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# Development of Oligomeric Phthalonitrile Resins for Advanced Composite Applications

*Palaniappan Selvakumar, Muthusamy Sarojadevi**

**Summary:** Phthalonitrile endcapped oligomers containing aromatic ether and imide linkages have been synthesized and characterized. The phthalonitrile terminated oligomers were prepared in two step (one spot) method by the reaction of an excess amount of pyromellitc dianhydride (PMDA) with aromatic diamines, in a *N,N*-dimethylacetamide (DMAc)/toluene solvent mixture to form anhydride terminated oligomeric intermediate that was terminated by the reaction with 4-(aminophenoxy) phthaloitrile. The average molecular weights of the prepared oligomers were determined by GPC analysis. The oligomeric phthalonitrile monomers have been converted to network polymers using 4,4'-diaminodiphenyl sulfone (DDS) (5.0 wt %) curing additive at elevated temperatures. Differential scanning calorimetric (DSC) analysis was used to follow the polymerization as the oligomeric phthalonitrile/diamine mixtures and prepolymers. An isothermal rheometric analysis was conducted to determine the complex viscosity of the prepolymers during polymerization reaction. Viscosity increases as a function of time due to crosslinking, which depends upon the concentration and reactivity of the curing agent. The TGA analysis of cured resins showed superior thermal and thermo-oxidative stability. The temperature of 10% weight loss from TGA are in the range of 498-511 °C in $N_2$ and 448–461 °C in air atmosphere. Char yield at 800 °C is 41.7–50.2% in air and 70.6–83.1% in $N_2$.

**Keywords:** high temperature materials; phthalonitrile oligomers; polymerisation; thermal properties; thermosets

## Introduction

Polymeric materials with good mechanical and thermo-oxidative properties along with relative ease of processability are in high demand for use as advanced composite applications. It is well known that in order for network materials to retain high thermal stability it is necessary for these materials to have high levels of aromatic and heterocyclic ring structure within the network. Such systems allow for good mechanical properties and thermo-oxidative stability simultaneously. Full usage of such polymers has been limited by their brittleness and intractability. The downside with incorporating such characteristics within the network has been brittleness.[1–3] Structural modifications such as the incorporation of flexible linkages into the polymeric backbone are necessary to enhance processability without sacrificing thermal stability and mechanical properties.[4,5] For advanced composite applications, it is essential to have resin systems that have low melting point, low viscosity for fabrication of composite materials and large processing window. In addition, the composite industry requires matrix materials that may be easily processed via commercial fabrication process such as filament winding, pultrusion and resin transfer moulding (RTM).[2]

Phthalonitrile polymers belong to an important class of high performance thermosetting materials, having superior properties like formation of void free composites, high

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Department of Chemistry, Anna University, Chennai-600 025, India
Fax: 91 44 22200660;
E-mail: msrde2000@yahoo.com

glass transition temperatures ($T_g$), very low moisture absorption and thermal resistance.[6] These polymers contain a substantial proportion of aromatic structures which leads to high mechanical strength, high modulus and dimensional stability. These resins have wide range of potential applications such as composite matrices, adhesives, solar panels and electrical conductors.[3,4] Keller et al have developed various structural modifications such as aromatic ether, thioether, sulphone and imide linkages between terminal phthalonitrile functional units. The polymerization of these monomers has been investigated using a variety of curing additives. Polymerization of the phthalonitrile resin takes place in two steps through the terminal cyano groups *via* an addition mechanism. The first step involves addition of the diamine curing agent to the monomer in the melt phase to initiate the polymerization and quenched to room temperature. This quenched amorphous solid product is called B-stage resin or prepolymer which can be kept indefinitely at ambient temperatures. In the second step, prepolymer product is heated at elevated temperature for an extended period of time.[5–7] The Polymerization can be easily controlled by the concentration of the curing additive and the cure temperature.

In phthalonitrile oligomers the linking group between the two ortho dinitrile groups separates the dinitrile groups enough to permit polymerization. They are bis(o-dicyanophenyl) compounds that can be cross-linked thermally by the formation of triazine ring structure to produce void free thermosets with high cross-linking density. The main route of the development of high temperature polymers is the incorporation of thermally stable structural units such as aromatic or heteroaromatic rings within the network of the polymeric system.[8–10] Through the design of a polymeric system with these highly stable structural units and with flexible linkages, the desired thermo-oxidative stability can be achieved with processability. No volatiles are generated from this reaction and the aromatic diamine curing agents are usually compatible with the monomers. The time and temperature needed for polymerization can be reduced by curing the phthalonitrile monomers in the presence of aromatic diamine curing agents.[11–15] The trimerisation of nitrile groups leading to the formation of triazine rings takes place only at high temperatures.

Phthalonitrile networks are tough materials with excellent thermo-oxidative stability. However, extensive curing times and temperatures are needed to achieve these properties. In addition, the processability of these resins is limited as the rigidity of the phthalonitrile monomers increases. Research efforts are needed to improve the processability of phthalonitrile resins system, by significantly decreasing the temperature and time necessary to achieve networks with high properties.[16–20]

It is therefore proposed to synthesize phthalonitrile endcapped oligomers with variable aromatic ether and imide linkages having different molecular weights by using aromatic dianhydride and diamines with the endcapping reagent 4-(aminophenoxy) phthalonitrile and subsequently cure into thermally stable and void free polymer system for advanced composite applications.

## Experimental Part

### Materials

4-nitrophthalonitrile was synthesized according to the procedure given in a previous study.[11] *N*-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and toluene were purchased from SRL, India. These solvents were purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves. Phthalimide, p-aminophenol, 4,4′-diaminodiphenylsulphone and anhydrous potassium carbonate were used as received from E-Merck, India. 4-chloronitrobenzene, 10% palladium on activated charcoal, 2,2′-bis(4-hydroxyphenyl)propone (bisphenol-A) and 1,5-dihydroxynaphthalene were purchased from Lancaster, India. Thionylchloride and hydrazine monohydrate were purchased from Fischer, India, and used without further purification.

### Measurements

Fourier Transform Infra Red (FT-IR) spectra were recorded on a Perkin Elmer RX-1 spectrometer using KBr disk at a scanning range from 4000 to 400 cm$^{-1}$. $^1$H-NMR and $^{13}$C-NMR spectra were obtained on a Joel Ex-400 spectrometer (400MHz) using $CDCl_3$ and DMSO-$d_6$ as solvents and the chemical shifts were calibrated by using 1% TMS as reference. Elemental analysis was carried out with a Perkin Elmer model 2400. Gel permeation chromatographic studies were carried out in Polymer Laboratories PL-GPC 50 integrated GPC system with a well chrom-K 2301 refractive index detector. 5μm PL gel mixed-C column and *N,N*-dimethylformamide (DMF) as the eluent for the oligomers were used. A TA Instruments AR-2000 Rheometer, in conjunction with an environmental testing chamber for temperature control, was used to monitor changes in the viscosity of phthalonitrile prepolymer melts in air at various temperatures. The viscosity measurement was used to determine the optimum level of curing additive concentration and processing temperature. DSC analysis was performed on a $Q_{10}$ series TA instruments Differential scanning calorimeter using 3 mg of the sample crimped in aluminium pans at a heating rate of 10 °C/min and a flow rate of 40ml/min. Thermo gravimetric analysis data were obtained on a $Q_{100}$ series TA instruments in flowing Nitrogen/air at a heating rate of 20 °C/min.

#### *4-nitrophthalonitrile*

This compound was synthesized and purified according to the procedure reported by J.G. Young et al; [21] m.p. 140–142 °C (Lit. m.p. 141 °C); IR. (KBr) shows absorptions at 2235 cm$^{-1}$ (C≡N), 1530 and 1295 cm$^{-1}$ (asymmetric and symmetric stretching vibrations of N=O). $^1$H NMR (400MHz, DMSO-$d_6$) $\delta$ (ppm) = 9.02 (s, 1H), 8.67 (d, 1H), 8.42 (d, 1H).

Elemental analysis for $C_8H_3N_3O_2$: calculated: C, 55.59%; H, 1.73%; N, 24.2%; Found: C, 56.08%; H, 1.92%; N, 23.01%.

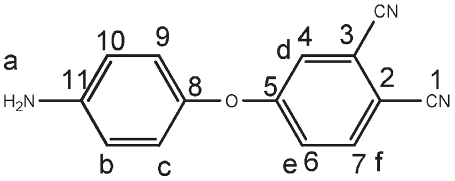
#### *Synthesis of Diamines*

The diamine compounds 1,5-bis(4-aminophenoxy)naphthalene and 2,2′-[bis(4-aminophenoxyphenyl)propane] were synthesized and purified according to the procedure reported by Tsu-Shang Leu et al.[22] The structures of the prepared compounds were confirmed by spectral analysis.

#### *Synthesis of 4-(aminophenoxy) phthalonitrile (APPH)*

This compound was synthesized by the nucleophilic nitro displacement reaction.[23,24] 4-aminophenol (5.4g; 0.05mol), potassium carbonate (6.9g; .05mol) and 4-nitrophthalonitrile (8.65g; 0.05mol) were taken in a single necked RB flask. Approximately 55 ml of dry DMF was added to the solution while stirring. The solution was allowed to react for 24 hours at room temperature under nitrogen atmosphere. The 4-(aminophenoxy)phthalonitrile was precipitated by adding the solution to ice cold water forming a dark brown colored precipitate. The solid product was collected by vacuum filtration, allowed to air-dry overnight; yield 11.9 g (88%). The FT-IR spectrum (KBr) shows absorptions at 3340 (–NH), 2233 (C≡N), 1250 & 1070 cm$^{-1}$ (C–O–C). $^1$H NMR (400MHz, DMSO-$d_6$) $\delta$ (ppm) = 5.23 (s, 1H), 6.78 (d, 2H), 6.85 (d, 2H), 7.37 (d, 1H), 7.71 (s, 1H), 8.12 (d, 1H). $^{13}$C NMR (400MHz, DMSO-$d_6$) $\delta$ (ppm) = $C_1$- 115.8, $C_2$- 109.0, $C_3$- 115.6, $C_4$- 121.8, $C_5$- 162.0, $C_6$- 122.5, $C_7$- 132.6, $C_8$- 147.0, $C_9$- 118.3, $C_{10}$- 116.0, $C_{11}$- 141.5.

Elemental analysis: Calculated: C, 71%; H, 3.82%; N, 17.8%; Found: C, 69.80%; H, 4.15%; N, 16.93%.



### *Synthesis of Phthalonitrile Endcapped Oligomers (PEO)(Ia)*

To a 500 ml RB flask equipped with a Dean-stark trap and a condenser was added pyromellitic dianhydride (6.54g, 0.03mol) and 40 ml of dry (*N,N*-dimethylformamide) DMF. After flushing the solution with nitrogen for 20 minutes, 1,5-bis(4-aminophenoxy)naphthalene (6.8g, 0.02 mol) was added in one portion and the reaction temperature was increased to 45 °C. The resulting solution was stirred for 1 hour under ambient conditions. The temperature of the reaction mixture was increased to 90 °C and held at this temperature for 2 hours. The reaction mixture was cooled to room temperature and 4-(aminophenoxy) phthalonitrile (8.4g, 0.03 mol) was added in one portion. The reaction medium was stirred under ambient conditions for 1 hour and at 90 °C for 2 hours. At this time, toluene (25 ml) was added to the reaction mixture. The reaction content was heated to reflux for about 16 hours. During the reaction, water that was formed as a by-product was removed by azeotropic method using Dean-starck trap.[25] After removing the toluene by distillation and cooling, the mixture was poured into 200 ml of absolute ethanol. The product was collected by filtration and dried; yield 15.8g (82%). The similar procedure with different stoichiometric ratio was adopted for the preparation of oligomer Ib and Ic. FT-IR (KBr, $cm^{-1}$); 2230 ($C\equiv N$), 1778, 1725($C=O$), 1243 (C–O). $^1H$ NMR (400MHz, DMSO-$d_6$) $\delta$ (ppm) = 7.15–7.30 (m, aromatic), 7.35–7.65 (m, aromatic), 7.92–8.05 (m, aromatic), 8.15–8.40 (m, aromatic), 8.50–8.57 (m, aromatic)

### *Synthesis of Phthalonitrile Endcapped Oligomers (PEO) (IIa)*

The procedure adopted was similar to **Ia,** pyromellitic dianhydride (6.54g, 0.03 mol), 2,2′-[bis(4-aminophenoxyphenyl)propone] (8.2g, 0.02 mol) and 4-(aminophenoxy) phthalonitrile (8.4g, 0.03 mol) were reacted in toluene/ *N,N*-dimethylformamide (DMF) solvent mixture: yield 16.2 g (84%). FT-IR (KBr, $cm^{-1}$); 2233 ($C\equiv N$), 1776, 1728 ($C=O$), 1245 (C–O). $^1H$ NMR (400MHz, DMSO-$d_6$) $\delta$ (ppm) = 1.94–1.99 (m, $CH_3$), 7.05–7.28 (m, aromatic), 7.34–7.58 (m, aromatic), 7.88–8.03 (m, aromatic), 8.39–8.62 (m, aromatic). The similar procedure with different stoichiometric ratio was adopted for the preparation of oligomer IIb and IIc.

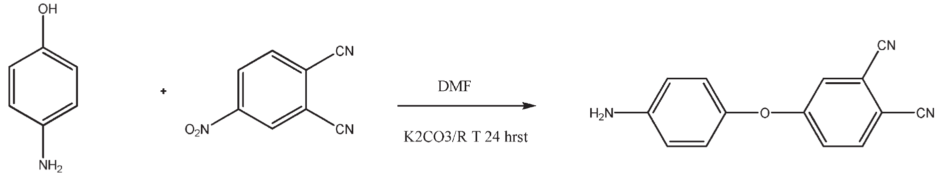
### *Synthesis of Prepolymers (B-stage Resin)*

A typical prepolymer synthesis was accomplished by weighing 50 g of the phthalonitrile endcapped oligomer Ia in a 100 ml reaction kettle, then placing on a preheated hot plate at 255 °C and heating until homogeneity occurred. The curing agent (DDS) was added, stirred for 15 min in air and quenched the prepolymer melt composition to room temperature.[2] This quenched product is called a B-staged resin or a prepolymer, which has the $T_g$ in the range of 155–165 °C and this amorphous solid is soluble in common organic solvents such as *N,N*-dimethylformamide(DMF), *N,N*-dimethylacetamide(DMAc), 1-methyl-2-pyrrolidone(NMP).[2,5] In addition, the prepared prepolymers can be stored under room temperature for infinite time and this technique is useful for making prepregs.

## Results and Discussion

### Synthesis of Phthalonitrile Endcapped Oligomers(PEO) (Ia–c & IIa–c)

As shown in Scheme 1, new phthalonitrile endcapped oligomers containing variable ether and imide linkages were prepared from the reaction of excess stoichiometric ratio of pyromellitic dianhydride (PMDA) and aromatic diamines, 1,5-bis(4-aminophenoxy)naphthalene, 2,2′-[bis(4-aminophenoxyphenyl)propane] to yield dianhydride terminated polyamic acid intermediate. This was followed by the reaction with end-capping agent 4-(-aminophenoxy) phthalonitrile to obtain phthalonitrile endcapped oligomers (PEO). This reaction was carried out in a toluene/DMF mixture, which permit the azeotropic distillation of the water formed as a by-product. Once no more water collection was observed, toluene was then removed by distillation and the product was precipitated in ethanol.



**Scheme 1.**
Synthesis of 4-(aminophenoxy) phthalonitrile (APH).

The FT-IR spectrum of representative oligomers Ia is given in Figure 1. The absorption around 2230 cm$^{-1}$ corresponds to nitrile (C≡N) group and two characteristic absorptions around1770 and 1725 cm$^{-1}$, attributed to the asymmetric and symmetric stretching vibrations of imide carbonyl (C–O) group. In addition bands were observed at 1370 (C–N stretch), 1102, and 716 cm$^{-1}$ (imide ring deformation). The $^{1}$H NMR spectrum (expanded) of phthalonitrile oligomer Ia in DMSO-$d_6$ is shown in Figure 2. All the proton signals are observed in broad range and multiplets. The proton signal ranges are 7.15–7.30 (m, aromatic), 7.35–7.65 (m, aromatic), 7.92–8.05 (m, aromatic), 8.15–8.40 (m, aromatic), and 7.50–8.57 (m, aromatic).[1] From the $^{1}$H NMR spectral data, the formation of oligomers which leads to the enhancement of molecular weight was confirmed.

### Gel Permeation Chromatography Analysis

Polymer Laboratories PL-GPC 50 integrated GPC system, equipped with a chrom-K 2301 refractive index (RI) detector, was used to measure the molecular weight for the oligomer samples. The 5μm PL gel mixed-C GPC column (4.6mm ×300mm length) was a Styragel HR 5E and 4E. The flow rate of eluent was 0.35 ml/min, and the injection volume was 50μl. The column temperature was usually controlled at 50 °C. Extra-pure DMF (HPLC grade, SRL, India) was used as a solvent and eluent after filtered through 0.2μm Teflon membranes. Molecular weights and polydispersity indexes were determined using narrow molecular weight polystyrene standards (polymer labs, UK) calibration. GPC average molecular weight and PI(polydispersity index) values of the oligomers (Ia–c & IIa–c) are summarized in Table 1.

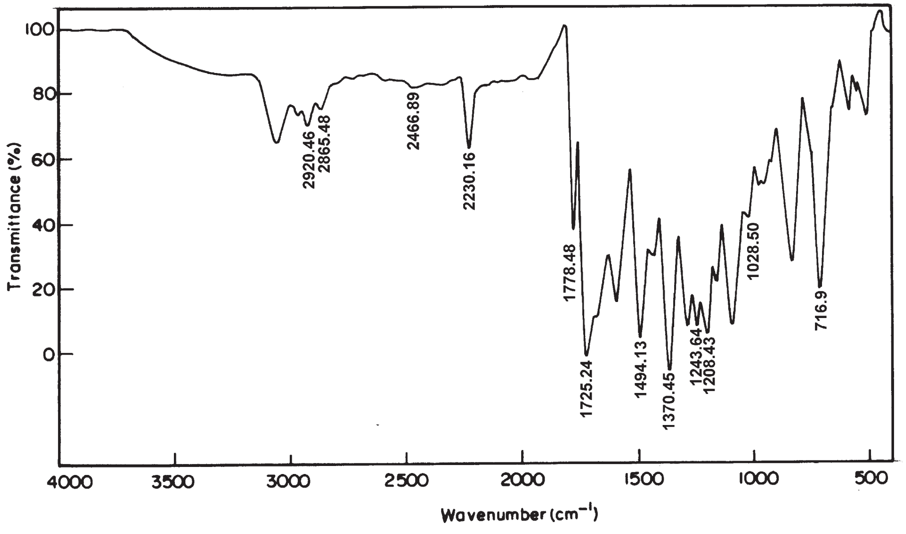


**Figure 1.**
FT-IR spectrum of phthalonitrile endcapped oligomer Ia.

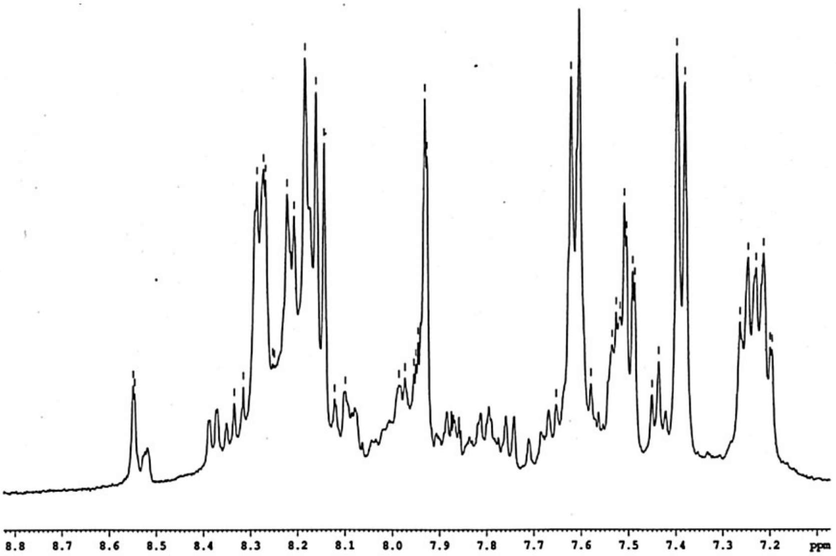


***Figure 2.***
$^1$H NMR spectrum of phthalonitrile encapped oligomer Ia.

As expected, the molecular weights distributions (MWD) of the new oligomers are dependent on the dianhydride/diamine molar ratio used: an increase of dianhydride ratio corresponds to the increment of molecular weight and decrease of molecular weight distribution. The molecular weights of the oligomers are in the range of 2480–4673 depending upon the ratio of diamine and dianhydride added.[16] The molecular weight distribution of the oligomers was analyzed using polymer labs cirrus GPC software.

## Cure Cycle Determination

### Rheometric Studies

Rheometric studies on phthalonitrile end-capped oligomer prepolymers were performed with three different concentrations of curing agent (4.0, 4.5 and 5.0 wt %) to monitor the melt viscosity during polymerization. An isothermal analysis at 290 °C was performed to determine the amine concentration needed for polymerization reaction. Viscosity increases as a function of time due to crosslinking, which depends upon the concentration and reactivity of the curing agent and molecular weight of the oligomers. During the crosslinking process, the nitrile groups react in the presence of diamine to form triazine ring structures.[5] A plot of viscosity change vs. time at 290 °C as a function of temperature for PEO prepolymer Ia containing 4.0 to 5.0% by weight of DDS is shown in Figure 3. It was observed that the viscosity increases more gradually over one hour for the prepolymers

***Table 1.***
GPC analysis results of oligomer Ia-c & IIa-c (relative to polystrene standards).

| S. No | Diamine/dianhydride ratio (mol) | Molecular weight (g mol$^{-1}$) | | | PI |
|---|---|---|---|---|---|
| | | Mn | Mw | Mp | |
| Ia | 1:1.5 | 2042 | 2480 | 4480 | 1.0905 |
| Ib | 1:2.0 | 3003 | 3818 | 5123 | 1.2854 |
| Ic | 1:2.5 | 3927 | 4560 | 5769 | 1.4654 |
| IIa | 1:1.5 | 2148 | 2530 | 4765 | 1.1081 |
| IIb | 1:2.0 | 3429 | 4012 | 5520 | 1.3034 |
| IIc | 1:2.5 | 4103 | 4973 | 6102 | 1.5072 |

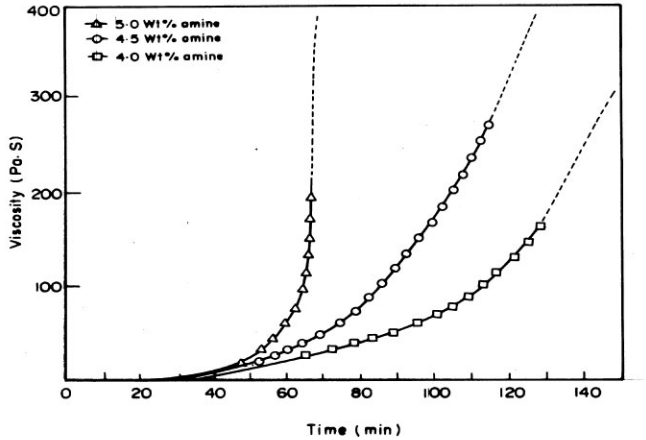


***Figure 3.***
complex viscosity of phthalonitrile encapped oligomer (Ia) at 290 °C.

containing the initial concentration of 4.0 and 4.5 wt % of amine. At a higher amine concentration (5.0 wt %) viscosity increases at a faster rate. Based on these observations, 5.0 wt % of amine content was considered as optimum level of curing agent concentration for polymerization.

### DSC Cure Studies of Oligomer/Diamine Mixture

The polymerizations of oligomers were studied by DSC analysis. The DSC cure thermogram of the oligomer Ia with 4.0 wt % diamine (DDS) mixtures is shown in Figure 4. The DSC scan exhibits a small endotherm around 178–180 °C and a large endotherm between 237–244 °C, corresponding to the diamine and monomer melting transitions, respectively.

A broad exotherm immediately after the melting peak was observed for all three oligomers (Ia–c & IIa–c). This exotherm corresponds to the reaction of the nitrile group of the oligomer in the presence of the aromatic diamine. The cure reaction was initiated at 272 °C and the exotherm completed at 312 °C. This oligomer/diamine crude mixture exhibits very low processing window (~28 °C) defined as the difference between the melting point

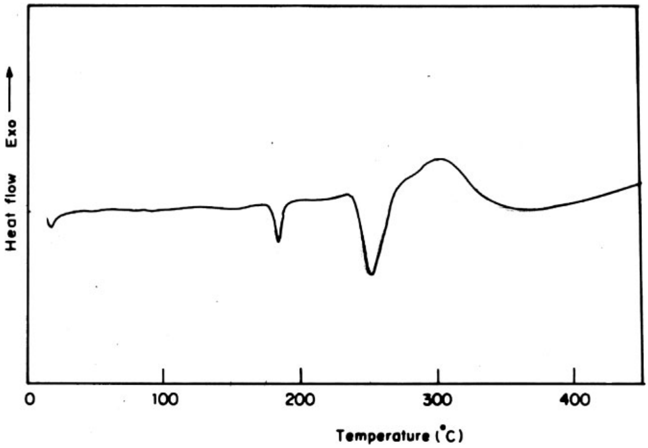


***Figure 4.***
DSC cure curve of oligomer Ia/5wt% diamine (DDS) mixture.

and the curing temperature. Processability is somewhat difficult because of a very short processing window.

### DSC cure Studies of Oligomeric Prepolymers

Initially the oligomers Ia-c were heated at 260–265 °C and degassed under reduced pressure to remove residual solvent. The temperature was reduced to 240 °C and 5.0 wt % of diamine (DDS) was added with stirring in air atmosphere. After homogeneity occurred the prepolymer melt composition (B-stage resin) was quenched to room temperature. The DSC cure thermogram of the oligomer prepolymers (Ia-c) is shown in Figure 5. The prepolymers exhibit a melting transition around 168–176 °C and the exotherm around 274–307 °C corresponds to the crosslinking reaction. This observation showed that the processing window increased ($\sim$28 °C $\rightarrow$ $\sim$100 °C) by the formation of prepolymers.

From the rheometric and DSC analysis results, a new cure cycle has been developed for the polymerization of phthalonitrile endcapped oligomers. The samples had been cured by oven in air atmosphere at 260 °C for 5 h, 280 °C for 5 h, 325 °C for 10 h and post-cured at 325 °C for 5 h and 380 °C for 10 h, respectively. The FT IR spectrum shows decreasing intensity of the nitrile absorption and increasing intensity of absorptions due to triazine ring at 1530 and 1365 cm$^{-1}$, confirming the formation of crosslinked network bonds through the formation of triazine rings.

### Thermal and Oxidative Properties

The thermal and oxidative properties of Ia–c & IIa–c were evaluated between 30–800 °C in TGA chamber at a heating rate of 20 °C/ min under nitrogen/air atmosphere. The results of thermal analysis for all investigated oligomers are summarized in Table 2. Figure 6 shows the thermal stability of Ia–c in nitrogen atmosphere. All the three oligomers show good thermal stability upto 450 °C and begin to lose weight at higher temperatures and 70.6–83.1% of char yield remaining at 800 °C. The temperature at 10% weight loss is in the range of 498–511 °C. As the temperature exposure of Ia was increased for additional 10 h at 380 °C, an improvement in the thermal stability was observed (curves'd'). Therefore, the polymeric stability was found to be dependant on cure cycle and post cure temperatures.[26–30]

Figure 7 shows the thermo-oxidative stability of Ia–c in air atmosphere. All the three oligomers did not exhibit obvious weight loss before the scanning temperature reached 430 °C in air atmosphere, indicating that no thermal decomposition occurred. The temperature at 10% weight

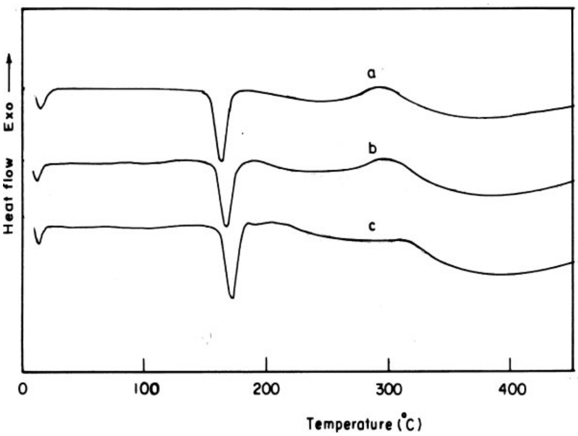


***Figure 5.***
DSC cure curves of phthalonitrile prepolymers Ia–c.

***Table 2.***
Thermal properties of oligomers Ia–c and IIa–c.

| S. No | DSC cure temp (°C) | | | TGA | | | |
|---|---|---|---|---|---|---|---|
| | Initial | Peak | Final | $T_{10}$ (%) wt loss in °C | | Char yield (%) | |
| | | | | Air | $N_2$ | Air | $N_2$ |
| Ia | 269 | 282 | 308 | 448 | 498 | 44.2 | 74.5 |
| Ib | 273 | 289 | 317 | 456 | 504 | 47.4 | 80.0 |
| Ic | 278 | 294 | 329 | 461 | 511 | 50.2 | 83.1 |
| IIa | 264 | 278 | 302 | 443 | 492 | 41.7 | 70.6 |
| IIb | 269 | 282 | 314 | 452 | 501 | 45.3 | 75.4 |
| IIc | 276 | 298 | 330 | 459 | 509 | 49.1 | 81.3 |

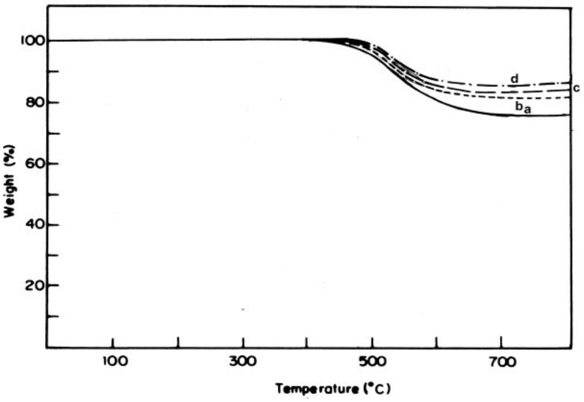


***Figure 6.***
TGA thermogram of phthalonitrile polymers Ia-c in $N_2$ atmosphere: 10 hrs additional postcured at 380 °C (curve'd').

loss was in the range of 448–461 °C. In addition on further heating to 800 °C, the residual weight retentions were found to be 44.2–46.7%, implying that these oligomers possess good oxidative stability. When the post cure temperature of Ia was increased from 325 to 380 °C for additional 10 h, the onset degradation temperature increased

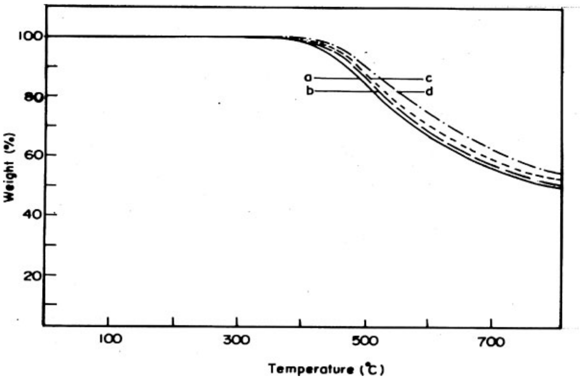
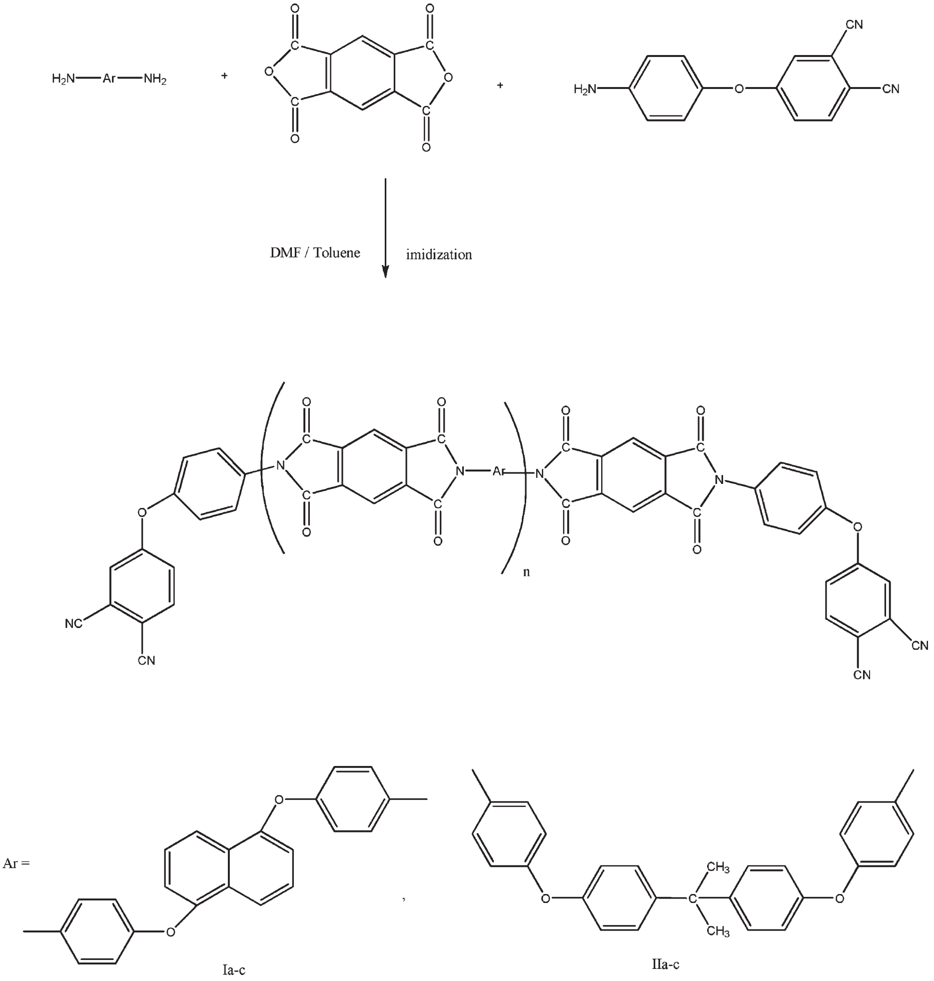


***Figure 7.***
TGA thermogram of phthalonitrile polymers Ia-c in air atmosphere: 10 hrs additional postcured at 380 °C (curve'd').



***Scheme 2.***
Synthesis of phthalonitrile endcapped oligomers (PEO).

(curves'd') to 454 °C and showed improvement in oxidative stability and the char yield. Once the degradation process commences, the catastrophic breakdown occurs at a rate dependent on the postcure conditions. In essence, as the postcure temperature and exposure time were increased, the polymeric stability diminished at elevated temperatures. From these results it is obvious that the polymers have high thermal stability that could be attributed to the incorporation of imide units, ether and phenyl groups in the backbone and triazine rings.[31,32] As the molecular weight of the oligomers increased, an improvement of the thermal stability was observed.

## Conclusions

A series of aromatic ether and imide linkage containing phthalonitrile encapped oligomers were prepared by a two step, one pot method. The formation of the oligomers was confirmed by FT IR and $^1$H NMR analysis. The average molecular weights of the phthalonitrile oligomers ranges were in the range of 2480–4673. The complex viscosity studies observed that, the viscosity increases at a faster rate with 5wt% diamine concentration. The cure reaction of the oligomers has been investigated with 5wt% of aromatic diamine (DDS) curing additive. The new resins exhibit better thermal and thermo-oxidative properties then current commercially available high temperature thermosetting resins.

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