get different type of spacers in between the phthalonitrile units for comparison of thermal behavior after curing. The synthesis of these ortho-linked oligomeric monomers may be carried out through simple nucleophilic displacement of the nitro group in 4-nitrophthalonitrile by potassium salt of diols in a continued purge of nitrogen in aprotic solvent such as DMF or DMSO.

\[
\begin{align*}
\text{HO-Ar-OH} & + \quad \text{O}_2\text{N} \quad \text{CN} \\
\text{CN} & \quad \text{CN} \\
& \quad \text{CN} \\
& \quad \text{O}_2\text{N} \\
\text{K}_2\text{CO}_3 & \quad \text{DMF or DMSO} \\
\text{NC} & \quad \text{O}-\text{Ar}-\text{O} \\
\text{CN} & \quad \text{CN}
\end{align*}
\]

\((58a, 58b, 58c)\)

Scheme 2.1: Synthesis of ortho-linked oligomeric phthalonitrile monomers

The diols a and b are commercially available, the diol c (2,5-bis(2-hydroxyphenyl)1,3,4-oxadiazole) may be synthesized by condensation reaction of 2-hydroxy benzoic acid with hydrazine sulphate in polyphosphoric acid (PPA), involving hydrazide as an intermediate.

\[
\begin{align*}
\text{OH} & \quad \text{COOH} + \quad \text{N}_2\text{H}_4\cdot\text{SO}_4 \\
& \quad \text{PPA} \\
\text{58c}
\end{align*}
\]

Scheme 2.2: Synthesis of 2,5-bis(2-hydroxyphenyl)1,3,4-oxadiazole
2.3.1.2 Synthesis of Self-catalyzed Oligomeric Phthalonitrile Monomers with Imide-ether Linkages

The synthesis of these oligomeric monomers may be accomplished in three steps.

**Step I: Synthesis of Aminophenoxy phthalonitriles**

Aminophenoxy phthalonitriles 59 may be prepared by the reaction of 4-nitrophthalonitrile with potassium salt of different isomers of aminophenol in anhydrous DMF and K₂CO₃. Different substituted amino phenols may be used for comparison.

\[
\text{H}_2\text{N} \quad \text{OH} \quad + \quad \text{O}_2\text{N} \quad \text{CN} \quad \text{CN} \quad \text{CN} \quad \text{K}_2\text{CO}_3 \quad \text{DMF} \quad \rightarrow \quad \text{H}_2\text{N} \quad \text{O} \quad \text{CN} \quad \text{CN} \quad \text{CN} \quad (59a, 59b, 59c)
\]

Scheme 2.3: Synthesis of Aminophenoxy phthalonitriles

**Step II: Synthesis of 4-[(4-nitrophthalimidyl)phenoxy]phthalonitriles**

4-[(4-nitrophthalimidyl)phenoxy]phthalonitriles 60 may be prepared by the reaction of 4-nitrophthalic anhydride with 4-(aminophenoxy)phthalonitriles in acetic acid/cyclohexane mixture. The various substituted 4-(aminophenoxy)phthalonitriles may be used for comparison.

\[
\text{O} \quad \text{H}_2\text{N} \quad \text{CN} \quad \text{CN} \quad \text{CN} \quad \text{O}_2\text{N} \quad \text{CH}_3\text{CO}_2\text{H}/\text{Cyclohexane} \quad \rightarrow \quad \text{O}_2\text{N} \quad \text{N} \quad \text{O} \quad \text{CN} \quad \text{CN} \quad \text{CN} \quad (60a, 60b, 60c)
\]

Scheme 2.4: Synthesis of 4-[(4-nitrophthalimidyl)phenoxy]phthalonitriles

**Step III: Synthesis of 4-[(4-aminophthalimidyl)phenoxy]phthalonitriles**

4-[(4-aminophthalimidyl)phenoxy]phthalonitriles 61 may be prepared by reduction with ammonium formate over 10 % Pd/C in N,N-dimethylacetamide.

\[
\text{O}_2\text{N} \quad \text{N} \quad \text{O} \quad \text{CN} \quad \text{CN} \quad \text{CN} \quad 	ext{HCOONH}_4/\text{Pd-C} \quad \text{DMAc} \quad \rightarrow \quad \text{H}_2\text{N} \quad \text{O} \quad \text{CN} \quad \text{CN} \quad \text{CN} \quad (61a, 61b, 61c)
\]

Scheme 2.5: Synthesis of 4-[(4-aminophthalimidyl)phenoxy]phthalonitriles
2.3.1.3 Synthesis of Self-catalyzed Oligomeric Phthalonitrile Monomers with Amide-ether Linkages

The synthesis of these oligomeric monomers may also be accomplished in three steps.

**Step I: Synthesis of N-(hydroxylphenyl)-4-nitrobezamides**

N-(hydroxylphenyl)-4-nitrobezamides 62 may be synthesized by reaction of aminophenols with 4-nitrobenzoyl chloride in inert atmosphere, in the presence of propylene oxide which acts as an acid scavenger.

\[
\begin{align*}
\text{O}_2\text{N} &\quad \text{Cl} \\
\text{O} &\quad + \\
\text{H}_2\text{N} &\quad \text{OH} \\
\text{NMP/PO} &\quad \text{O}_2\text{N} \\
\text{HN} &\quad \text{O} \\
\text{OH} &\quad \text{NH}_2\text{NH}_2 \\
\text{Pd-C, EtOH} &\quad \text{H}_2\text{N} \\
\text{O}_2\text{N} &\quad \text{Cl} \\
\text{O} &\quad + \\
\text{H}_2\text{N} &\quad \text{OH} \\
\text{NMP/PO} &\quad \text{O}_2\text{N} \\
\text{HN} &\quad \text{O} \\
\text{OH} &\quad \text{NH}_2\text{NH}_2 \\
\text{Pd-C, EtOH} &\quad \text{H}_2\text{N} \\
\end{align*}
\]

Scheme 2.6: Synthesis of N-(hydroxylphenyl)-4-nitrobezamides

**Step II: Synthesis of N-(hydroxylphenyl)-4-aminobezamides**

N-(hydroxylphenyl)-4-aminobezamides 63 may be synthesized by catalytic reduction of N-(hydroxylphenyl)-4-nitrobezamides by drop wise addition of hydrazine monohydrate. The various substituted aminophenols may be used for comparison.

\[
\begin{align*}
\text{O}_2\text{N} &\quad \text{HN} \\
\text{O} &\quad \text{OH} \\
\text{NH}_2\text{NH}_2 &\quad \text{Pd-C, EtOH} \\
\text{H}_2\text{N} &\quad \text{HN} \\
\text{O} &\quad \text{OH} \\
\end{align*}
\]

Scheme 2.7: Synthesis of N-(hydroxylphenyl)-4-aminobezamides

**Step III: Synthesis of 4-amino-N-[(3,4-dicyanophoxy)phenyl]benzamides**

4-amino-N-[(3,4-dicyanophoxy)phenyl]benzamides may be synthesized by the reaction of 4-nitro phthalonitrile with potassium salt of N-(hydroxylphenyl)-4-aminobezamides, in anhydrous DMSO and K₂CO₃.

\[
\begin{align*}
\text{H}_2\text{N} &\quad \text{HN} \\
\text{O} &\quad \text{OH} \\
\text{O}_2\text{N} &\quad \text{CN} \\
\text{K}_2\text{CO}_3, \text{NMP} &\quad \text{H}_2\text{N} \\
\text{CN} &\quad \text{O} \\
\end{align*}
\]

Scheme 2.8: Synthesis of 4-amino-N-[(3,4-dicyanophoxy)phenyl]benzamides
2.3.2 Synthesis of Polymers

2.3.2.1 Synthesis of Diol-based Phthalonitrile Polymers

The diol-based phthalonitrile oligomeric monomers may be melted and degassed for fifteen minutes in order to remove the moisture and solvent residue. Then 5 weight % of bis[4-(4-aminophenoxy)phenyl]sulfone (p-BAPS) will be added as a curing agent to the melt with vigorous stirring and quenched after 5 minutes. The resulting green dark phthalonitrile prepolymer or B-staged resins will be heated according to the heating profile; 170°C for 2h, 200°C for 2h, 250°C for 3h, 315°C for 5h and then postcured at 375°C for 5h in open atmosphere.

2.3.2.2 Synthesis of Self-catalyzed Phthalonitrile Polymers

The self-catalyzed monomers may be heated according to the heating profile; 170°C for 1h, 200°C for 2h, 250°C for 3h, 315°C for 5h and then postcured at 375°C for 5h in open atmosphere without adding curing agent.

2.3.3 Characterization

The synthesized compounds in each step and the polymers will be characterized by the use of following techniques.

i. FT-IR
ii. \(^1\text{H}-\text{NMR}\)
iii. \(^{13}\text{C}-\text{NMR}\)
2.3.4 Thermal Studies

Thermal studies may be carried out to find the behavior of the sample as a function of temperature. Herein we may be use some conventional techniques including differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and complex melt viscosity for the analysis and characterization of the synthesized prepolymers and polymers.
Herein we will describe the experimental procedures, characterization and instrumentation used for the synthesis of the following series of monomers. The series-A and B monomers obtained by the reaction of ortho-linked diols and amino phenols with 4-nitrophthalonitrile respectively. The series C and D obtained from the reaction of 4-(aminophenoxy)phthalonitriles with 4-nitrophthalic anhydride and N-(hydroxyphenyl)-4-aminobenzamides with 4-nitrophthalonitrile respectively.

A-Series From ortho-linked diols and 4-nitrophthalonitrile
B-Series From Amino phenols and 4-nitrophthalonitrile
C-Series From 4-(aminophenoxy)phthalonitriles and 4-nitrophthalic anhydride
D-Series From N-(hydroxyphenyl)-4-aminobenzamides and 4-nitrophthalonitrile

A-series monomers were terminated with cyano reactive end groups, while in series B, C, and D the monomers were ended with amino and cyano groups.

3.1 Reagents and Solvents

3.1.1 Reagents
4-nitrophthalonitrile, bis[4-(4-aminophenoxy)phenyl]sulfone (p-BAPS) and 4-nitrophthalic anhydride (Alpha. Shijiazhuang China Chemical Co. Ltd) Biphenol-2,2'-diol, catechol, 2-hydroxy benzoic acid and hydrazine sulfate (Beijing Beihua Fine Chemicals Co. China) were used as supplied. 2-aminophenol, 3-aminophenol, and 4-aminophenol (Sinopharm Chemical reagent) were used as received. Ammonium formate, 4-nitrobenzyol chloride, propylene oxide (PO), hydrazine monohydrate and 10 % Pd-C were obtained from Sigma-Aldrich and used as received. Potassium carbonate (Fluka) was dried at 150 °C under vacuum.

3.1.2 Solvents
Dimethyl sulfoxide (DMSO) (Fisher Scientific Co.), N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc) (Sigma-Aldrich) were purified by distillation under reduced pressure over calcium hydride (CaH2) and were stored over 4 Å molecular sieves. N,N-dimethylformamide (DMF), (Beijing Beihua Fine Chemicals Co. China) was purified by distillation over phosphorus pentoxide under reduced pressure and was
stored over 4 Å molecular sieves. Ethanol, Methanol and Tetrahydrofuran were distilled after refluxing for six hours with pre-heated Calcium oxide (CaO). Acetic Acid, Cyclohexane (C₆H₁₂) and Acetonitrile (CH₃CN) (Fluka) were used as received.

3.2 Instrumentation

Rf values were calculated by using precoated silica gel glass backed plates Kiesel gel 60F₂₅₄ Merck (Germany) using ethyl acetate: pet-ether (1:3), mostly as a developing solvents. Purity of each compound was ascertained by thin layer chromatography. The purification of synthesized compounds was achieved mostly by the crystallization technique or otherwise by column chromatography, whenever required. The melting points of the compounds were determined by Gallenkamp apparatus. The Fourier transform infrared (FT-IR) spectral data were recorded on Bruker 27 IR spectrometer using KBr disks. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AV 400 NMR or Bruker AV 300 NMR spectrometers with DMSO-d₆ as the solvent and tetramethylsilane (TMS) as internal standard. Differential scanning calorimetry (DSC) experiments were performed with Mettler Toledo DSC822e differential scanning calorimeter at heating rate of 10 °C/min under nitrogen atmosphere with flow rate of 50ml/min. Complex viscosity measurements were performed on a Physica MCR-300 mechanical spectrometer at a ramp rate of 4 °C/min in air and the top parallel plate was oscillated at a fixed strain of 10 % and a fixed angular frequency of 100 rad/s. Sample specimen discs of 2.5 cm diameter and 1 mm thickness were prepared by compression molding at room temperature under high pressure. Thermogravimetric analysis (TGA) was conducted with a Netzsch STA 409PC instrument, using approximately 10 mg of samples under controlled flux of nitrogen/air at 10 °C /min. The glass transition temperature (Tg) of the polymers was identified as the peak temperature of the tan δ curves obtained by dynamic mechanical analysis performed on a DMA 242 C (Netzsch, Germany) instrument with a driving frequency of 1.0 Hz, single cantilever mode, and a scanning rate of 5 °C/min in nitrogen.
3.3 Synthesis of Monomers

3.3.1 Synthesis of Diol-based Phthalonitrile Monomers

3.3.1.1 2,2’-Bis(3,4-dicyanophenoxy)biphenyl (1d)

A mixture of biphenyl-2,2’-diol (9.31 g, 0.05 mol) and anhydrous K$_2$CO$_3$ (15.0 g, 108 mmol) was dissolved in 100 mL of DMSO and 100 mL of benzene. The flask was equipped with a nitrogen inlet, a Dean–Stark trap, and a condenser. The mixture was heated with stirring at 120 °C for 6 h under a thin stream of nitrogen to remove the water formed as a by-product by azeotropic distillation with benzene. After reaching room temperature and removal of water; add 4-nitrophthalonitrile (17.66 g, 10mmol). The reaction was continued with stirring at 40 °C for 40 h under nitrogen. Then the mixture was cooled to room temperature and poured into 1 L of cold water. The precipitated solid was collected by filtration and dried. The product was purified by crystallization from ethanol.

Yield: 83 % (18.2 g); pale-yellow needles; m.p.:156.0 °C. (lit: 155.0–156.0 °C). FT-IR (KBr, υ, cm$^{-1}$): 3069, 2233, 1598, 1565, 1489, 1254. $^1$H-NMR (400 MHz, DMSO-$d_6$): δ(ppm)

7.97 (d, $J = 8.72$ Hz, 2H), 7.53 (s, 2H), 7.46 (t, $J = 8.24$ Hz, 2H), 7.45 (d, $J = 7.72$ Hz, 2H), 7.34 (t, $J = 7.44$ Hz, 2H), 7.19 (d, $J = 8.36$ Hz, 2H), 7.17 (d, $J = 7.96$ Hz, 2H). $^{13}$C-NMR (400 MHz, DMSO-$d_6$): δ(ppm) 161.0, 151.5, 136.6, 132.9, 130.9, 129.8, 126.5, 122.9, 122.4, 121.0, 117.0, 116.3, 115.7, 108.5.

3.3.1.2 1,2-Bis(3,4-dicyanophenoxy)benzene (1e)

Catechol (11.02 g, 100 mmol) and 4-nitrophthalonitrile (34.62 g, 200 mmol) were added to the suspension of anhydrous K$_2$CO$_3$ (27.6g, 200 mmol) in 300 mL N,N-dimethylformamide. The mixture was stirred at room temperature for 24 h. Next, the precipitated solid was collected and washed thoroughly with methanol and water. The yield of the crude product was 34.0 g (93.92 %). The crude product was purified by crystallization from acetonitrile/methanol (1:1) to afford the purified product.
Yield: 71 % (25.7 g); colorless needles; m.p.: 188.7 °C (lit. 190.1–190.6 °C\textsuperscript{75}). FT-IR (KBr, \textit{\upsilon}, cm\textsuperscript{-1}): 3082, 2232, 1588, 1566, 1486, 1246. \textsuperscript{1}H-NMR (400 MHz, DMSO-\textit{d}_{6}): \delta (ppm) 8.01 (d, \textit{J} = 8.82 Hz, 2H), 7.73 (s, 2H), 7.40-7.45 (m, 4H), 7.33 (d, \textit{J} = 8.76 Hz, 2H). \textsuperscript{13}C NMR (400 MHz, DMSO-\textit{d}_{6}): \delta (ppm) 160.7, 145.2, 136.7, 128.4, 123.9, 122.4, 122.0, 117.2, 116.3, 155.8, 109.2.

### 3.3.1.3 4,4’-[(1,3,4-oxadiazole-2,5-diyl)bis(1,2-phenylene)]bis(oxy)dipthalonitrile (1f)

(a) 2,5-Bis (2-hydroxyphenyl)1,3,4-oxadiazole

Hydrazine sulfate (10.0 g, 78 mmol) was added to 300g polyphosphoric acid (PPA). The reaction mixture was heated at 80 °C and then 4-hydroxy-benzoic acid (19.7 g, 156 mmol) was added. The mixture was heated at 125°C for 8 h. The reaction mixture was heated to 140 °C for additional 2 h to ensure ring closing. The reaction mixture was poured into 1 L of water to precipitate out the product. The precipitated solid was filtered and dried in vacuum oven. The product was purified by thoroughly washing with cold methanol.

(b) 4,4’-[(1,3,4-oxadiazole-2,5-diyl)bis(1,2-phenylene)]bis(oxy)dipthalonitrile (1f)

2,5-Bis(2-hydroxyphenyl)1,3,4-oxadiazole (4.0 g, 15 mmol) and 4-nitrophthalonitrile (5.44g, 3 mmol) were added to a suspension of K\textsubscript{2}CO\textsubscript{3} (4.8g, 30 mol) in 100 mL of DMF. The reaction mixture was heated at 60 °C for about 5 h and stirred continuously. The reaction mixture was poured into 500 mL of water, after which the precipitated solid was collected and washed thoroughly with methanol and water, and dried overnight under vacuum at 70 °C.
Yield: 90 % (6.8 g); off-white crystals; m.p.: 265.7 °C. FT-IR (KBr, ν, cm⁻¹): 3074, 2232, 1615, 1596, 1545, 1491, 1313, 1281, 1252.

1H-NMR (400 MHz, DMSO-d₆): δ(ppm) 8.07 (d, J = 8.80 Hz, 2H), 8.04 (d, J = 8.08 Hz, 2H), 7.78 (s, 2H), 7.75 (t, J = 7.83 Hz, 2H), 7.54 (t, J = 7.47 Hz, 2H), 7.36-7.41 (m, 4H). 13C NMR (400 MHz, DMSO-d₆): δ(ppm) 161.7, 161.4, 151.6, 136.8, 134.6, 130.9, 127.4, 123.4, 123.0, 122.4, 117.2, 116.9, 116.3, 116.8, 109.0.

3.3.2 General Method for the Synthesis of 4-(aminophenoxy)phthalonitriles (2o–p)

Aminophenol (10.9 g 100 mol) and 4-nitrophthlonitrile (17.3 g 100 mol) were added to a suspension of anhydrous K₂CO₃ (13.8 g, 100 mol) in 50 mL DMF. The reaction mixture was heated at 85 °C for 8 h under nitrogen atmosphere and then poured slowly into aqueous NaOH (1 mol/L) solution. The precipitate so formed was filtered and dried in vacuum oven at 70 °C to afford the required product and used in the next step without further purification.

3.3.2.1 4-(2-aminophenoxy)phthalonitrile (2o)

Yield: 94 % (22.0 g); light brown; m.p.: 122.0 °C. FT-IR (KBr, ν, cm⁻¹): 3446, 3365, 3038, 2233, 1606, 1564, 1485, 1249. 1H-NMR (400 MHz, DMSO-d₆): δ(ppm) 8.04 (d, J = 8.65, 1H), 7.62 (s, 1H), 7.18 (d, J = 8.01, 1H), 7.03 (t, J = 7.18, 1H), 6.94 (d, J = 7.65, 1H), 6.85 (d, J = 7.74, 1H), 6.60 (t, J = 8.00, 1H), 5.12 (s, 2H). 13C-NMR (100 MHz, DMSO-d₆): δ(ppm): 161.8, 141.3, 139.2, 136.6, 127.6, 122.3, 122.1, 121.0, 117.1, 117.0, 116.7, 116.6, 116.0, 107.7.

3.3.2.2 4-(3-aminophenoxy)phthalonitrile (2m)

Yield: 88 % (20.7 g); light yellow; m.p.: 172.5 °C (lit 172.0-173.0 °C). FT-IR (KBr, ν, cm⁻¹): 3444, 3365, 3039, 2231, 1608, 1564, 1487, 1249. 1H-NMR (400 MHz, DMSO-d₆): δ(ppm) 8.07 (d, J = 8.7, 1H), 7.72 (s, 1H), 7.34 (d, J = 8.7, 1H), 7.10 (t, J = 8.0, 1H), 7.48 (d, J = 8.09, 1H), 6.29 (s, 1H), 6.24 (d, J = 7.99, 1H), 5.39 (s, 2H). 13C-NMR (100 MHz, DMSO-d₆): δ(ppm) 161.8, 155.0, 151.5, 136.6, 131.1, 122.9, 122.2, 117.0, 116.4, 115.9, 111.9, 108.0, 107.2, 105.4.
3.3.2.3 4-(4-aminophenoxy)phthalonitrile (2p)

Yield: 96 % (22.6 g); deep brown; m.p.: 131.0 °C (lit 134.0 °C\(^9\)). FT-IR (KBr, \(\bar{\nu}\), cm\(^{-1}\)): 3454, 3371, 3043, 2231, 1600, 1562, 1510, 1487, 1251. \(^1\)H-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 8.02 (d, \(J = 8.8\), 1H), 7.60 (s, 1H), 7.24 (d, \(J = 8.8\), 1H), 6.85 (d, \(J = 8.40\), 2H), 6.63 (d, \(J = 7.20\), 2H), 5.18 (s, 2H). \(^{13}\)C-NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 163.1, 147.4, 143.4, 136.6, 121.9, 121.8, 121.1, 116.9, 116.5, 115.9, 115.40, 107.4.

3.3.3 General Method for the Synthesis of 4-[(4-nitrophthalimidyl)-phenoxy]phthalonitriles (3o–p)

Aminophenoxy phthalonitrile (15.00 g, 63 mmol) and 4-nitrophthalic anhydride (12.31 g, 63 mmol) were added to a mixture of 250 mL acetic acid and 30 mL cyclohexane in a 500 mL flask equipped with a Dean–Stark trap. The mixture was heated at 110 °C under nitrogen for 12 h. The water formed during reaction was trapped in Dean–Stark tube quantitatively. After reaching room temperature, the reaction mixture was poured into 700 ml of cool water, after which the solid precipitate was collected and dried in a vacuum oven at 70 °C. The purified product was obtained after crystallization from acetonitrile.

3.3.3.1 4-[2-(4-nitrophthalimidyl)phenoxy]phthalonitrile (3o)

Yield: 67 % (17.3 g); light pink; m.p.: 110.0 °C. FTIR (KBr, \(\bar{\nu}\), cm\(^{-1}\)): 3076, 2225, 1785, 1725, 1585, 1539, 1496, 1342, 1251. \(^1\)H-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm): 8.67 (d, \(J = 8.13\), 1H), 8.57 (s, 1H), 8.20 (d, \(J = 8.13\), 1H), 8.07 (d, \(J = 8.75\), 1H), 7.74 (s, 1H), 7.66 (t, \(J = 7.55\), 1H), 7.64 (d, \(J = 8.09\), 1H), 7.51 (t, \(J = 8.76\), 1H), 7.39 (d, \(J = 7.82\), 2H). \(^{13}\)C-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 164.9, 164.6, 160.0, 151.7, 150.4, 136.2, 135.9, 132.7, 131.68, 131.0, 130.0, 126.3, 125.3, 123.2, 123.1, 122.5, 121.3, 118.6, 116.5, 115.7, 115.2, 109.0.
3.3.3.2 4-[3-(4-nitrophthalimidyl)phenoxy]phthalonitrile (3m)

Yield: 72 % (18.6 g); light pink; m.p.: 185.0 °C. FT-IR (KBr, v, cm⁻¹): 3087, 2231, 1776, 1726, 1589, 1539, 1487, 1349, 1251. \(^1\)H-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 8.67 (d, \(J = 8.13, 1H\)), 8.58 (s, 1H), 8.22 (d, \(J = 8.14, 1H\)), 8.15 (d, \(J = 8.73, 1H\)), 7.90 (s, 1H), 7.67 (t, \(J = 7.98, 1H\)), 7.48 (d, \(J = 8.72, 1H\)), 7.43 (d, \(J = 7.99, 1H\)), 7.33 (s, 1H), 7.32 (d, \(J = 8.77, 1H\)). \(^{13}\)C-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 165.2, 164.9, 160.3, 154.1, 151.6, 136.5, 136.2, 133.3, 132.9, 131.0, 130.0, 125.0, 124.2, 123.4, 122.6, 119.9, 118.7, 118.3, 116.9, 115.8, 115.4, 108.9.

3.3.3.3 4-[4-(4-nitrophthalimidyl)phenoxy]phthalonitrile (3p)

Yield: 70 % (18.0 g); light pink; m.p.: 198.0 °C. FT-IR (KBr, v, cm⁻¹): 3091, 2229, 1787, 1724, 1589, 1539, 1508, 1481, 1349, 1249. \(^1\)H-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm): 8.68 (d, \(J = 8.14, 1H\)), 8.59 (s, 1H), 8.23 (d, \(J = 8.15, 1H\)), 8.14 (d, \(J = 8.69, 1H\)), 7.93 (s, 1H), 7.59 (d, \(J = 8.62, 2H\)), 7.49 (d, \(J = 8.20, 1H\)), 7.38 (d, \(J = 8.62, 2H\)). \(^{13}\)C-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 165.4, 165.2, 160.4, 153.8, 151.6, 136.5, 136.3, 133.0, 129.8, 129.4, 128.7, 125.0, 123.5, 122.7, 120.5, 118.2, 116.84, 115.9, 115.4, 108.8.

3.3.4 General Method for the Synthesis of 4-[(4-aminophthalimidyl)phenoxy]phthalonitriles (4o–p)

A mixture of 4-[(4-nitrophthalimidyl)phenoxy]phthalonitrile (16 g, 39 mmol), ammonium formate (124 g, 1970 mmol), and 1.0 g of 10 % Pd–C were added to 100 ml N, N-dimethylacetamide (DMAc). The reaction contents were allowed to stir at ambient temperature under nitrogen for 20 h. The stirred mixture was filtered to remove Pd–C and poured the filtrate to 1000 mL cool water. The precipitated solid was filtered and dried. The pure product was obtained by crystallization from methanol.
3.3.4.1 4-[2-(4-aminophthalimidyl)phenoxy]phthalonitrile (4o)

Yield: 77 % (11.4 g), yellow, m.p.: 100.0 °C. FT-IR (KBr, υ, cm⁻¹): 3471, 3363, 3080, 2229, 1772, 1714, 1614, 1589, 1568, 1500, 1379, 1249. ¹H-NMR (400 MHz, DMSO-d₆): δ(ppm) 8.04 (d, J = 8.76, 1H), 7.67 (s, 1H), 7.58 (d, J = 8.8, 1H), 7.57 (t, J = 8.76, 1H), 7.50 (d, J = 8.67, 1H), 7.45 (t, J = 8.67, 1H), 7.33 (d, J = 8.67, 2H), 6.91 (s, 1H), 6.82 (d, J = 8.25, 1H), 6.59 (s, 2H). ¹³C-NMR (100 MHz, DMSO-d₆): δ(ppm) 167.4, 166.9, 160.8, 155.9, 151.0, 136.7, 134.8, 132.0, 131.5, 126.8, 126.1, 124.8, 123.3, 122.8, 121.9, 117.7, 117.0, 116.6, 116.3, 115.8, 109.2, 107.7.

3.3.4.2 4-[3-(4-aminophthalimidyl)phenoxy]phthalonitrile (4m)

Yield: 88 % (13.0 g), deep yellow, m.p.: 204.1 °C. FT-IR (KBr, υmax, cm⁻¹): 3485, 3363, 3078, 2229, 1759, 1706, 1616, 1589, 1562, 1489, 1377 1251. ¹H-NMR (400 MHz, DMSO-d₆): δ(ppm) 8.14 (d, J = 8.67, 1H), 7.87 (s, 1H), 7.62 (d, J = 7.98, 1H), 7.30 (s, 1H), 7.24 (d, J = 7.75, 1H), 7.00 (s, 1H), 6.87(d, J = 8.01, 1H), 6.60 (s, 2H). ¹³C-NMR (100 MHz, DMSO-d₆): δ(ppm) 167.5, 167.1, 161.0, 155.9, 154.3, 137.0, 134.8, 134.7, 131.1, 126.0, 124.6, 123.6, 122.9, 119.5, 119.2, 117.8, 117.3, 116.9, 116.4, 116.0, 109.2, 107.7.

3.3.4.3 4-[4-(4-aminophthalimidyl)phenoxy]phthalonitrile (4p)

Yield: 71 % (10.5 g); deep yellow, m.p.: 242.3 °C. FT-IR (KBr, υ, cm⁻¹): 3489, 3384, 3043, 2229, 1759, 1706, 1614, 1597, 1566, 1510, 1382, 1257. ¹H-NMR (400 MHz, DMSO-d₆): δ(ppm) 8.12 (d, J = 8.79, 1H), 7.88 (s, 1H), 7.59 (d, J = 8.09, 1H), 7.51 (d, J = 7.75, 2H), 7.45 (d, J = 8.77, 1H), 7.31 (d, J = 7.49, 2H), 7.01 (s, 1H), 6.87 (d, J = 8.22, 1H), 6.55 (s, 2H). ¹³C NMR (100 MHz, DMSO-d₆): δ(ppm): 167.0, 166.8, 160.7, 157.4, 153.0, 136.4, 133.7, 129.3, 125.4, 124.9, 123.2, 122.4, 120.4, 119.7, 117.2, 116.8, 115.9, 115.4, 108.6, 107.1.
3.3.5 General Method for the Synthesis of \(N\)-(hydroxyphenyl)-4-nitrobezamides (1a–c)

Aminophenol (3.69 g, 338 mmol) was added to 70 mL dry \(N\)-methyl-2-pyrrolidone (NMP) under a constant flow of nitrogen. The reaction mixture was stirred at 0 °C for half an hour and then 20 mL (PO) was added. After five minutes, \(p\)-nitrobenzoyl chloride (6.24 g, 338 mmol) was added and the reaction mixture was stirred for an additional half an hour at the same temperature. After reaching room temperature, the reaction mixture was stirred for an additional 8 h. The reaction mixture was poured into water, and the solid precipitate was filtered, washed with hot water repeatedly, and dried overnight under vacuum at 80 °C.

3.3.5.1 \(N\)-(2-hydroxyphenyl)-4-nitrobezamide (1a)

\[
\begin{align*}
\text{Chemical Formula: } & C_{13}H_{10}N_{2}O_{4} \\
\text{Exact Mass: } & 258.06
\end{align*}
\]

Yield: 97 % (8.4 g); light yellow, m.p.: 206.0 °C. FT-IR (KBr, \(\nu_{\text{cm}^{-1}}\)): 3300–3420, 3035, 1655, 1610, 1550, 1522, 1438, 1351. \(^1\) H-NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 9.85 (s, 1H), 9.74 (s, 1H), 8.36 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 8.19 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 7.60 (d, \(J = 8.02 \text{ Hz}, 1\text{H}\)), 7.04-7.10 (m, 2H), 6.93 (d, \(J = 8.00 \text{ Hz}, 1\text{H}\)), 6.81-6.86 (m, 1H). \(^{13}\) C-NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 164.7, 151.0, 150.0, 141.2, 130.1, 127.3, 126.0, 124.5, 120.95, 119.9, 116.9.

3.3.5.2 \(N\)-(3-hydroxyphenyl)-4-nitrobezamide (1b)

\[
\begin{align*}
\text{Chemical Formula: } & C_{13}H_{10}N_{2}O_{4} \\
\text{Exact Mass: } & 258.06
\end{align*}
\]

Yield: 98 % (8.5 g); yellow, m.p.: 214.0 °C. FT-IR (KBr, \(\nu_{\text{cm}^{-1}}\)): 3310–3405, 3033, 1662, 1605, 1545, 1525, 1440, 1353. \(^1\) H-NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 10.44 (s, 1H), 9.49 (s, 1H), 8.37 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 8.16 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 7.35 (s, 1H), 7.15 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 6.54 (t, \(J = 7.89 \text{ Hz}, 1\text{H}\)). \(^{13}\) C-NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 165.0, 158.7, 150.0, 141.6, 140.9, 130.2, 124.5, 112.1, 108.5.

3.3.5.3 \(N\)-(4-hydroxyphenyl)-4-nitrobezamide (1c)

\[
\begin{align*}
\text{Chemical Formula: } & C_{13}H_{10}N_{2}O_{4} \\
\text{Exact Mass: } & 258.06
\end{align*}
\]

Yield: 92 % (8.0 g); deep yellow, m.p.: 266.0 °C. FT-IR (KBr, \(\nu_{\text{cm}^{-1}}\)): 3300–3405, 3030, 1660, 1600, 1550, 1520, 1441, 1352. \(^1\) H-NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 10.36 (s, 1H), 9.36 (s, 1H), 8.36 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 8.16 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 7.35 (s, 1H), 7.15 (d, \(J = 8.00 \text{ Hz}, 2\text{H}\)), 6.54 (t, \(J = 7.89 \text{ Hz}, 1\text{H}\)). \(^{13}\) C-NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 165.0, 158.7, 150.0, 141.6, 140.9, 130.2, 124.5, 112.1, 108.5.
2H), 8.15 (d, J = 8.00 Hz, 2H), 7.53 (d, J = 8.02 Hz, 2H), 6.75 (d, J = 8.02 Hz, 2H). $^{13}$C-NMR (75 MHz, DMSO-$d_6$): δ(ppm) 164.2, 155.0, 149.9, 141.8, 131.2, 130.0, 124.5, 123.3, 116.0.

3.3.6 General Method for the Synthesis of N-(hydroxyphenyl)-4-aminobezamides (2a–c)

N-(hydroxyphenyl)-4-nitrobenzamide (7.5 g, 29 mmol), 0.3 g of 10 % Pd–C, and 350 mL ethanol were heated in a 500 mL flask to 85 oC. Over a period of 1 h, 10 ml of hydrazine monohydrate was added to the stirring mixture drop wise. The reaction continued at reflux for another 4 h after addition of the hydrazine monohydrate. The reaction continued at reflux for another 4 h after addition of the hydrazine monohydrate. In order to redissolve the precipitated product, 70 ml of tetrahydrofuran was added to the suspension and refluxing continued for an additional 1 h. The mixture was filtered to remove the Pd–C and the filtrate was poured into water. The product was filtered, washed with hot water, and vacuum dried overnight at 70 oC.

3.3.6.1 N-(2-hydroxyphenyl)-4-aminobezamide (2a)

Yield: 88 % (5.8 g); off-white powder, m.p.: 231.0 oC

FT-IR (KBr, υ, cm $^{-1}$): 3270–3330, 3025, 1644, 1605, 1595, 1520, 1435, 1345. $^1$H-NMR (300 MHz, DMSO-$d_6$): δ(ppm) 9.82 (s, 1H), 9.23 (s, 1H), 7.63-7.72 (m, 3H), 6.80-6.98 (m, 3H), 6.58 (d, $J$ = 8.02 Hz, 2H), 5.82 (s, 2H). $^{13}$C-NMR (75 MHz, DMSO-$d_6$): δ(ppm) 166.5, 153.4, 149.6, 130.3, 127.7, 126.0, 124.0, 121.0, 120.2, 117.4, 113.7.

3.3.6.2 N-(3-hydroxyphenyl)-4-aminobezamide (2b)

Yield: 88 % (5.8 g); white powder, m.p.: 221.0 oC. FT-IR (KBr, υ, cm $^{-1}$): 3270–3325, 3027, 1647, 1600, 1598, 1525, 1438, 1340. $^1$H-NMR (300 MHz, DMSO-$d_6$): δ(ppm) 9.61 (s, 1H), 9.30 (s, 1H), 7.68 (d, $J$ = 8.05 Hz, 2H), 7.33 (s, 1H) 7.02-7.15 (m, 3H), 6.58 (d, $J$ = 8.03 Hz, 2H), 6.42 (d, $J$ = 7.91 Hz, 1H), 5.73 (s, 2H). $^{13}$C-NMR (75 MHz, DMSO-$d_6$): δ(ppm) 166.2, 158.4, 153.0, 141.9, 130.3, 130.0, 122.3, 113.5, 111.9, 111.0, 108.3.
3.3.6.3 N-(4-hydroxyphenyl)-4-aminobezamide (2c)

Yield: 96 % (6.3 g); white powder, m.p.: 262.0 °C. FT-IR (KBr, \(\bar{\nu}\), cm\(^{-1}\)): 3285–3320, 3034, 1641, 1608, 1581, 1535, 1436, 1360. \(^1\)H-NMR (300 MHz, DMSO-\(d_6\)): \(\delta(\text{ppm})\) 9.53 (s, 1H), 9.16 (s, 1H), 7.65 (d, \(J = 8.00\) Hz, 2H), 7.46 (d, \(J = 8.00\) Hz, 2H), 6.68 (d, \(J = 8.03\) Hz, 2H), 6.55 (d, \(J = 8.03\) Hz, 2H), 5.67 (s, 2H). \(^13\)C-NMR (75 MHz, DMSO-\(d_6\)): \(\delta(\text{ppm})\) 165.9, 154.2, 152.8, 132.2, 130.2, 123.2, 122.5, 115.9, 113.6.

3.3.7 General Method for the Synthesis of 4-amino-N-[(3,4-dicyanophenoxy)phenyl]bezamides (3a–b)

4-Nitrophthalonitrile (2.27 g, 0.0131 mol) and K\(_2\)CO\(_3\).(1.81 g, 0.0131 mol) were added to a solution of N-(hydroxyphenyl)-4-aminobenzamides (3.00 g, 0.0131 mol) in 40 mL DMSO. The reaction mixture was stirred under nitrogen for 40 h or until the 4-nitrophthalonitrile was consumed. The contents were poured into 200 mL of ice cold water and a few drops of hydrochloric acid (HCl) were added until the solution was neutralized. The precipitated solid was filtered and washed with water and cold ethanol. The product was dried overnight under vacuum at 70 °C.

3.3.7.1 4-amino-N-[2-(3,4-dicyanophenoxy)phenyl]benzamide (3a)

Yield: 80 % (3.7 g); light brown, m.p.: 100.0 °C. FT-IR (KBr, \(\bar{\nu}\), cm\(^{-1}\)): 3650–3153, 3078, 2227, 1637, 1600, 1585, 1521, 1344, 1272, 1170, 1109, 1055, 837, 761. \(^1\)H-NMR (300 MHz, DMSO-\(d_6\)): \(\delta(\text{ppm})\) 9.03 (s, 1H), 7.75 (d, \(J = 8.52\) Hz, 1H), 7.52 (d, \(J = 8.52\) Hz, 2H), 7.25-7.40 (m, 4H), 7.14 (s, 1H), 7.03 (d, \(J = 8.60\) Hz, 1H), 6.52 (d, \(J = 8.55\) Hz, 2H), 6.16 (s, 2H). \(^13\)C-NMR (75 MHz, DMSO-\(d_6\)): \(\delta(\text{ppm})\) 164.9, 155.2, 150.6, 146.1, 135.9, 132.5, 132.2, 127.6, 127.2, 126.5, 125.4, 119.0, 118.6, 118.0, 117.0, 116.4, 114.9, 113.5, 101.7.

3.3.7.2 4-amino-N-[3-(3,4-dicyanophenoxy)phenyl]benzamide (3b)

Yield: 78 % (3.5 g); light yellow, m.p.: 180.0°C. FT-IR (KBr, \(\bar{\nu}\), cm\(^{-1}\)): 3670–3168, 3035, 2231, 1639, 1604, 1510, 1485, 1438, 1284, 1251, 1184, 1143, 1089, 975, 981, 846, 686. \(^1\)H-NMR (300 MHz, DMSO-\(d_6\)): \(\delta(\text{ppm})\) 9.93 (s, 1H), 8.12 (d, \(J = 8.40\) Hz, 1H), 7.83 (s,
1H), 7.64-7.75 (m, 4H), 7.35-7.50 (m, 2H), 6.85 (d, $J = 8.75$ Hz, 1H), 6.58 (d, $J = 8.70$ Hz, 2H), 5.80 (s, 2H). $^{13}$C-NMR (75 MHz, DMSO-$d_6$): $\delta$(ppm) 164.4, 162.0, 154.8, 153.3, 142.9, 137.3, 131.4, 130.4, 123.7, 123.0, 121.6, 117.9, 117.7, 116.9, 116.4, 115.3, 113.5, 112.3, 109.1.

3.3.7.3 4-amino-$N$-[4-(3,4-dicyanophenoxy)phenyl]benzamide (3c)

Yield: 76 % (3.5 g); off white powder, m.p.: 240.0 °C. FT-IR (KBr, $\tilde{\nu}$, cm$^{-1}$): 3680–3160, 3070, 2229, 1649, 1606, 1586, 1510, 1406, 1313, 1251, 1205, 837. $^1$H-NMR (300 MHz, DMSO-$d_6$): $\delta$(ppm) 9.90 (s, 1H), 8.07 (d, $J = 8.50$ Hz, 1H), 7.86 (d, $J = 8.59$ Hz, 2H), 7.75 (s, 1H), 7.70 (d, $J = 8.40$ Hz, 2H), 7.34 (d, $J = 8.90$ Hz, 1H), 7.14 (d, $J = 7.70$ Hz, 2H), 6.59 (d, $J = 8.60$ Hz, 2H), 5.78 (s, 2H). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$(ppm) 166.3, 162.6, 153.2, 149.4, 138.6, 137.2, 130.5, 123.2, 122.8, 122.4, 121.8, 121.6, 117.6, 116.9, 116.4, 113.5, 108.7.

3.4 Synthesis of Polymers

3.4.1 General Method for the Synthesis of Diol based Phthalonitrile Polymers (P1d–1f)

The monomers were melted and degassed for fifteen minutes in order to remove the moisture and solvent residue. Then added 5 weight % of bis[4-(4-aminophenoxy)phenyl]sulfone (p-BAPS) as a curing agent to the melt with vigorous stirring and quenched after 5 minutes. The resulting green dark phthalonitrile prepolymer or B-staged resins were heated according to the heating profile; 170°C for 2h, 200°C for 2h, 250°C for 3h, 315°C for 5h and then postcured at 375°C for 5h in open atmosphere. The postcured products were then characterized and analyzed through different techniques.

3.4.1.1 Phthalonitrile Polymer of Monomer 1d (P1d)

FT-IR (KBr, $\tilde{\nu}$, cm$^{-1}$): 3069, 2224, 1600, 1522, 1473, 1436, 1355, 1225, 1095, 1010, 829, 750.

3.4.1.2 Phthalonitrile Polymer of Monomer 1e (P1e)

FTIR (KBr, $\tilde{\nu}$, cm$^{-1}$): 3063, 2224, 1603, 1521, 1487, 1354, 1217, 1099, 1010, 827, 748.
3.4.1.3 Phthalonitrile Polymer of Monomer 1f (P1f)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3076, 2227, 1720, 1599, 1521, 1481, 1348, 1232, 1093, 885, 829, 744.

3.4.2 General Method of Synthesis of Self-catalyzed Phthalonitrile Polymers
The self catalyzed monomers (2o–p, 4o–p, and 3a–b) were heated according to the heating profile; 170°C for 1h, 200°C for 2h, 250°C for 3h, 315°C for 5h and then postcured at 375°C for 5h in open atmosphere. The postcured products were then characterized and analyzed through different techniques.

3.4.2.1 Phthalonitrile Polymer of Monomer 2o (P2o)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3447, 3364, 3037, 2224, 1641, 1608, 1523, 1487, 1357, 1288, 1252, 1174, 1143, 1012, 974, 827,788.

3.4.2.2 Phthalonitrile Polymer of Monomer 2m (P2m)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3447, 3364, 3038, 2223, 1645, 1607, 1523, 1487, 1355, 1288, 1252, 1176, 1144, 1013, 974, 827,788.

3.4.2.3 Phthalonitrile Polymer of Monomer 2p (P2p)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3456, 3373, 3045, 2225, 1635, 1598, 1522, 1510, 1487, 1353, 1284, 1253, 1205, 1087, 1012, 953, 896, 835, 783.

3.4.2.4 Phthalonitrile Polymer of Monomer 4o (P4o)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3066, 2224, 1778, 1716, 1599, 1523, 1487, 1350, 1282, 1265, 1226, 1092, 1013, 827, 736.

3.4.2.5 Phthalonitrile Polymer of Monomer 4m (P4m)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3067, 2224, 1772, 1718, 1660, 1593, 1521, 1481, 1424, 1356, 1265, 1232, 1093, 1010, 942, 833, 783.

3.4.2.6 Phthalonitrile Polymer of Monomer 4p (P4p)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3068, 2226, 1772, 1716, 1659, 1598, 1519, 1478, 1435, 1359, 1266, 1229, 1082, 1015, 956, 831, 744.

3.4.2.7 Phthalonitrile Polymer of Monomer 3a (P3a)
FT-IR (KBr, \( \nu \), cm\(^{-1}\)): 3384, 3057, 2218, 1712, 1664, 1595, 1481, 1354, 1307, 1242, 1171, 1116, 1012, 821, 742.
3.4.2.8 Phthalonitrile Polymer of Monomer 3b (P3b)
FT-IR (KBr, ㎛, cm⁻¹): 3417, 3068, 2223, 1722, 1658, 1595, 1521, 1477, 1431, 1357, 1313, 1240, 1180, 1112, 1012, 964, 831, 756.

3.4.2.9 Phthalonitrile Polymer of Monomer 3c (P3c)
FT-IR (KBr, ㎛, cm⁻¹): 3425, 3066, 2223, 1722, 1660, 1597, 1523, 1500, 1469, 1355, 1309, 1209, 1113, 1010, 966, 829, 742.
Chapter – 4

RESULTS AND DISCUSSION

Phthalonitrile-based polymers are the materials that are superior in many aspects, which find their application in aerospace and marine industries. The materials in which backbone consists of aromatic and heterocyclic rings are getting much attention due to easy synthesis of their monomers and polymerization. In order to find the effects of various structural modifications such as ether, imide and amide linkages in the backbone; polymers were synthesized and was studied their behavior under the effect of heat.

Four series of the monomers were synthesized and polymerized. The first and second series involved the synthesis of Phthalonitrile monomers with ether linkage, while the third and fourth series with imide-ether and amide-ether linkages, respectively.

![General structures of the synthesized monomers](image)

Figure 4.1: General structures of the synthesized monomers

4.1 Synthesis of Diol based Phthalonitrile Monomers (1d–f)

4.1.1 2,2'-Bis(3,4-dicyanophenoxy)biphenyl (1d)

2,2'-Bis(3,4-dicyanophenoxy)biphenyl was synthesized in a single step following the reported method\(^\text{96}\). It involved nucleophilic displacement of nitro group in 4-nitrophthalonitrile by potassium salt of biphenyl-2,2'-diol in a continuous purge of nitrogen in anhydrous DMSO/benzene mixture as shown in Scheme 4.1. Benzene was used to remove water, formed as a by-product during reaction, by azeotropic distillation. The use of aprotic solvent like DMSO or DMF helps in dissolving the reactants without any reaction with base. Potassium carbonate was preferred because it does not hinder
biphenoxide during substitution of nitro group. The physical data of the compound 1e is given in the Table 4.1.

\[
\text{HO-A-CH}_2\text{OH} + 2 \quad \text{K}_2\text{CO}_3 \rightarrow \text{NC-CN} \quad \text{Curing Additive} \rightarrow \text{Thermoset (P1d, P1e)}
\]

**Scheme 4.1: Synthesis and polymerization of 1d and 1e**

FT-IR spectrum was in complete agreement with the proposed product. The spectrum indicated all the absorption bands related to the structure. The aromatic C–H stretching bands appeared at 3069 cm\(^{-1}\) and nitrile stretching band at 2223 cm\(^{-1}\). The C=C bonds in the aromatic rings were observed by two stretching bands at 1598 cm\(^{-1}\) and 1565 cm\(^{-1}\). The stretching band appeared at 1254 cm\(^{-1}\) associated with the C–O–C linkage, which confirmed the formation of the product, as shown in Table 4.2.

**Table 4.1: Physical data of compounds (1d–1f)**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Molecular formula</th>
<th>Molecular Weight</th>
<th>M.P. °C</th>
<th>Physical Appearance</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>C(<em>{28})H(</em>{14})O(_2)N(_4)</td>
<td>438.11</td>
<td>156.0</td>
<td>pale-yellow needles</td>
<td>83</td>
</tr>
<tr>
<td>1e</td>
<td>C(<em>{22})H(</em>{10})O(_2)N(_4)</td>
<td>362.08</td>
<td>188.7</td>
<td>colorless needles</td>
<td>71</td>
</tr>
<tr>
<td>1f</td>
<td>C(<em>{30})H(</em>{14})O(_3)N(_6)</td>
<td>506.11</td>
<td>265.7</td>
<td>off-white crystals;</td>
<td>90</td>
</tr>
</tbody>
</table>

\(^1\)H-NMR spectrum of the compound 1d indicated seven different aromatic protons, showing two triplet, four doublet and one singlet signals as shown in the Table 4.3. The protons H-a appeared as a doublet at 7.97 ppm, is highly deshielded due to its position ortho to the electron withdrawing nitrile group. The most shielded protons aperea at 7.17 ppm attributed to H-g due to ortho position to electron donating oxygen. The integration ratio of the protons is in complete agreement with the structure of the product. \(^{13}\)C-NMR spectrum further confirmed the formation of the product by the signals corresponded to the number of carbons in the aromatic region. The large upfield shift of C-a arises due to the anisotropic effect of nitrile triple bond. The C-c is more shielded compared to C-f due to electron donating effect of oxygen at ortho position,
although both are deshielded equally by nitrile group due to ortho position to them. The detailed $^{13}$C-NMR spectral data is shown in Table 4.4

### 4.1.2 1,2-Bis(3,4-dicyanophenoxy)benzene (1e)

1,2-Bis(3,4-dicyanophenoxy)benzene $^{75}$ was synthesized through a simple displacement of nitro group in 4-nitrophthalonitrile by potassium biphenoxide ion in an aprotic solvent DMF. The physical data of the compound 1e is shown in the Table 4.1.

FT-IR spectrum displayed all the stretching bands within the structure. The stretching bands at 3082 cm$^{-1}$ and 2232 cm$^{-1}$ corresponded to C–H aromatic and nitrile moieties respectively. The stretching bands at 1588 cm$^{-1}$ and 1566 cm$^{-1}$ attributed to the C=C bonds in the aromatic rings. The appearance of a stretching band at 1246 cm$^{-1}$ corresponded to the aromatic C–O–C linkage in the product, as presented in Table 4.2.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Absorption (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>3069</td>
</tr>
<tr>
<td>1e</td>
<td>3082</td>
</tr>
<tr>
<td>1f</td>
<td>3074</td>
</tr>
</tbody>
</table>

In the $^1$H-NMR spectrum of compound 1e, protons H-a showed as a doublet at 8.01 ppm, is highly downfield due to its position, ortho to the electron withdrawing nitrile group as shown in Table 4.3. The protons H-b and H-c appeared as singlet and doublet at 7.73 ppm and 7.33 ppm, respectively. The protons H-d, H-e, H-f, and H-g appeared as a multiplet in the range of 7.38–7.45 ppm. $^{13}$C-NMR spectrum displayed all the signals of the aromatic carbons within the structure of the compound. The C-d and C-g are highly deshielded carbons appeared at 160.6 ppm and 151.5 ppm respectively. The C-a and C-b appeared at 109.2 ppm and 115.8 ppm were shielded due to the anisotropic effect of nitrile moiety attached to them. The complete $^{13}$C-NMR spectral data of the compound 1e is given in the Table 4.4.
4.1.3 4,4’-[(1,3,4-oxadiazole-2,5-diyl)bis(2,1-phenylene)]bis(oxy)diphthalonitrile (1f)

Compound 1f was synthesized by simple nucleophilic displacement of nitro group in 4-nitrophthalonitrile by potassium salt of 2,5-bis(2-hydroxyphenyl)1,3,4-oxadiazole. In turn 2,5-bis(2-hydroxyphenyl)1,3,4-oxadiazole was synthesized by condensation reaction of 2-hydroxy benzoic acid with hydrazine sulphate in polyphosphoric acid (PPA) involving hydrazide as an intermediate. PPA was used due to its significant dehydration properties. High temperature is helpful for conversion of extended form of hydrazide into folded form and cyclodehydration of hydrazide groups. All the FT-IR, 1H-NMR and 13C-NMR spectroscopic data were in complete agreement with the proposed structure.

![Scheme 4.2: Synthesis and polymerization of 1f](image)

FT-IR spectrum showed all the bands within the structure of compound 1f. A stretching band at 3076 cm⁻¹ was observed due to aromatic C–H bond. It displayed the cyano absorption band at 2232 cm⁻¹. In addition, a band was observed at 1615 cm⁻¹ corresponded to C=N of oxadiazole ring. The absorption bands at 1596 and 1545 cm⁻¹ attributed the C=C in the aromatic rings. The spectrum also contains an absorption band at 1252 cm⁻¹ due to ether functionality in the compound as shown in Table 4.2.
Table 4.3: $^1$H-NMR spectral data of compounds (1d–1f)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Chemical shift(ppm), multiplicity, coupling constant(Hz) and intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-a</td>
</tr>
<tr>
<td>1d</td>
<td>7.97, d, 8.72, 2H</td>
</tr>
<tr>
<td>1e</td>
<td>8.01, d, 8.82, 2H</td>
</tr>
<tr>
<td>1f</td>
<td>8.07, d, 8.80, 2H</td>
</tr>
</tbody>
</table>

In the $^1$H-NMR spectrum of compound 1f, protons H-a showed a doublet at 8.07 ppm, highly downfield as usual due to its position ortho to the electron withdrawing nitrile group as shown in the Table 4.3. The protons H-b and H-c appeared as singlet and multiplet at 7.78 ppm and in the range of 7.36–7.41 ppm respectively. The protons H-d and H-g appeared as a multiplet in the range of 7.36–7.41 ppm and 8.04 ppm respectively. Protons H-e and H-f indicated as triplets at 7.75 ppm and 8.04 ppm respectively. $^{13}$C-NMR spectrum displayed all the signals of the aromatic carbons within the structure of the compound. The C-d, C-g and C-m are highly deshielded carbons appeared at 161.4 ppm, 151.6 ppm and 161.7 ppm respectively. The C-a and C-b appeared at 109.0 ppm and 116.8 ppm were shielded due to the anisotropic effect of nitrile moiety attached to them. The whole $^{13}$C-NMR spectral data of the compound 1f is given in the Table 4.4.
### Table 4.4: $^{13}$C-NMR spectral data of compounds (1d–1f)

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>Chemical shift (ppm), 1d</th>
<th>Chemical shift (ppm), 1e</th>
<th>Chemical shift (ppm), 1f</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>108.5</td>
<td>109.2</td>
<td>109.0</td>
</tr>
<tr>
<td>b</td>
<td>115.7</td>
<td>115.8</td>
<td>116.8</td>
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<tr>
<td>c</td>
<td>122.9</td>
<td>128.4</td>
<td>123.4</td>
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<tr>
<td>d</td>
<td>161.0</td>
<td>160.7</td>
<td>161.4</td>
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<tr>
<td>e</td>
<td>126.5</td>
<td>123.9</td>
<td>123.0</td>
</tr>
<tr>
<td>f</td>
<td>136.6</td>
<td>136.7</td>
<td>134.6</td>
</tr>
<tr>
<td>-CN</td>
<td>116.3, 117.0</td>
<td>116.3, 117.2</td>
<td>116.3, 116.9</td>
</tr>
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<td>g</td>
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<td>145.2</td>
<td>151.6</td>
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<td>122.0</td>
<td>122.4</td>
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<tr>
<td>i</td>
<td>129.8</td>
<td>122.4</td>
<td>130.9</td>
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<tr>
<td>j</td>
<td>122.4</td>
<td>122.4</td>
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<tr>
<td>l</td>
<td>130.9</td>
<td>145.2</td>
<td>117.2</td>
</tr>
</tbody>
</table>

### 4.2 Synthesis of 4-[(4-aminophthalimidyl)phenoxy]phthalonitriles

The 4-[(4-aminophthalimidyl)phenoxy]phthalonitriles were synthesized through a three-step synthetic route starting from aminophenols as shown in the scheme 4.4. The first step, all the three isomers of aminophenol were treated with 4-nitrophthalonitrile at 85 °C for 8h, to get 4-(aminophenoxy)phthalonitriles. These were further condensed with 4-nitrophthalic anhydride using acetic acid/cyclohexane mixture in the second step, followed by reduction of the nitro group in the third step.

#### 4.2.1 Synthesis of 4-(aminophenoxy)phthalonitriles (2o–p)

4-(aminophenoxy)phthalonitriles were synthesized by simple nitro displacement in 4-nitro phthalonitrile with potassium salt of different isomers of aminophenol. The reactions were carried out in anhydrous DMF and K₂CO₃. The physical data of the resulted products is shown in Table 4.5.
FT-IR spectra of the compounds $2o$, $2m$, and $2p$ displayed all the characteristic absorption bands within the structures as shown in Table 4.6. The FT-IR spectra characterized by stretching bands around 3450 cm$^{-1}$ and 3366 cm$^{-1}$, indicating the presence of amino group. The other characteristic bands observed around 3040 cm$^{-1}$ and 2232 cm$^{-1}$ attributed to aromatic C-H and nitrile moieties respectively. The most important characteristic band around 1250 cm$^{-1}$ attributed to ether group, which confirmed the formation of the products.

Scheme 4.3: Synthesis and polymerization of $2o$, $2m$ and $2p$

In the $^1$H-NMR spectra of compounds $2o$, $2m$ and $2p$, the proton $H-1$ gave doublet around 8.04 ppm, is highly deshielded as usual due to its position ortho to the electron withdrawing nitrile group. The protons $H-2$ and $H-3$ appeared as doublet and singlet round about 7.24 ppm and 7.65 ppm respectively. The amino protons appeared as singlet at 5.25 ppm. The other protons belonging to aromatic ring having amino group appeared in the range of 6.40–7.10 ppm as shown Table 4.7. $^{13}$C-NMR spectra displayed all the related signals within the structures of compounds $2o$, $2m$ and $2p$. The C-1 and C-2 appeared round about 107.6 ppm and 116.8 ppm, shielded due to the anisotropic effect of nitrile group attached to them. The other carbons appeared in the range of approximately 115.5–155.4 ppm. The complete $^{13}$C-NMR spectral data of the compound $2o$, $2m$ and $2p$ are given in the Table 4.8.
Table 4.5: Physical data of compounds (2o, m–4o, m–p)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Molecular formula</th>
<th>Molecular Weight</th>
<th>M.P. °C</th>
<th>Physical Appearance</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2o</td>
<td>C14H9O1N3</td>
<td>235.07</td>
<td>121.7</td>
<td>light brown</td>
<td>94</td>
</tr>
<tr>
<td>3o</td>
<td>C22H10O5N4</td>
<td>410.07</td>
<td>110.0</td>
<td>light pink</td>
<td>67</td>
</tr>
<tr>
<td>4o</td>
<td>C22H12O3N4</td>
<td>380.09</td>
<td>100.0</td>
<td>yellow</td>
<td>77</td>
</tr>
<tr>
<td>2m</td>
<td>C14H9O1N3</td>
<td>235.07</td>
<td>172.5</td>
<td>light yellow</td>
<td>88</td>
</tr>
<tr>
<td>3m</td>
<td>C22H10O5N4</td>
<td>410.07</td>
<td>185.0</td>
<td>light pink</td>
<td>72</td>
</tr>
<tr>
<td>4m</td>
<td>C22H12O3N4</td>
<td>380.09</td>
<td>204.1</td>
<td>deep yellow</td>
<td>88</td>
</tr>
<tr>
<td>2p</td>
<td>C14H9O1N3</td>
<td>235.07</td>
<td>130.9</td>
<td>deep brown</td>
<td>96</td>
</tr>
<tr>
<td>3p</td>
<td>C22H10O5N4</td>
<td>410.07</td>
<td>198.0</td>
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<tr>
<td>4p</td>
<td>C22H12O3N4</td>
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<td>deep yellow</td>
<td>71</td>
</tr>
</tbody>
</table>

4.2.2 Synthesis of 4-[(4-nitrophthalimidy)phenoxy]phthalonitriles (3o-p)

4-[(4-nitrophthalimidy)phenoxy]phthalonitriles were prepared by condensation of 4-nitrophthalic anhydride with 4-(aminophenoxy)phthalonitriles in acetic acid and cyclohexane mixture. Cyclohexane was used to remove water, formed as a by-product during imidization, by azeotropic distillation. The imidization take place through the amic acid route. The physical data of the resulted products is shown in Table 4.5.

FT-IR spectra showed all the characteristic absorption bands of the compounds within the structures of 3o, 3m, and 3p as shown in Table 4.6. The FT-IR spectra characterized by stretching bands around 3085 cm⁻¹ and 2228 cm⁻¹, attributed to aromatic C–H and nitrile moieties respectively. The most important characteristic bands around 1780 cm⁻¹ and 1725 cm⁻¹, attributed to imide group and disappearance of the bands attributed to amino group, confirmed the formation of the products. The other characteristic bands observed round about 1487 cm⁻¹ and 1349 cm⁻¹ attributed to nitro group. The band around 1251 cm⁻¹ attributed to ether group.
Scheme 4.4: Synthesis and polymerization of 4o, 4m and 4pa

Table 4.6: FT-IR data of compounds (2o, m, p – 4o, m, p)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2o</td>
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<td>2233</td>
<td>1606, 1564</td>
<td>1249</td>
<td>3446, 3363</td>
<td></td>
<td></td>
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<tr>
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<td>3076</td>
<td>2225</td>
<td>1585, 1539</td>
<td>1251</td>
<td>3471, 3363, 1785, 1725, 1496, 1342</td>
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<td></td>
</tr>
<tr>
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<td>3080</td>
<td>2229</td>
<td>1589, 1568</td>
<td>1249</td>
<td>3471, 3363, 1772, 1714</td>
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<td></td>
</tr>
<tr>
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<td>2231</td>
<td>1608, 1564</td>
<td>1249</td>
<td>3444, 3365</td>
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<td></td>
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<td>3m</td>
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<td>2231</td>
<td>1589, 1539</td>
<td>1251</td>
<td>1776, 1726, 1487, 1349</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>3078</td>
<td>2229</td>
<td>1589, 1562</td>
<td>1251</td>
<td>3485, 3363, 1759, 1706</td>
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<td></td>
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<td>1600, 1562</td>
<td>1251</td>
<td>3454, 3371</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3p</td>
<td>3091</td>
<td>2229</td>
<td>1589, 1539</td>
<td>1249</td>
<td>1787, 1724, 1481, 1349</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4p</td>
<td>3043</td>
<td>2229</td>
<td>1597, 1566</td>
<td>1257</td>
<td>3489, 3384, 1759, 1706</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the ¹H-NMR spectra of compounds 3o, 3m and 3p, the proton H-1 gave doublet around 8.10 ppm, is highly deshielded as usual due to its ortho position to the electron withdrawing nitrile group. The protons H-2 and H-3 appeared as doublet and singlet
around 7.40 ppm and 7.70 ppm respectively. The protons, H-4 to H-8 belonging to the middle aromatic rings B appeared in the range of 7.38–7.91 ppm. The protons set H-10 gave a doublet around 8.67 ppm, is highly deshielded due to electron withdrawing group at ortho position. The protons H-9 and H-11 in ring C appeared as doublet and singlet around 8.22 ppm and 8.58 ppm respectively as shown Table 4.7. 13C-NMR spectra showed all the related signals within the structures of compounds 3o, 3m and 3p. The C-1 and C-2 appeared around 108.9 ppm and 118.7 ppm, shielded due to the anisotropic effect of nitrile group attached to them. The other carbons from C-3 to C-12 of rings A and B appeared in the range of approximately 115.2–160.4 ppm. The C-13 and C-14 of imide group appeared around 165.0 ppm highly deshielded due sp2 hybridization and no hydrogen attached to them. The C-16 and C-18 appeared round about 121.0 ppm and 128.0 ppm, should be deshielded more due to ortho position to electron withdrawing nitro group but however they are shielded due to intramolecular electric field of nitro group. This shift the bonding electrons of C-H bond to carbon atom, as a result the electronic density at ortho carbons increased. The other carbons in ring C appeared in the range of approximately 113.2–152.4 ppm. The complete 13C-NMR spectral data of the compound 3o, 3m and 3p are given in the Table 4.8.

4.2.3 Synthesis of 4-[(4-aminophthalimidyl)phenoxy]phthalonitriles (4o–p)

4-[(4-aminophthalimidyl)phenoxy]phthalonitriles were prepared by reduction with ammonium formate over 10 % Pd/C in N, N-dimethylacetamide. Ammonium formate donates hydrogen in this catalytic system, which is highly selective to nitro group reduction and did not show any effect on other reducible group such as nitrile group within the compound. The physical data of the resulted products is shown in Table 4.5.

In the FT-IR spectra of the compounds 4o, 4m, and 4p all the characteristic absorption bands within the structures were observed as shown in Table 4.6. The stretching bands around 3080 cm⁻¹ and 2229 cm⁻¹ attributed to aromatic C–H and nitrile moieties, respectively. The most important characteristic bands round about 3482 cm⁻¹ and 3372 cm⁻¹ attributed to amine and disappearance of the bands attributed to nitro group, confirmed the formation of the products. The shifting of imide bands around 1760 cm⁻¹ and 1710 cm⁻¹ due to electron donating effect of amino group is another evidence of the formation amine. The band around 1252 cm⁻¹ attributed to ether group.
Table 4.7: $^{13}$H-NMR spectral data of (2o, m, p–4o, m, p)

![Diagram]

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Chemical shift (ppm), multiplicity, coupling constant(Hz) and intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-1</td>
</tr>
<tr>
<td>2o</td>
<td>8.04, d, 8.65, 7.18, s, 1H, 7.62, 1H</td>
</tr>
<tr>
<td>3o</td>
<td>8.07, d, 8.75, 7.39, s, 1H, 7.74, 1H</td>
</tr>
<tr>
<td>4o</td>
<td>8.04, 8.76, 7.53, 1H, 8.67, s, 1H</td>
</tr>
<tr>
<td>2m</td>
<td>8.07, 8.7, 7.34, d, 7.72, s, 1H, 6.29, 1H</td>
</tr>
<tr>
<td>3m</td>
<td>8.15, 8.73, 7.32, d, 7.90, s, 1H, 7.33, 1H</td>
</tr>
<tr>
<td>4m</td>
<td>8.14, 8.67, 7.62, d, 7.9, 8.1H, 7.30, s, 1H</td>
</tr>
<tr>
<td>2p</td>
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</tr>
<tr>
<td>3p</td>
<td>8.14, 8.69, 7.59, d, 7.93, s, 1H, 7.38, 1H</td>
</tr>
<tr>
<td>4p</td>
<td>8.12, 8.79, 7.59, d, 7.88, s, 1H, 7.31, 1H</td>
</tr>
</tbody>
</table>

In the $^1$H-NMR spectra of compounds 4o, 4m, and 4p, the proton H-1 gave doublet round about 8.08 ppm, is highly deshielded due to its position ortho to the electron withdrawing nitrile group. The protons H-2 and H-3 appeared as doublet and singlet around 7.45 ppm and 7.70 ppm respectively. The protons from H-4 to H-8 belonging to the middle aromatic rings B appeared in the range of 7.32–7.90 ppm. The amine protons appeared at 6.60 ppm. The shifting of protons H-9, H-10 and H-11 of the ring C to a shielded region compared to the starting materials due to shielding effect of amino group
as shown Table in 4.7. $^{13}$C-NMR spectra displayed all the characteristic signals within the structures of compounds 4o, 4m and 4p. The C-1 and C-2 appeared around 107.7 ppm and 117.2 ppm, shielded due to the anisotropic effect of adjacent nitrile groups. The other carbons from C-3 to C-12 of rings A and B appeared in the range of approximately 110–162 ppm. The C-13 and C-14 of imide group appeared around 167.0 ppm highly deshielded due sp$^2$ hybridization and no hydrogen attached to them. The C-16 and C-18 appeared around 110 ppm and 120 ppm, shifted upfield due to amino group at ortho position, indicated the formation of the products. The other carbons in ring C appeared in the range of approximately 123.2–157.3 ppm. The complete $^{13}$C-NMR spectral data of the compound 4o, 4m and 4p are given in the Table 4.8.

Table 4.8: $^{13}$C-NMR spectral data of (2o, m, p–4o, m, p)

<table>
<thead>
<tr>
<th>carbon No.</th>
<th>13C-$\delta$ (ppm), Compounds</th>
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</thead>
<tbody>
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<td>1</td>
<td>107.7</td>
</tr>
<tr>
<td>2</td>
<td>116.7</td>
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<tr>
<td>3</td>
<td>121.0</td>
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<td>4</td>
<td>161.8</td>
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<td>5</td>
<td>122.3</td>
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<td>20</td>
<td>150.4</td>
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<tr>
<td>-CN</td>
<td>116.0</td>
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4.3 Synthesis of 4-amino-N-[(3,4-dicyanophenoxy)phenyl]benzamides

The 4-amino-N-[(3,4-dicyanophenoxy)phenyl]benzamides were synthesized in three steps as shown in the Scheme 4.5. The first step, N-(hydroxyphenyl)-4-nitrobezamides were synthesized by condensation reaction between commercially available aminophenol with 4-nitrobenzoyl chloride. This was followed by catalytic reduction of nitro group in the second step and finally the target compounds were obtained through nucleophilic displacement of the nitro group in 4-nitrophthalonitrile by potassium salt of N-(hydroxyphenyl)-4-aminobezamides in a continued purge of nitrogen.

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{Cl} \\
\text{O} & \quad \text{H}_2\text{N} \\
\text{H} & \quad \text{OH} \\
\text{O} & \quad \text{Cl}
\end{align*}
\]

\text{NMP/PO} \quad \text{NH}_2\text{NH}_2 \quad \text{Pd-C, EtOH}

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{HN} \\
\text{O} & \quad \text{H}_2\text{N} \\
\text{O} & \quad \text{CN}
\end{align*}
\]

\[
\text{K}_2\text{CO}_3, \text{NMP}
\]

\[
\text{Thermosets} \quad \text{(P3a, P3b, P3c)}
\]

Scheme 4.5: Synthesis and polymerization of 3a, 3b and 3c

4.3.1 Synthesis of N-(hydroxyphenyl)-4-nitrobezamides (1a–c)

N-(hydroxyphenyl)-4-nitrobezamides were synthesized by condensation reaction of aminophenol with 4-nitrobenzoyl chloride in inert atmosphere. The reaction was kept at freezing temperature with slow addition of 4-nitrobenzoyl chloride. The reaction was carried out in the presence of propylene oxide which acts as an acid scavenger. The physical data of the resulted products is shown in Table 4.9.
Table 4.9: Physical data of compounds (1a, b, c–3a, b, c)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Molecular formula</th>
<th>Molecular Weight</th>
<th>M.P. °C</th>
<th>Physical Appearance</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>C13H10O2N2</td>
<td>258.06</td>
<td>206.0</td>
<td>light yellow</td>
<td>97</td>
</tr>
<tr>
<td>2a</td>
<td>C13H12O2N2</td>
<td>228.09</td>
<td>231.0</td>
<td>off-white powder</td>
<td>88</td>
</tr>
<tr>
<td>3a</td>
<td>C21H14O2N4</td>
<td>354.11</td>
<td>100.0</td>
<td>light brown</td>
<td>80</td>
</tr>
<tr>
<td>1b</td>
<td>C13H10O2N2</td>
<td>258.06</td>
<td>214.0</td>
<td>yellow</td>
<td>98</td>
</tr>
<tr>
<td>2b</td>
<td>C13H12O2N2</td>
<td>228.09</td>
<td>221.0</td>
<td>white powder</td>
<td>88</td>
</tr>
<tr>
<td>3b</td>
<td>C21H14O2N4</td>
<td>354.11</td>
<td>180.0</td>
<td>light yellow</td>
<td>78</td>
</tr>
<tr>
<td>1c</td>
<td>C13H10O2N2</td>
<td>258.06</td>
<td>266.0</td>
<td>deep yellow</td>
<td>92</td>
</tr>
<tr>
<td>2c</td>
<td>C13H12O2N2</td>
<td>228.09</td>
<td>262.0</td>
<td>white powder</td>
<td>88</td>
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<tr>
<td>3c</td>
<td>C21H14O2N4</td>
<td>354.11</td>
<td>240.0</td>
<td>off-white powder</td>
<td>76</td>
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</table>

FT-IR spectra of the compounds 1a, 1b, and 1c illustrated all the characteristic absorption bands within the structures as shown in Table 4.10. The FT-IR spectra characterized by stretching bands in the range of 3300-3450 cm⁻¹ and bending band at 1605 cm⁻¹ assigned to amide group. The other characteristic bands were observed around 3030 cm⁻¹ and 1660 cm⁻¹ attributed to aromatic C–H and amide carbonyl moieties respectively. The nitro group gave two bands around 1440 cm⁻¹ and 1253 cm⁻¹ attributed to asymmetric stretching and symmetric stretching respectively.

In the ¹H-NMR spectra of compounds 1a, 1b, and 1c, the proton H-1' and H-2' gave doublets around 8.36 ppm and 8.16 ppm respectively as shown in Table 4.11. They are highly deshielded as usual due to their position ortho to the electron withdrawing nitro and amide groups. The protons H-3' to H-7' appeared around 6.75–8.15 ppm. The amide and hydroxyl protons appeared at 10.30 ppm and 9.50 ppm respectively. ¹³C-NMR spectra displayed all the related signals within the structures of compounds 1a, 1b, and 1c. The C-1' and C-4' appeared round about 150.0 ppm and 140.0 ppm, deshielded due to nitro and amide groups attached to them respectively. The C-3' appeared at 124.4 ppm, shielded due to intramolecular electric field of nitro group. The C-5' observed at 164.4 ppm. The signals of the rest carbons were observed in the range of 112.5–158.7 ppm. The complete ¹³C-NMR spectral data of the compound 1a, 1b, and 1c is given in the Table 4.12.
Table 4.10: FT-IR data of compounds (1a, b, c–3a, b, c)

<table>
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<td>3c</td>
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<td></td>
<td>3680–3160</td>
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4.3.2 Synthesis of \(\text{N-(hydroxyphenyl)-4-aminobezamides (2a–c)}\)

\(\text{N-(hydroxyphenyl)-4-aminobezamides}\) were synthesized by catalytic reduction of \(\text{N-(hydroxyphenyl)-4-nitroobezamides}\) by drop wise addition of hydrazine monohydrate. Hydrazine hydrate is not only highly selective reducing agent to nitro group but also produces harmless by-products during the course of reaction, such as nitrogen and water. The physical data of the resulted products is shown in Table 4.9.

FT-IR spectra of the compounds 2a, 2b, and 2c\(^{98}\) indicated all the characteristic absorption bands within the structures as shown in Table 4.10. The FT-IR spectra characterized by stretching bands in the range of 3250–3335 cm\(^{-1}\) and bending band at 1600 cm\(^{-1}\) assigned to amide group. The other characteristic bands observed around 3028 cm\(^{-1}\) and 1644 cm\(^{-1}\) attributed to aromatic C–H and amide carbonyl moieties respectively. The disappearance of nitro bands and appearance of new bands in the range of 3270–3325 cm\(^{-1}\), attributed to amino group, confirmed the formation of products. Similarly the shifting of amide carbonyl band to 1644 cm\(^{-1}\) due to electron donating effect of amino group also confirmed the reduction of nitro group.
Table 4.11: $^1$H-NMR spectral data of compounds (1a, b, c–3a, b, c)

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Chemical shift (ppm), multiplicity, coupling constant (Hz) and intensity</th>
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<td>3c</td>
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R = -NO₂, -NH₂
Table 4.12: $^{13}$C-NMR spectral data of (1a, b, c–3a, b, c)

R = -NO$_2$, -NH$_2$

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<th>carbon No.</th>
<th>$^{13}$C-$\delta$(ppm), Compounds</th>
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<tr>
<td>1'</td>
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<tr>
<td>2'</td>
<td>124.5 113.7 113.5 124.5 113.5 113.5 124.5 113.6 113.5</td>
</tr>
<tr>
<td>3'</td>
<td>130.1 130.3 132.5 130.2 130.3 130.4 130.0 130.2 130.5</td>
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<td>4'</td>
<td>141.2 124.0 127.6 140.9 122.3 123.7 141.8 122.5 123.2</td>
</tr>
<tr>
<td>5'</td>
<td>164.7 166.5 164.9 165.0 166.2 164.4 164.2 165.9 166.3</td>
</tr>
<tr>
<td>6'</td>
<td>127.3 127.7 132.2 141.6 141.9 142.9 131.2 132.2 137.2</td>
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<tr>
<td>7'</td>
<td>150.0 149.6 146.1 108.5 108.3 112.3 123.3 123.2 122.8</td>
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<tr>
<td>8'</td>
<td>116.9 117.4 117.0 158.7 158.4 154.8 116.0 115.9 121.6</td>
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<tr>
<td>9'</td>
<td>126.0 126.0 127.2 112.1 111.9 117.7 155.0 154.2 149.4</td>
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<tr>
<td>10'</td>
<td>121.0 121.0 125.4 130.2 130.0 131.4 116.0 115.9 121.6</td>
</tr>
<tr>
<td>11'</td>
<td>120.0 120.2 118.6 112.1 111.0 116.4 123.3 123.2 122.8</td>
</tr>
<tr>
<td>12'</td>
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<td>13'</td>
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<tr>
<td>-CN</td>
<td>114.9, 116.4 115.2, 116.9 116.4, 116.9</td>
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In the $^1$H-NMR spectra of compounds 2a, 2b, and 2c, the proton H-1' appeared as doublet round about 6.56 ppm, highly shielded compared to their nitro counterparts due to amino group at ortho position as shown in Table 4.11. The protons H-2' to H-7' appeared around 6.42–7.72 ppm. A singlet round about at 5.25 ppm attributed to amino protons and confirmed the formation of the product. The amide and hydroxyl protons appeared at 9.70 ppm and 9.23 ppm respectively. $^{13}$C-NMR spectra displayed all the related signals within the structures of compounds 2a, 2b, and 2c. The C-2' and C-4' appeared round about 113.6 ppm and 123.0 ppm, are deshielded compared to nitro counterparts due to amino group at ortho and para position to them respectively. The C-5' observed at 166.0 ppm is highly deshielded. The signals of the rest carbons were observed in the range of 111.5–153.4 ppm, nearly at the same position as their precursors. The complete $^{13}$C-NMR spectral data of the compound 2a, 2b, and 2c is given in the Table 4.12.

4.3.3 Synthesis of 4-amino-N-[(3,4-dicyanophenoxy)phenyl]benzamides (3a–c)

4-amino-N-[(3,4-dicyanophenoxy)phenyl]benzamides were synthesized by simple nitro displacement in 4-nitrophthalonitrile with potassium salt of N-(hydroxyphenyl)-4-aminobezamides. The reaction was carried out in anhydrous DMSO and K$_2$CO$_3$. The physical data of the resulted products is shown in Table 4.9.

FT-IR spectra of the compounds 3a, 3b, and 3c displayed all the characteristic absorption bands within the structures as shown in Table 4.10. The FT-IR spectra characterized by stretching bands in the range of 3150–3650 cm$^{-1}$ and bending band at 1600 cm$^{-1}$ assigned to amide group. The other characteristic bands observed around 3070 cm$^{-1}$ and 1645 cm$^{-1}$ attributed to aromatic C–H and amide carbonyl moieties respectively. The disappearance of hydroxyl band and appearance of new band at 1252 cm$^{-1}$ attributed to ether groups, confirmed the formation of products. The appearance of bands in the range of 3160–3650 cm$^{-1}$ and a new band at 2229 cm$^{-1}$ attributed to amine and nitrile groups, respectively, confirmed the formation of products.

In the $^1$H-NMR spectra of compounds 3a, 3b, and 3b, the proton H-1' and H-2' appeared as doublet round about 6.58 ppm and 7.60 ppm as shown in Table 4.11. The protons H-3' to H-7' appeared round about 7.03–7.75 ppm. The disappearance of hydroxyl signal and appearance of new signals in the range of 7.14–8.12 ppm attributed to the protons of new ring C confirmed the formation of the products. The structures of compounds 3a,
3b, and 3c were also confirmed by $^{13}$C-NMR spectroscopy. The appearance of additional eight signals in the aromatic region i.e. 108.2–162.6 ppm confirmed the formation of the products. The signals of the rest carbons were observed in the range of 112.3–166.3 ppm nearly the same position as their precursors. The complete $^{13}$C-NMR spectral data of the compound 3a, 3b, and 3c is given in the Table 4.12.

### 4.4 Syntheses of Prepolymer and Polymer of Diol based Monomers (P1d–f)

The diol based phthalonitrile monomers changed into prepolymer, after adding of bis[4-(4-aminophenoxy)phenyl]sulfone ($p$-BAPS) to their corresponding melted form in order to get a homogenous mixture. Prepolymers (B-stage) are stable under room temperature and can be used at any time as a matrix in fabrication of composites, characterization and curing. The use of $p$-BAPS helps in catalyzing the polymerization and was preferred due to high stability and low reactivity. The reaction is very slow, that is why the mixture was heated at different temperature, even above the curing temperature, for different intervals in order to insure complete curing. The thermal cycle used to insure complete curing included a five-step thermal cure cycle was employed for composite panel fabrication. The cycle included dwells at 170 °C for 2h, 200 °C for 2h, 250 °C for 3h, 315 °C for 5h and 375 °C for 5h.

The FT-IR spectrum confirmed the crosslinked structure of polymer P1d. In the polymer structure all the characteristic bands were observed as like that of the monomer including some additional peaks around 1522 and 1355 cm$^{-1}$ and around 1010 cm$^{-1}$ indicated the formation of triazine and phthalocynine rings respectively. In the FT-IR spectrum the intensity of the stretching band of nitrile group decreased compare to the precursor as well as shifted from 2233 to 2224 cm$^{-1}$ after crosslinking. It shows that all cyno groups did not trimirize to triazine rings completely even after post-curing, due to steric hindrance.

Similarly the FT-IR spectrum of the polymeric structure P1e indicated some additional stretching bands along the all characteristic bands of the precursor. These new stretching bands around 1521 and 1354 cm$^{-1}$ and around 1010 cm$^{-1}$ confirm the formation of triazine and phthalocynine rings respectively. The decrease in intensity of nitrile group and shifting to 2224 cm$^{-1}$, is a strong evidence of the formation of triazine ring. The FT-IR spectrum of polymer P1f indicated additional stretching bands at 1521 and 1348 cm$^{-1}$ showing the formation of triazine ring. The small but significant decrease in intensity of
nitrile group and shifting to 2227 cm\(^{-1}\) compared to the precursor is another evidence of the formation of triazine ring.

4.5 Syntheses of Polymer of Self-catalyzed Monomers

4.5.1 Syntheses of Polymer of 4-(aminophenoxy)phthalonitriles (P2o–p)

FT-IR spectra were recorded in KBr pellets. They were a little bit broadened and of low intensity because of large particle size. However, they still provided some useful information about the structure of the cross-linked products. FT-IR spectra indicated some additional bands along with their corresponding precursors. These new stretching bands around 1522 and 1353 cm\(^{-1}\) and around 1012 cm\(^{-1}\) confirm the formation of triazine and phthalocynine rings respectively. The small but significant decrease in intensity of nitrile group and shifting to 2224 cm\(^{-1}\) compared to their corresponding precursors is another strong evidence of the formation of triazine ring. Herein, the intensity of nitrile group is lower compared to diol based phthalonitriles/diamine. This is due to stable and higher concentration of amino containing self catalyzed compound, which catalyze the polymerization. The absorption band around 1252 cm\(^{-1}\) attributed to ether linkage indicated that curing at high temperatures does not cause any decomposition in the skeleton of the cross-linked polymers\(^99\).

4.5.2 Syntheses of Polymer of 4-[(4-aminophthalimidyl)phenoxy]-phthalonitriles (P4o–p)

FT-IR spectra confirmed all the concerned bands within the structure of the cross-linked products. They showed some additional bands along their corresponding precursors. These new stretching bands around 1520 and 1356 cm\(^{-1}\) and around 1013 cm\(^{-1}\) confirm the formation of triazine and phthalocynine rings respectively. The decrease in intensity of nitrile group and shifting to lower wavelength compared to their corresponding precursors confirm the formation of triazine ring. The other absorption band around 1772 cm\(^{-1}\) (asymmetric C=O) and 1718 cm\(^{-1}\) (symmetric C=O) attributed to imide linkage, indicated that curing at high temperatures does not cause any decomposition in the skeleton of the cross-linked polymers\(^100\).
4.5.3 Syntheses of the Polymer of 4-amino-N-[(3,4-dicyanophenoxy)-
phenyl]benzamides (P3a–c)

FT-IR spectra confirmed the structure of the final cross-linked products. They displayed all the characteristic bands with some additional bands along their corresponding precursors. These new stretching bands around 1522 and 1357 cm\(^{-1}\) and around 1011 cm\(^{-1}\) confirm the formation of triazine and phthalocynine rings respectively. The decrease in intensity of nitrile group and shifting to lower wavelength around 2223 cm\(^{-1}\) compared to their corresponding precursors confirm the formation of triazine ring. The other absorption band around 3410 cm\(^{-1}\) (-NH- amide) and 1680 cm\(^{-1}\) (C=O) and around 1240 cm\(^{-1}\) attributed to amide and ether linkages, indicated that curing at high temperatures does not cause any decomposition in the skeleton of the cross-linked polymers.

4.6 Thermal Analyses of Prepolymers and Polymers

Thermal analysis helps us to find the behavior of the sample as a function of temperature. Herein we used some conventional techniques including: differential scanning calorimetry (DSC), Thermo gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and complex melt viscosity for the analysis and characterization of the synthesized prepolymers and polymers.

4.6.1 Differential Scanning Calorimetric (DSC) Analysis

The DSC results of both diol-based phthalonitrile prepolymers and the self-catalyzed monomers are shown here in Table 4.13. The DSC thermograms were recorded at a heating rate of 10°C per minute under nitrogen with a flow rate of 50 mL per minute.

The polymerization reactions of monomers 1d, 1e, and 1f were studied by DSC analysis up to 400 °C in the presence of 5 mol % of p-BAPS\(^{98}\) as shown in the Figure 4.2 (a). In addition to endothermic peak in the curve, an exothermic transition peak is also observed for each monomer. These are attributed to melting transition and to the reaction with p-BAPS, respectively. The heat absorbed during melting of monomer 1d and 1e is in the range of 81–110 J g\(^{-1}\) is comparatively lower than that of p-biphenyl\(^{86}\) and resorcinol-based\(^{78}\) phthalonitriles (120–150 J g\(^{-1}\)). This low melting enthalpy indicates that these ortho-linked phthalonitriles are less crystalline than meta or para-linked phthalonitriles due to less packing of monomers. However, the melting enthalpy for the monomer 1f, melted at 265.7°C, is comparatively high showing high degree of crystallinity. For monomer 1e, the reaction temperature is at about 243.0 °C; whereas the reaction temperature is shifted to higher temperature at about 264.0 °C and 390.0 °C for monomer
1d and 1f respectively. This might be due to the reactivity of monomers towards p-BAPS. The monomer 1d and 1f with bulky size made it more difficult for the curing additive to find the reactive ends and to continue the reaction compared to monomer 1e, having a small size. Moreover, curing enthalpy varied from 15-17 \text{j g}^{-1}, did not show any significant effect of structure variation in the monomer backbone.

Figure 4.2: DSC thermograms of monomers 1d–1f (a) and 2o–2p(b)

The polymerization reactions of monomers 2o, 2m and 2p were studied by DSC analysis up to 400 °C as shown in the Figure 4.2 (b). They exhibited both endothermic and exothermic transition peaks for each monomer, attributed to melting and cross-linking respectively. These endothermic transitions around 121.7 °C, 172.5 °C and 131.0 °C corresponded to the melting point of 2o, 2m and 2p respectively. These differences in melting points indicated that melting has relation with the position of amino group. The high melting point of 2m due to coplanarity of donor and accepter groups and close packing structure, compared to 2o and 2p. These low melting temperatures of 2o and 2p are very helpful in processability. The heat absorbed during melting of monomer 2o, 2m and 2p in the range of 110–140 J g^{-1} is higher than that of ortho biphenyl and Catechol-based phthalonitriles, showing comparatively high crystallinity. These curing peaks around 261.6 °C, 240.9 °C and 236.0 °C corresponded to the highest temperature of curing of the monomers 2o, 2m and 2p respectively. The curing temperature of 2o is comparatively high due to non-coplanarity and hindering of amino group at ortho position, which makes it difficult to find the reactive ends and to continue the reaction compared to monomer 2m and 2m. Moreover, curing enthalpy of these monomers was higher than bisphthalonitride monomers/diamine and hydroxyl catalyzed phthalonitriles due to high concentration of catalyzing amino group, which made them more
The curing enthalpies of monomers \( 2o, 2m \) and \( 2p \) were 251.6 J g \(^{-1}\), 203.5 J g \(^{-1}\) and 232.5 J g \(^{-1}\) respectively. This variation in the enthalpy of monomers showed significant effect of the position of amino group in the monomer structure.

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<th>Monomer code</th>
<th>Melting point (°C) (DSC)</th>
<th>Curing peak Temp. (°C)</th>
<th>Monomer code</th>
<th>Melting point (°C) (DSC)</th>
<th>Curing peak Temp. (°C)</th>
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</table>

The polymerization of monomers \( 4o, 4m \) and \( 4p \) were analyzed by DSC up to 400 °C as displayed in the Figure 4.3 (c), where the endotherms attributed to melting and exotherms corresponded to curing reaction respectively. These endothermic transitions around 100.0 °C, 204.0 °C and 242.0 °C corresponded to the melting point of \( 4o, 4m \) and \( 4p \) respectively. These differences in melting points indicated that melting has the relationship with the structures of monomers. The lower melting point of \( 4o \), around 100°C due to unclosed packing structure especially by incorporating of 1,2-linked unit (catechol) compared to 1,3 and 1,4-linked units in \( 4m \) and \( 4p \) respectively. The heat absorbed during melting of monomer \( 4o, 4m \) and \( 4p \) in the range of 4-75 J g \(^{-1}\) is higher than that of aminophenoxy-based phthalonitriles. These lower values of melting enthalpies indicted that these monomers were less crystalline than their lower molecular weight precursors. These curing peaks were around in the range of 266.0–274.5 °C as usual, indicating no effect of configuration of monomers on curing temperature. The curing enthalpies were in the range of 99-105 J g \(^{-1}\). These comparable values showed that the structural changes within the backbone of monomer have no considerable effect on the cross-linking.
The curing of the monomers 3a, 3b and 3c were analyzed by DSC up to 400 °C as displayed in the Figure 4.3 (d). The melting transition occurred around 88.0 °C, 181.0 °C and 239.0 °C for monomers 3a, 3b and 3c respectively. These differences in melting points reflect that melting transition is strongly related to the structure of monomers as mentioned above. The heat absorbed during melting of monomer 3a, 3b and 3c is 5.36 J g⁻¹, 163.20 J g⁻¹ and 130.82 J g⁻¹, respectively, which was higher than the heat for their imide-based phthalonitrile. These higher melting enthalpies indicated that these monomers were more crystalline than their imide counterparts due to intermolecular hydrogen bonding. On the other hand, the rather low melting enthalpy of monomer 3a compared to monomers 3b and 3c is due to the fact that its structure does not allow for the same levels of intermolecular interaction. Curing peaks were observed at 318.6 °C, 252.9 °C and 308.6 °C for monomers 3a, 3b and 3c respectively. These variations indicated the effect of different monomer linkages. The curing enthalpies were 170.65 J g⁻¹, 221.54 J g⁻¹ and 90.42 J g⁻¹ for monomers 3a, 3b and 3c respectively. This variation in enthalpy of monomers shows significant effect of the linkages on the structure of monomer.

4.6.2 Rheometric Analysis

Processability is the main feature keeping in mind during polymer formation. Several approaches have been made for enhancing the processing of thermosets which include the formation of oligomers and the introduction of flexible chain like ether etc, in the monomer back bone. Keeping this idea in mind and some other similar studies, it was found that processability can be improved by low melting monomers or oligmers. In
order to achieve this goal some structural changes were made in the monomer backbone to reduce its linearity, chain to chain interaction and chain packing. Therefore, flexible ether linkages along with other groups were incorporated into the monomer backbones that interconnected the amino group on one end, which act as an auto-catalyst and terminal phthalonitrile units on the other end.

Rheometric studies during polymerization were carried out at 270°C on prepolymer made with 5 mol % p-BAPS as a function of time. Bis[4-(4-aminophenoxy)phenyl]-sulfone (p-BAPS) was selected because of its high stability and low reactivity in order to have high processing window. Processing window is the temperature difference between the melting point and the curing temperature. Typical complex viscosity ($\eta^*$) vs time plots for prepolymer are presented in Figure 4.4 (a). The results revealed that 1e has higher tendency to cure than 1d, and in turn higher than 1f. This order related to the fact that the monomer 1d with bulky size have slower polymerization rate than monomer 1e. There was no change in viscosity of monomer 1f, indicated no polymerization under the prevailing condition. This might be attributed to the large or rigid structure of monomer 1f. Since, the rheological behavior of a material is a key factor in determining its processability. Therefore, variation in the complex viscosity of monomer 1f blend was determined as a function of temperature at the rate of 4 °C /min. The results indicated that the melt viscosity of monomer 1f increases around 390 °C. This relatively low and stable melt viscosity of these monomers with 5 % of p-BAPS afforded sufficient processing window for the various composite structures by resin transfer molding (RTM), resin infusion molding and filament winding.
Rheometric study was also carried out to investigate the melt viscosity of the monomers 2o, 2m and 2p as a function of temperature. The viscosity of each monomer decreased sharply above its melting point and increased sharply at curing temperature as shown in Figure 4.4 (b). The phenomenon was coincided generally with the non-isothermal DSC. It was found that all the three monomers maintained very low viscosity (<1 Pa.s) in the range of temperature between the melting point and the curing temperature, which is highly suitable for resin transfer molding or resin infusion molding, etc. It was noticed that 2o had the widest “processing window” (>120 °C) and 2m had the narrowest. This is due to low melting temperature and high curing temperature of 2o as explained above under DSC analysis.

![Figure 4.5: Complex viscosity (η*) of monomers 4o–4p(c) and 3a–3c(d)](image)

The melt viscosity changes of monomers 4o, 4m and 4p, accompanying the curing reactions as a function of temperature, were also monitored by rheometric studies. Viscosity measurements were recorded as a function of temperature for the polymerization of all the three monomers as shown in Figure 4.5 (c). The viscosity of 4o first decreased and then remained constant from 135 °C to 235 °C. Above 235 °C, the viscosity increased abruptly as the curing reaction progressed. The viscosity of 4m remained constant in the range of 205 °C to 245 °C and then suddenly increased above 245 °C. However, the viscosity of 4p increased suddenly after melting. The relatively low viscosity of all the monomers at moderate temperatures and relatively high processing window of 4o is one of the key features that advantageously affect their processing to thermosets. The relatively high processing window of 4o is due to its low melting temperature as explained above.
The rheometric analysis of monomers 3a, 3b and 3c were performed during polymerization, as a function of temperature as shown in Figure 4.5 (d). These measurements were made from 75 °C to 375°C. It was found that the viscosity of each monomer decreased sharply above its melting point and increased suddenly close to the curing temperature. The phenomenon coincided generally with the DSC analysis. It was found that all the three monomers maintained very low viscosity in the processing window between the melting point and the initiation of polymerization. The results showed a reasonable processing window (ΔT ~ 50–200 °C depending on the monomer) between melting point and curing temperature. Their low melt viscosity and large processing window make them suitable candidates for resin transfer molding or resin infusion molding, among other liquid composite processing technologies. It was noticed that 3a had the widest processing window (~ 200 °C) and 3b had the narrowest window. This is due to lower melting temperature and high curing temperature of 3a as explained above under DSC analysis.

4.6.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed to find the thermal stability of the post cured monomers up to 900 °C. They were carried out both in nitrogen and air atmospheres. The thermal stability, as usual, expressed as 5 % weight loss temperature (T5%) as shown in Table 4.14. The thermal stability and residual mass given by TGA are very helpful in finding their uses.

The thermal stability of thermosetting phthalonitrile polymers P1d, P1e, and P1f both under nitrogen and air atmospheres are indicated in the Figure 4.6 (a) and Table 1.14. It has been noted that the polymers containing ortho-linked units are relatively unstable to thermal decomposition. Therefore, it is of great interest to know the influence of incorporating the ether linkage into ortho-linked structures that otherwise is well-known for their thermal stability. The results indicated that each polymer showed different behavior due to different size and structure of the precursors. For the polymers P1d, P1e, and P1f, 5 % weight loss temperature (T5%) were 444.0 °C, 489.6 °C and 511.8 °C under nitrogen atmosphere, respectively. The char yield in the range of 64.4–67.9 %, at 900 °C, under nitrogen atmosphere. Additionally, heating in air showed 5 % weight loss temperature at 436.5 °C, 488.0 °C, and 500.0 °C, respectively, with sudden decomposition occurring between 600–800 °C. The higher thermal stability of the P1f is due to the presence of oxadiazole ring as shown by comparing the 5 % weight loss
The introduction of the oxadiazole ring is very effective in improving thermal stability. This would be the contribution of polarity and rigidity of oxadiazole ring. The higher thermal stability of the polymer P1e in comparison to P1d is due to smaller size of the monomer of the former, which in turn formed more highly crosslinked networks due to higher density of cyano groups. The high char yield of the polymer P1e and P1f in comparison to P1d is due to higher crosslink density. This high char yield (64.4–67.9 %) is the indication of high fire-resistance materials.

**Table 4.14: TGA data of the polymers**

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>TGA(°C)</th>
<th>% Char yield (N₂) (900°C)</th>
<th>Polymer code</th>
<th>TGA(°C)</th>
<th>% Char yield (N₂) (900°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1d</td>
<td>444.0</td>
<td>436.5</td>
<td>P4o</td>
<td>528.8</td>
<td>520.0</td>
</tr>
<tr>
<td>P1e</td>
<td>489.6</td>
<td>488.0</td>
<td>P4m</td>
<td>525.4</td>
<td>513.7</td>
</tr>
<tr>
<td>P1f</td>
<td>511.8</td>
<td>500.0</td>
<td>P4p</td>
<td>527.5</td>
<td>513.7</td>
</tr>
<tr>
<td>P2o</td>
<td>527.0</td>
<td>505.0</td>
<td>P3a</td>
<td>517.1</td>
<td>496.0</td>
</tr>
<tr>
<td>P2m</td>
<td>524.0</td>
<td>512.0</td>
<td>P3b</td>
<td>506.1</td>
<td>500.7</td>
</tr>
<tr>
<td>P2p</td>
<td>528.0</td>
<td>518.0</td>
<td>P3c</td>
<td>531.0</td>
<td>501.8</td>
</tr>
</tbody>
</table>

The TGA data for polymer P2o, P2m and P2p under nitrogen and air atmospheres are shown in Figure 4.6 (b) and Table 4.14. The 5% weight loss temperatures under nitrogen and air were in the ranges 524–528 °C and 505–518 °C respectively, indicating high thermal and thermo-oxidative stability compared to polymer P1d to P1f. In addition, it was found that the char yields ranged from 72–74 % at 900 °C under nitrogen, showed high crosslink networks. These results revealed that the introduction of amino group, which acting as an internal catalyst, enhanced extent of curing due to high amino concentration.
The TGA of the polymers P4o, P4m, and P4p were performed both under nitrogen and air atmospheres between 25 °C to 900 °C as shown in Figure 4.7 (c). The results of these analyses indicated that the polymers P4o, P4m, and P4p retained 95 weight % in the ranges of 525.5–529 °C and 514–520 °C under flowing nitrogen and air respectively. They showed char yields ranged from 62.5–70 % at 900 °C under nitrogen atmosphere. Thermal stability of these polymers was comparable to the polymers derived from monomers 2o–p, despite the differences in skeleton structures. However the char yields of these polymers (62.5-70 %) were less in comparison to the polymers (72–74 %) obtained from smaller monomers due to higher average molecular mass, which has inverse relation with crosslink density, between the interacting groups.
The TGA of the polymers P3a, P3b, and P3c were performed both under nitrogen and air atmospheres between 25 to 900 °C as shown in Figure 4.7 (d) and Table 4.14. The results of these studies indicated that the polymers P3a, P3b, and P3c had 5 % weight loss temperatures the ranging from 506–531 °C in nitrogen atmosphere and from 496–502 °C in air, respectively. They showed char yields ranging from 66–75 % at 900 °C under nitrogen atmosphere. Thermal stability of these polymers was lower than the polymers P4o–P4p, due to the differences in molecular structures. These polymers have amide group, which are comparatively less stable than imide groups in their imide analogues. However the char yields of these polymers (66–75 %) were higher than the polymers (62.5–70 %) obtained from monomers 4o–p due to lower average molecular mass between the crosslinking groups.

4.6.4 Dynamic Mechanical Analysis (DMA)

Rheometric studies were carried out to find the effect of variation in structure and different temperature treatment on the dynamic mechanical properties of the phthalonitrile polymers. Here we present the storage moduli (E’) and damping factors (tan δ) from 25 °C to around 500 °C. Glass transition temperature (Tg) was considered the peak of tan δ, because of ease in measurement.

![Figure 4.8: Storage moduli and damping factors of polymers P1d (a) & P1e (b)](image)

The DMA studies of the polymers P1d, P1e, and P1f, cured with 5 mol% of p-BAPS to a maximum temperature of 375 °C for 5 h, were evaluated up to 500 °C to estimate storage moduli and the glass transition temperatures as shown in Figure 4.8 (a,b), Figure 4.9 (a) and Table 4.15. The polymer P1f was additionally cured at 400°C for 5 h, due to its large size, for complete curing29. The measurements showed different dynamic mechanical properties of the polymers depending on different chemical structure under
same and different condition of temperature treatment. The polymers P1d, P1e, and P1f, showed storage moduli around 4200, 1800 and 2000 MPa at 40 °C respectively. The high storage modulus for polymer P1d is probably due to higher crosslink density and rigid structure. The storage moduli of P1e and P1f were comparable; even they have different structures and different heat treatments, due to smaller size of polymer P1e precursor and rigid structure of polymer P1f precursors. The polymer P1e and P1f showed a drop in the storage moduli with the increase of temperature up to 500 °C to around 20–40% of their initial values. This decrease in modulus attributed to the molecular relaxation and removal of internal stresses in the polymer network. The damping factor of polymer P1d exhibited a maximum after fall of storage moduli at 350 °C and then decreased continuously with increasing temperature due to increase in segmental motion of the polymer while changing from glassy to rubbery state. The broadness of the tan δ curve is due to wide distribution of molecular weights or due to unequal distribution of cross-links or due to formation of various polymeric structures. In case of polymer P1e there was no distinct transition, even with the gradual decrease of storage modulus, indicating high degree of curing. On the other hand for the polymer P1f heated up to 400 °C, both storage modulus and tan δ curve were remained almost flat with the increase of temperature. This behavior is a result of rigid back bone and high crosslink density at elevated temperature, which hindered the segmental motion of the polymer chains.

Figure 4.9: Storage moduli and damping factors of polymers P1f(a) and P2o–P2p(b)
The DMA data of the polymers \( P_{2o}, P_{2m} \) and \( P_{2p} \) is shown in Figure 4.9 (b) and Table 4.15. The different dynamic mechanical behavior of the polymers depends upon different chemical structure under same condition of temperature treatment. The polymers \( P_{2o}, P_{2m} \) and \( P_{2p} \), displayed storage moduli of 1040, 835 and 980 MPa at 40°C respectively. The high moduli observed for \( P_{2o} \) and \( P_{2p} \) compared to \( P_{2m} \), as a result of their higher crosslinking densities. The storage moduli of the aforementioned polymers decrease slowly with the increase of temperature up to 560 °C to around 30% of their initial values due to releasing stresses in the polymer networks. The starting temperature of the decreasing of storage modulus for all the three polymeric materials was about only 10 °C lesser than the decomposing temperature of the cured monomers. The damping factor of each polymer exhibited a maximum after fall of storage modulus around 560 °C and then decreased continuously with increasing temperature due to change from glassy to rubbery state. This behavior indicated that all these self-catalyzed polymers showed dynamic mechanical properties of a glassy state up to 560 °C. This characteristic behavior made them suitable candidate for the usage as high temperature polymeric materials.

### Table 4.15: DMA data of the polymers cured at 375 °C

<table>
<thead>
<tr>
<th>Polymer Code</th>
<th>( E' ) (MPa) rt.</th>
<th>( T_g ) (°C)</th>
<th>Polymer Code</th>
<th>( E' ) (MPa) rt.</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1d</td>
<td>4200</td>
<td>350</td>
<td>P4o(^a)</td>
<td>1450</td>
<td>465</td>
</tr>
<tr>
<td>P1e</td>
<td>1800</td>
<td>&gt;500</td>
<td>P4m(^a)</td>
<td>1500</td>
<td>435</td>
</tr>
<tr>
<td>P1f(^b)</td>
<td>2000</td>
<td>&quot;</td>
<td>P4p(^a)</td>
<td>1975</td>
<td>465</td>
</tr>
<tr>
<td>P2o</td>
<td>1040</td>
<td>&quot;</td>
<td>P4o</td>
<td>1450</td>
<td>&gt;500</td>
</tr>
<tr>
<td>P2m</td>
<td>835</td>
<td>&quot;</td>
<td>P4m</td>
<td>1575</td>
<td>&quot;</td>
</tr>
<tr>
<td>P2p</td>
<td>980</td>
<td>&quot;</td>
<td>P4m</td>
<td>1575</td>
<td>&quot;</td>
</tr>
<tr>
<td>P3a</td>
<td>2150</td>
<td>&quot;</td>
<td>P4p</td>
<td>2700</td>
<td>&quot;</td>
</tr>
<tr>
<td>P3b</td>
<td>2070</td>
<td>&quot;</td>
<td>P4p</td>
<td>2700</td>
<td>&quot;</td>
</tr>
<tr>
<td>P3c</td>
<td>1950</td>
<td>&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Cured at 350(°C) \(^b\) Cured at 400(°C)
The rheometric measurements provided by DMA for the polymers P4o, P4m, and P4p were very helpful to find the effect of isomeric changes and temperature as shown in Figure 4.10 (a,b), Figure 4.11 (a) and Table 4.15. The polymers P4o, P4m, and P4p cured up to 350 °C, displayed storage moduli ranging from 1450-2000 MPa at 25 °C. The higher moduli observed for P4p compared to others is a result of higher crosslink density. The storage moduli of the aforementioned polymers increased with the increase of curing temperature up to 375 °C due to enhancing cross-linking. However, there was no any increase in storage modulus of P4o, indicating the completion of cross-linking before the last round. The storage moduli of these polymers are comparatively higher than aminophenoxy phthalonitrile based polymers due to rigid polymer backbone having imide group. Damping factor of each polymer cured up to 350 °C exhibited a maximum after fall of storage modulus around 450°C and then decreased continuously with increasing temperature due to change from glassy to rubbery state. However, upon heating to 375 °C, the tan δ curves remained flat approximately up to 500 °C, due to high crosslink density. This behavior indicated that these polymers remained in glassy state up to 500 °C.

Figure 4.10: Storage moduli and damping factors of polymers P4o(a) and P4m(b)

Figure 4.11: Storage moduli and damping factors of polymers P4p(a) and P3a–P3b(b)
The rheometric measurements were carried out to find only the effect of structural change on dynamic mechanical properties of P3a, P3b, and P3c as shown in Figure 4.11 (b) and Table 4.15. The polymers P3a, P3b, and P3c cured up to 375 °C, showed storage moduli ranged at 2150, 2070 and 1950 MPa respectively, at 25 °C. The higher moduli observed for P3a is probably of higher crosslink density. The storage moduli of the aforementioned polymers decrease with the increase of measuring temperature in order to release internal stresses within the polymer network. The storage moduli of P3a and especially P3c almost remain flat with increase of temperature, due to high cross-linking. However, there was a steady decrease in storage modulus of P3b, indicating more stresses within the polymer. The storage moduli of these polymers are comparatively higher than aminophenoxy phthalonitrile based polymers and their imide analogue except P4p, due to high cross link density. The damping factor (tan δ) of each polymer cured up to 375 °C, remained flat approximately up to 500 °C, due to high cross link density. This behavior indicated that these polymers remained in glassy state up to 500 °C.

4.7 Conclusions

Phthalonitrile resins were prepared from two kinds of monomers; one having the self-catalyzing amino groups and the other has ortho-linked ether linkage without any catalyzing group in the molecular structure. The properties of these monomers and the polymers prepared from them were studied and the following conclusions were drawn:

1. The thermal stability and char yield of the polymers obtained from self-catalyzed monomers is higher than the polymers obtained from diol-based phthalonitrile monomers.

2. Among the polymers obtained from diol-based monomers, the 5 % weight loss temperature of the polymer obtained from the monomer having oxadizole ring is higher, both under nitrogen and air.

3. The char yield of the polymers obtained from self-catalyzed monomers is higher for the polymers obtained from the monomers having only ether linkages.

4. The char yield of the polymers obtained from self-catalyzed monomers having imide-ether or amide-ether linkages is approximately the same.
5. The processing window of the diol-based monomers increases with the increase in size of the monomer. In case of self-catalyzed monomers, the monomers having amino group at ortho position or ortho-linkages have broad processing window comparatively.

6. The storage moduli and glass transition temperature ($T_g$) increase with the curing temperature and curing time.

7. Among the polymers obtained from diol-based monomers, the polymers synthesized from the catechol or oxadiazole based monomers have higher storage moduli and glass transition temperature than the polymer obtained from biphenyl based monomer.

8. Among the polymers obtained from self-catalyzed monomers, the polymers having imide-ether or amide-ether linkages have higher moduli than the polymer having only ether linkages.


