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Synthesis, Characterization and Thermal Properties of Imide-Containing Phthalonitrile Polymers

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A series of novel imide-containing phthalonitrile polymers with flexible aryl ether units have been synthesized and characterized. Bisphenol monomers were synthesized by a multi-step synthesis involving a condensation reaction between aromatic aldehydes and 2,6-dimethyl phenol, respectively. The bisphenols obtained were reacted with 4-nitrophthalonitrile to form aryl ether linkage containing bisphthalonitriles. These products were hydrolyzed to tetra carboxylic acid, which were subsequently converted into corresponding dianhydrides. The obtained dianhydrides were reacted with synthesized 4-(4′-aminophenoxy) phthalonitrile by thermal imidization leading to the formation of imide-containing phthalonitrile monomers. The synthesized monomers were cured with 3.5 wt% of aromatic diamine, 4,4′-diaminodiphenylsulphone(DDS). The structure and properties of all compounds synthesized were confirmed by using elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, DSC, TGA and rheometric studies. The cure temperatures are found to be in the range of 283–302°C, the temperature of 5% and 10% weight loss from TGA are in the range of 433–492°C in N_2 and 424–478°C in air, char yield at 800°C is 40–51%.

Keywords: Phthalonitrile, ether and imide linkage, cure behavior, thermal stability, rheometric studies

1 Introduction

Demand in fiber-reinforced composites for advance aerospace applications has lead to the search for high temperature polymers which are easily processed and exhibit high thermal and oxidative stability. Nowadays, epoxy and polyimides are used for advanced composites. These resins have superior mechanical properties and are lighter than the metals, but lack of thermal stability to operate at high temperatures and tend to oxidize and become brittle over time. Conventional epoxy–based composites are limited to a maximum service temperature of 120°C. This has been a problem with water absorption, engineering reliability and requires low temperature prepreg storage. While aromatic polyimides have a greater thermal stability than epoxy resins, their use has not been as extensive as epoxy resins because of their insolubility in organic solvents, their poor reproducibility on account of the release of water which often splits polymeric chains and trapped solvents in the final resin (1–3). A major problem is in processing blister and void-free components using these matrix resins due to the volatilization of low boiling component that is generated during the step growth synthesis (4, 5).

Phthalonitrile polymers belong to a class of high performance thermosetting materials, possessing unusually high heat and thermal resistance. These resins have wide range of applications such as composite matrices, adhesives, solar panels and electrical conductors (3, 4). These resins have superior properties like formation of void free composites, very low moisture absorption, excellent dimensional stability due to the absence of moisture-induced distortions, and high thermo-oxidative stability. These polymers contain a substantial proportion of aromatic structures which leads to high mechanical strength, high modulus and dimensional stability. Such polymeric materials also contain flexible segments to permit conventional processing and to prevent brittleness (6–8).

These polymers are prepared from phthalonitriles in which the linking group (aromatic groups, aliphatic and unsaturated, aromatic and diamine groups, sulfone and ketone groups) between the two ortho dinitrile groups separates the dinitrile groups enough to permit polymerization. They are bis(o-dicyanophenyl) compounds, and can be crosslinked thermally by the formation of triazine ring structure to produce void free thermosets with high crosslinking density. The main method for the development of high temperature polymers is the incorporation of thermally stable structural units such as aromatic or

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*Address correspondence to: M. Sarojadevi, Department of Chemistry, Anna University, Chennai-600 025, India. Ph: (+91) 44 22203158; Fax: (+91) 44 22200660; E-mail: msrde2000@yahoo.com heteroaromatic rings within the network of the polymeric system. 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 (9–11). It has also been reported that the neat polymerization of phthalonitrile resin is difficult even under extreme thermal conditions, because these monomers do not contain active hydrogen. The slow rate of polymerization can be attributed to the rigidity of the linking sites, which reduces the mobility of the reaction sites or to the absence of initiating agent (3). Aromatic diamines are considered to be suitable curing agents for phthalonitrile polymerization. These diamines generate an active intermediate, which reacts with the excess of phthalonitrile functionalities (12–14). No volatiles are generated from this reaction and they are usually compatible with the monomer. The time and temperature needed for polymerization can be reduced by curing the phthalonitrile monomers in the presence of aromatic diamine curing agents (15). Most of the aromatic amines, particularly 4,4′-diaminodiphenylsulphone (DDS) have the thermal stability at elevated temperatures necessary to enhance polymerization in the present process. Aliphatic amines, however, are less desirable due to their thermo-oxidative instability. Polymerization can be carried out by heating in air in the presence of amine catalyst for several hours at high temperatures by addition polymerization. The possible cross-linking structures include phthalocyanine, triazine and isoindoline depending on the reaction conditions and co reactants used. The network structure is primarily from the formation of isoindoline. The trimerisation of nitrile groups leading to the formation of triazine rings takes place only at high temperatures (16).

Phthalonitrile resins and networks are reasonably tough materials with exceptional thermo-oxidative stability. However, extensive curing times and temperatures are necessary to achieve these properties. Furthermore, the processability of these resins is limited as the crystallinity of the phthalonitrile monomers is high. Research efforts are needed to improve the processability of phthalonitrile resins, by significantly decreasing the temperature and time necessary to achieve networks with high properties. It is therefore proposed to synthesize a new polyimide resin end capped with orthophthalonitrile groups using aromatic dianhydrides with the end capping reagent 4-(4′-aminophenoxy) phthalonitrile and subsequently cure into thermally stable and void free polymer systems with high modulus and low moisture absorption by addition polymerization at high temperature without evolution of volatiles.

2 Experimental

2.1 Materials

4-nitrophthalonitrile was synthesized according to the procedure given in a previous study (17). *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF) 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, acetic acid, p-aminophenol, 4,4′-diaminodiphenylsulphone, 2,6-dimethyl phenol, benzaldehyde and anisaldehyde were purchased from Lancaster, India. 4,4-dimethoxy benzaldehyde, hydrochloric acid and anhydrous potassium carbonate were used as received from E-Merck, India. Thionylchloride and acetic anhydride (Fischer, India) were used without further purification.

2.2 Measurements

Fourier Transform Infra Red (FT-IR) spectra were recorded on a Perkin-Elmer RX-1 spectrometer using a KBr disk at a scanning range from 4000 to 400 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Jeol Ex-400 spectrometer (400 MHz) using DMSO-d_6 as solvent and the chemical shifts were calibrated by using 1% TMS as reference. Elemental analysis was carried out with a Perkin-Elmer model 2400. The viscosity measurements were performed on a TA Instruments AR-2000 Rheometer, with an environmental testing chamber for temperature control. 40 mm diameter parallel plates were used in the test chamber of the rheometer. The melt viscosity of the phthalonitrile prepolymers were monitored in air at 290°C as a function of time. 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 40 ml/min. Thermo gravimetric data were obtained on a Q_{100} series TA instruments in flowing Nitrogen/air at a heating rate of 20°C/min.

2.3 Synthesis of Monomers

2.3.1. *4-Nitrophthalonitrile*

This compound was synthesized and purified according to the procedure reported by J.G. Young et al. (17); m.p. 140–142°C (Lit. m.p. 141°C); IR. (KBr) shows absorptions at 2235 cm^{-1} ($C\equiv N$), 1530 and 1295 cm^{-1} (asymmetric and symmetric stretching vibrations of N=O). ^{1}H-NMR (400 MHz, DMSO-d_6)δ (ppm) = 9.02 (s, 1H), 8.67 (d, 1H), 8.42 (d, 1H). Elemental analysis for $C_8H_3N_3O_2$: Calcd: C, 55.59%; H, 1.73%; N, 24.2%; Found: C, 56.08%; H, 1.92%; N, 23.01%

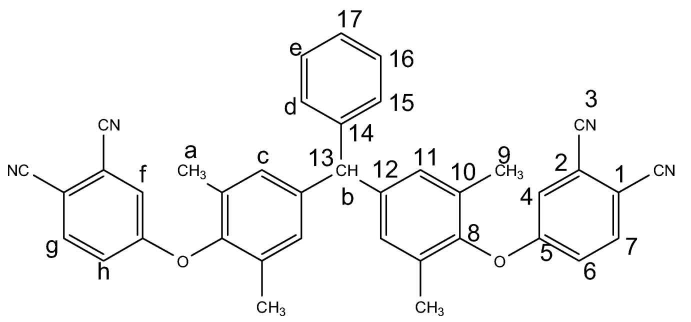
2.3.2. *Synthesis of bis (4-hydroxy-3,5-dimethyl) phenyl methane (HDPM) (Ia)*

A 250 ml three-necked round bottom flask equipped with a reflux condenser and nitrogen inlet was charged with 2,6-dimethylphenol (12.2 g; 0.1 mol). Dry HCl (10.9 ml;

0.1 mol) was added into the reaction vessel for a time period of 30 min. To this mixture, benzaldehyde (5.3 g; 0.05 mol) was added dropwise and stirred at room temperature for 1 h. Then, the reaction mixture was refluxed for about 6 h. The reaction mixture was cooled and the pH was adjusted to 7 using sodium hydroxide solution. The solid product obtained was filtered, washed repeatedly with methanol, and dried in a vacuum oven; yield 14.2 g (86%); IR (KBr) 3585–3595 (O—H), 2920 cm^{-1} (CH_3); ^{1}H-NMR (400 MHz, DMSO-d_6) δ (ppm) = 2.23 (s, 12H, H_b), 4.52 (s, 2H, H_a), 5.35 (s, 1H, H_c), 6.76 (s, 4H, H_d), 7.12 (d, 2H, H_e), 7.33 (dd, 3H, H_f). ^{13}C-NMR (400 MHz, DMSO-d_6)δ (ppm) = C_1- 152.2, C_2-15.2, C_3-125.5, C_4-128.5, C_5-135.8, C_6-56.9, C_7-143.4, C_8-127.8, C_9-129.3, C_{10}-126.3. Elemental analysis: Calcd: C, 83%; H, 7.2%; Found: C, 82.6%; H, 7.12%. Bisphenols Ib and Ic were also prepared using a similar procedure starting from anisaldehyde and 2,6 dimethoxy benzaldehyde, respectively.

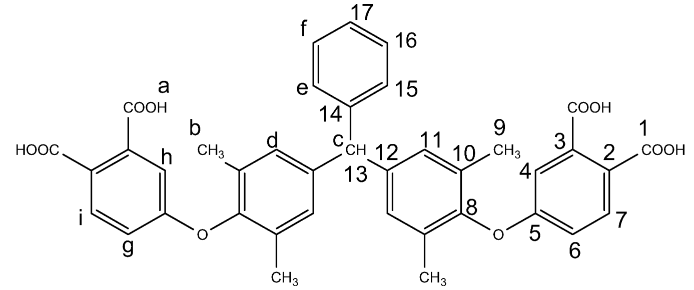
2.3.3. *Synthesis of 1,1-bis (4-(4′-dicyanophenoxy)-3,5-dimethylphenyl benzyl methane (DDBM) (IIa)*

To a 250 ml three-necked flask was added HDPM(Ia) (8.3 g; 0.025 mol), 4-nitrophthalonitrile (8.65 g; 0.05 mol), anhydrous potassium carbonate (10.35 g; 0.075 mol) and 30 ml of dry DMSO as the solvent. The reaction mixture was stirred at room temperature for 24 h under nitrogen atmosphere. The resultant solution was slowly poured into rapidly stirring DI water (800 ml) to precipitate the monomer. The monomer was collected by vacuum filtration and washed with methanol to remove residual starting materials and DMSO. The purified bisphthalonitrile monomer was collected by vacuum filtration and dried under ambient condition; yield 12.8 g; (83%), FT-IR (KBr) 2242 (C≡N), 1297 and 1076 cm^{-1} (C—O—C); ^{1}H-NMR (400 MHz, DMSO-d_6)δ (ppm) = 2.1 (s, 12H, H_a), 5.63 (s, 1H, H_b), 6.89 (s, 4H, H_c), 7.14 (d, 2H, H_d), 7.25 (dd, 3H, H_e), 7.75 (d, 2H, H_f), 8.16 (s, 2H, H_g), 8.73 (d, 2H, H_h).^{13}C-NMR (400 MHz, DMSO-d_6)δ (ppm) = C_1-115.8, C_2-109.0, C_3-115.5, C_4-121.8, C_5-162.0, C_6-122.5, C_7-132.6, C_8-147.6, C_9-15.0, C_{10}-128.1, C_{11}-126.8, C_{12}-136.3, C_{13}-56.9, C_{14}-143.4, C_{15}-128.3, C_{16}-129.3, C_{17}-126.3. Elemental analysis: Calcd: C, 80.13%; H, 4.79%; N, 9.58% Found: C, 80.17%; H, 4.91%; N, 9.62%. Bisphthalonitriles IIb and IIc were prepared starting from bisphenols Ib and Ic respectively adopting a similar procedure.



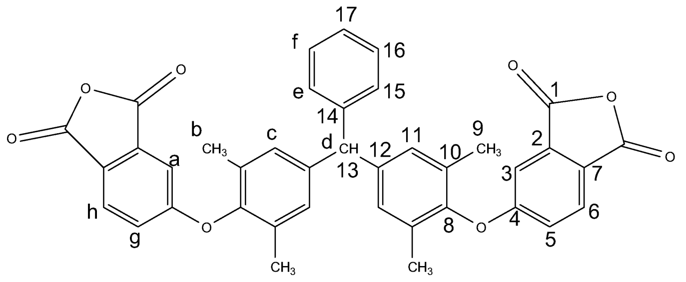
2.3.4. *Synthesis of 1, 1-bis (4-(4′-dicarboxyphenoxy)-3,5-dimethyl phenyl) benzyl Methane (DDPBM) (IIIa)*

A mixture of 2,6-bis (ether dinitrile) (IIa) (7.72 g; 0.015 mol) and potassium hydroxide (24.3 g; 0.4327 mol) in 60 ml of ethanol and 60 ml of distilled water was stirred at refluxing temperature until no further ammonia was generated. The time taken to reach this stage was about 36 h. The resulting hot, clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool, and the pH value was adjusted by adding dilute hydrochloric acid to near 3. The precipitate formed was collected by filtration, washed repeatedly with water, and dried under vacuum; yield 6.9 g (80%), FT-IR (KBr) 3400–3550 (O—H), 1758 (C=O), 1228 cm^{-1} (C—O—C); ^{1}H-NMR (400 MHz, DMSO-d_6)δ (ppm) =10.6 (s, 4H, H_a), 2.12 (s, 12H, H_b), 5.62 (s, 1H, H_c), 6.96, 7.01 (s,4H, H_d), 7.14(d, 2H, H_e), 7.23 (dd, 3H, H_f),7.67 (d, 2H, H_g), 7.69 (d, 2H, H_h), 7.8 (s, 2H, H_i).^{13}C-NMR (400 MHz, DMSO-d_6) δ (ppm) = C_1-169.4, C_2-126.0, C_3-132.6, C_4-117.6, C_5-162.1, C_6-122.6, C_7-129.9, C_8-147.6, C_9-15.0, C_{10}-128.1, C_{11}-126.8, C_{12}-136.3, C_{13}-56.9, C_{14}-143.4, C_{15}-128.3, C_{16}-129.3, C_{17}- 126.3. Elemental analysis: Calcd: C, 70.90%; H, 4.84%; N, 24.24%. Found: C, 70.23%; H, 4.79%; N, 24.58%. The diacids IIIb and IIIc were prepared in a similar way starting from IIb and IIc, respectively.



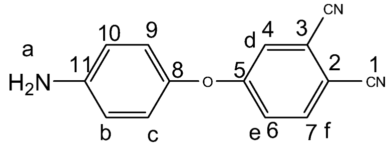
2.3.5. *Synthesis of 1,1-bis (4-(4′- dicarboxyphenoxy)-3,5-dimethyl phenyl) benzyl methane dianhydride (DDBD) IVa*

A mixture of bis(3, 4-dicarboxyphenoxy) ether diacid (IIIa) (6.5 g; 0.01 mol), acetic acid (30 ml), and acetic anhydride (30 ml) was stirred under reflux until a clear solution was obtained. The resulting hot, clear solution was filtered to remove any insoluble impurities. On cooling, the crystallized brown needles were collected, washed with dry toluene, and dried under vacuum; yield 5.2 g (84%). The IR spectrum shows absorptions at 1845 and 1785 (C=O) and 1194 cm^{-1} (C—O—C); ^{1}H-NMR (400 MHz, DMSO-d_6)δ (ppm) = 2.25 (s, 12H, H_b), 5.52 (s, 1H, H_d), 6.71 (s, 4H, H_c), 7.08 (d, 2H, H_e), 7.15 (dd, 3H, H_f), 7.35 (d, 2H, H_g), 7.75 (s, 2H, H_a), 8.30 (d, 2H, H_h).^{13}C-NMR (400 MHz, DMSO-d_6)δ (ppm) = C_1-163.5, C_2-129.4, C_3-118.2, C_4-162.1, C_5-122.6, C_6-129.9, C_7-122.8, C_8-147.6, C_9-15.6, C_{10}-128.1, C_{11}-126.8, C_{12}-136.3, C_{13}-58.7, C_{14}-143.4, C_{15}-128.3, C_{16}-129.3, C_{17}-126.3. Elemental analysis: Calcd: C, 75.0%; H, 4.48%; N, 20.51%. Found: C, 75.27%; H, 4.89%; N, 20.58%. The dianhydrides IVb and IVc were prepared in a similar way from IIIb and IIIc., respectively.



2.3.6. *Synthesis of 4-(4′-aminophenoxy)phthalonitrile (APPH)*

This compound was synthesized by the nucleophilic nitro displacement reaction. 4-Aminophenol (5.4 g; 0.05 mol), potassium carbonate (6.9 g; 0.05 mol) and 4-nitrophthalonitrile (8.65 g; 0.05 mol) 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 h at room temperature under nitrogen atmosphere. The 4-(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 and 1070 cm^{-1} (C–O–C). ^{1}H-NMR (400 MHz, DMSO-d$_6$)δ (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 (400 MHz, DMSO-d$_6$)δ (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: Calcd: C, 71%; H, 3.82%; N, 17.8%; Found: C, 69.80%; H, 4.15%; N, 16.93%.



2.3.7. *Synthesis of imide-containing phthalonitriles (ICPH) (Va)*

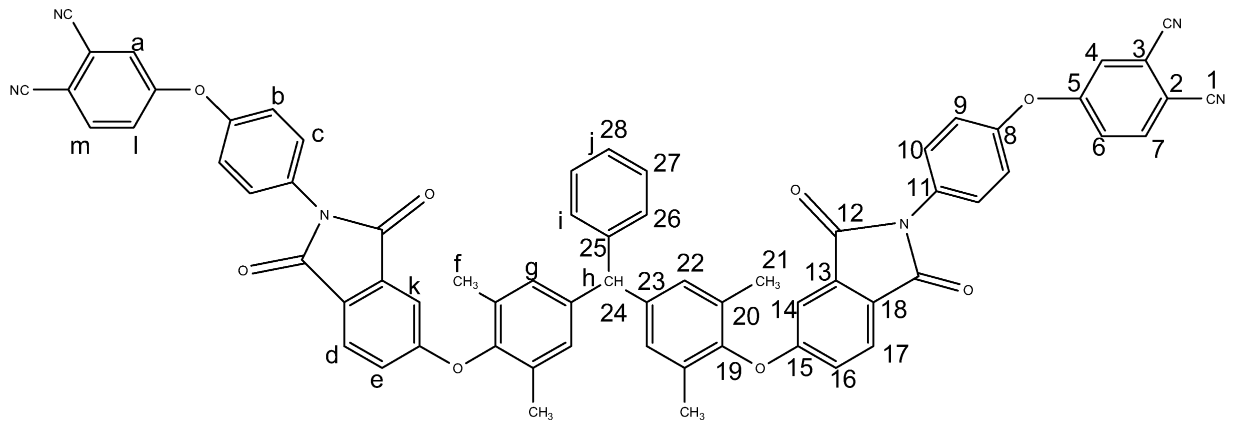
The ICPH(Va) was prepared as follows. To a 100 ml three-necked flask was added 2,6-bis (3,4-dicarboxyphenoxy) benzaldehyde dianhydride (6.3 g; 0.01 mol) and 30 ml of dry dimethylformamide (DMF). After flushing the solution with nitrogen for 30 min, 4-(4′-aminophenoxy) phthalonitrile (4.7 g; 0.02 mol) was added to the reaction flask under ambient conditions. The temperature of the reaction mixture was increased to 90°C and held at this temperature for 1 h. Toluene (30 ml) was added and the solution was heated to reflux. The water that was formed as a by-product was removed as azeotrope from the mixture using a Dean-Stark trap. Total reflux time was 12 h. After removing the toluene by distillation and cooling, the solidified product was removed from the reaction vessel, washed with ethanol, collected by filtration, and dried under vacuum; yield 8.9 g (82%). Monomers Vb and Vc were prepared using appropriate reagents adopting similar procedure.

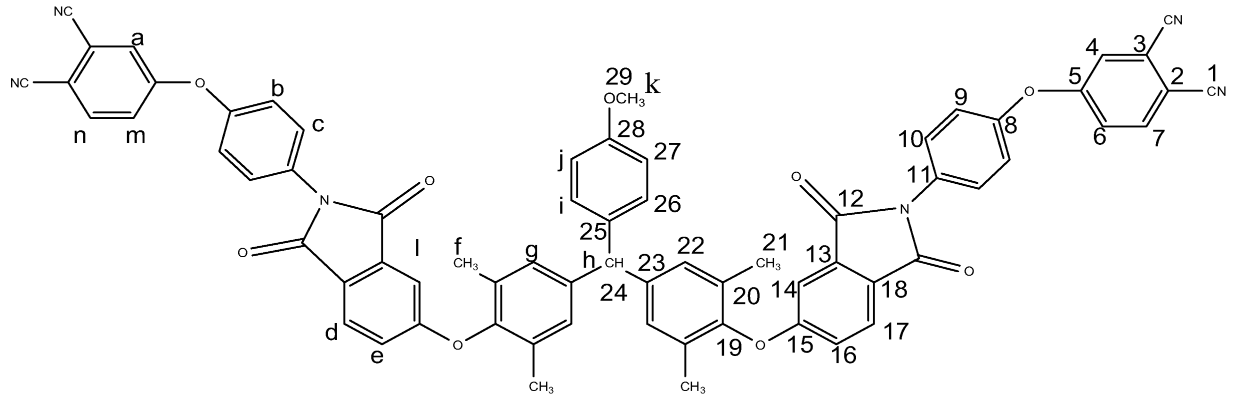
MonomerVa

FT-IR (KBr); 2242 (C≡N), 1257 cm^{-1} (C–O–C); ^{1}H-NMR (400 MHz, DMSO-d$_6$)δ (ppm) = 2.20 (s, 12H, H$_f$), 5.36 (s, 1H, H$_h$), 6.63 (s, 4H, H$_g$), 6.90 (d, 4H, H$_b$), 7.02 (d, 2H, H$_i$), 7.12 (dd, 3H, H$_j$), 7.35 (d, 2H, H$_c$), 7.38 (s, 2H, H$_a$), 7.45 (d, 2H, H$_m$), 7.62 (d, 2H, H$_l$), 7.66 (d, 4H, H$_e$), 7.81 (s, 2H, H$_k$), 8.1 (d, 2H, H$_d$).^{13}C-NMR (400 MHz, DMSO-d$_6$)δ (ppm) = C$_1$-115.9, C$_2$-114.5, C$_3$-116.8, C$_4$-131.6, C$_5$-141.5, C$_6$-132.9, C$_7$-133.4, C$_8$-132.6, C$_9$-128.1, C$_{10}$-122.1, C$_{11}$-131.4, C$_{12}$-167.1, C$_{13}$-131.8, C$_{14}$-115.0, C$_{15}$-160.5, C$_{16}$-121.0, C$_{17}$-127.3, C$_{18}$-125.2, C$_{19}$-147.6, C$_{20}$-128.1, C$_{21}$-16.2, C$_{22}$-126.3, C$_{23}$-136.3, C$_{24}$-56.9, C$_{25}$-143.4, C$_{26}$-128.3, C$_{27}$-129.3, C$_{28}$-126.3. Elemental analysis: Calcd: C, 76.0%; H, 3.96%; N, 7.93%. Found: C, 76.43%; H, 4.01%; N, 7.88%.

Monomer Vb

FT-IR (KBr); 2240 (C≡N), 1257 cm^{-1} (C–O–C); ^{1}H NMR (DMSO-d$_6$): 2.32 (s, 12H, H$_f$,), 3.73 (s, 3H, H$_k$),





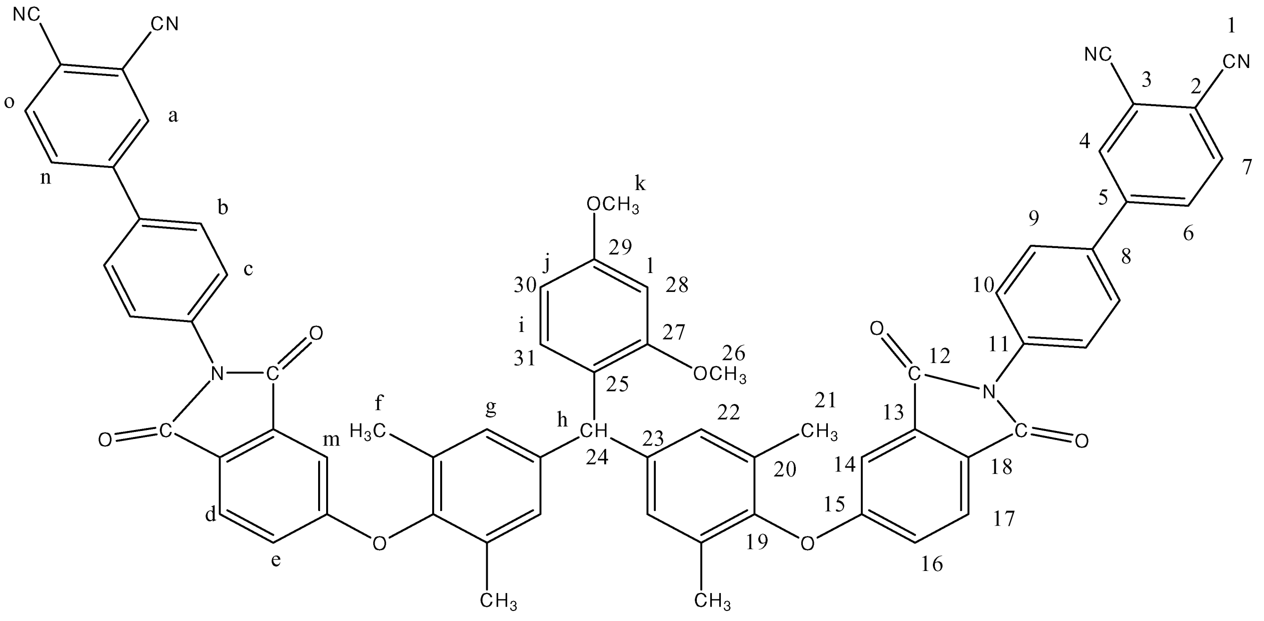
5.32 (s, 1H, H_h), 6.61 (s, 4H, H_g), 6.65 (d, 2H, H_j), 6.93 (d, 2H, H_i), 7.22 (d, 2H, H_e), 7.38 (d, 4H, H_b), 7.69 (d, 4H, H_c), 7.73 (s, 2H, H_n), 7.80 (s, 2H, H_l), 7.92 (s, 2H, H_a), 7.96 (d, 2H, H_m), 8.22 (s, 2H, H_d).^{13}C-NMR (400 MHz, DMSO-d_6)δ (ppm) = C_1-115.9, C_2-114.5, C_3-116.8, C_4-131.6, C_5-141.5, C_6-132.9, C_7-133.4, C_8-132.6, C_9-128.1, C_{10}-122.1, C_{11}-131.4, C_{12}-167.1, C_{13}-131.8, C_{14}-115.0, C_{15}-160.5, C_{16}-121.0, C_{17}-127.3, C_{18}-125.2, C_{19}-147.6, C_{20}-128.1, C_{21}-16.2, C_{22}-126.3, C_{23}-136.3, C_{24}-56.9, C_{25}- 143.4, C_{26}-128.5, C_{27}-117.3, C_{28}-158.3, C_{29}-58.2.

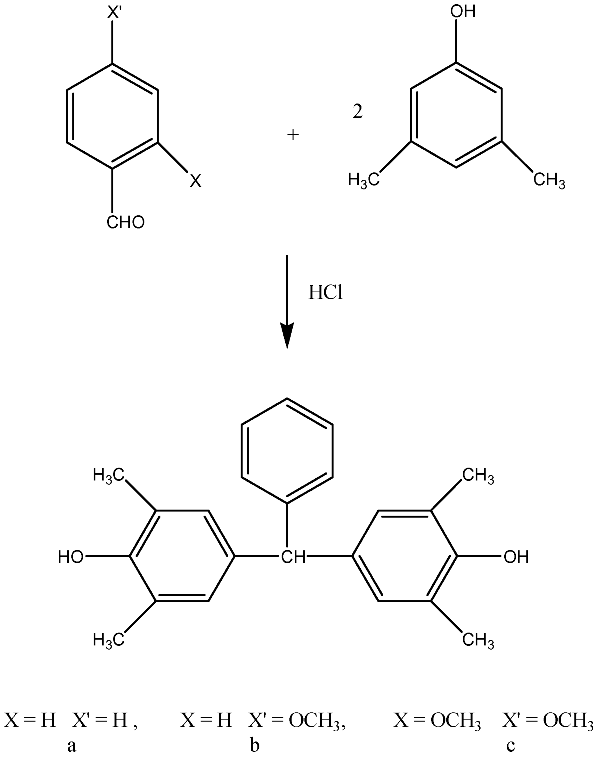
Monomer Vc

FT-IR (KBr pellet) 2237(C≡N), 1257 cm^{-1} (C–O–C); ^{1}H-NMR (DMSO-d_6): 2.32 (s, 12H, H_f,), 3.76 (s, 6H, H_k), 5.36 (s, 1H, H_h), 6.61 (s, 4H, H_g), 6.25 (d, 1H, H_j), 6.83 (d, 1H, H_i), 7.22 (d, 2H, H_e), 7.38 (d, 4H, H_b), 7.69 (d, 4H, H_c), 7.73 (s, 2H, H_o), 6.30 (s, 1H, H_l), 7.92 (s, 2H, H_a), 7.96 (d, 2H, H_n), 7.94 (s, 2H, H_m), 8.22 (s, 2H, H_d). ^{13}C-NMR (400 MHz, DMSO-d_6)δ (ppm) = C_1-115.9, C_2-114.5, C_3-116.8, C_4-131.6, C_5-141.5, C_6-132.9, C_7-133.4, C_8-132.6, C_9-128.1, C_{10}-122.1, C_{11}-131.4, C_{12}-167.1, C_{13}-131.8, C_{14}-115.0, C_{15}-160.5, C_{16}-121.0, C_{17}-127.3, C_{18}-125.2, C_{19}-147.6, C_{20}-128.1, C_{21}-16.2, C_{22}-126.3, C_{23}-136.3, C_{24}-47.9, C_{25}-123.4, C_{26}-56.7, C_{27}-159.3, C_{28}-102.8, C_{29}-161.2, C_{30}-108.7, C_{31}-132.5.

2.3.8. *Prepolymer and polymer synthesis*

A typical prepolymer synthesis was accomplished by weighing 50 g of the phthalonitrile monomer **Va (Vb or Vc)** 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. This quenched product is a B-staged resin or a prepolymer, which has the T_g in the range of 100–135°C and this amorphous solid is soluble in common organic solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP).





Sch. 1. Synthesis of bisphenols Ia–c.

3 Results and Discussion

3.1 Synthesis of Monomers

As shown in Scheme 1, new bisphenols were prepared by the condensation reaction between benzaldehyde/anisaldehyde/2,4-dimethoxy benzaldehyde and 2,6-dimethylphenol in the presence of HCl (18). The FT-IR spectrum of a representative bisphenol**(1a)** is given in Figure 1. The broad absorption around 3499 cm^{-1} corresponds to O—H group and the absence of C=O stretching vibration due to the aldehyde around 1730–1780 cm^{-1} confirms the formation of new bisphenol.

The synthesized bisphenols were reacted with 4-nitrophthalonitrile (Scheme 2) in the presence of K_2CO_3 to form bisphthalonitriles(IIa to IIc) (19, 20). The FT-IR spectrum of bisphthalonitrile**(IIa)** is shown in Figure 1. The spectrum contains absorption bands around 3050–3081 cm^{-1} due to the aromatic C-H stretching, in addition to the sharp band at 2237–2240 cm^{-1} due to the nitrile groups (C≡N) and the intense band at 1282–1288 cm^{-1} is due to the ether group. The ^{1}H-NMR spectrum of bisphthalonitrile in DMSO-d_6 is shown in Figure 2. The singlet appearing at 2.13 ppm is due to the methyl protons and that at 5.38 ppm corresponds to the methine proton. The aromatic proton signals appear in the range between 6.85–8.71 ppm. The representative ^{13}C-NMR spectrum of monomer IIa is shown in Figure 3. Methyl carbons appear at around 15.0–16.2 ppm and methine carbon appears in the range of 47.9–58.7 ppm. The characteristic carbon of the nitrile functionality is found at around 114.8–118.2 ppm. Aromatic carbons appear in the range of 109.0–162.0 ppm. The synthesized bisphthalonitriles were converted into tetra carboxylic acid by using KOH in ethanol as solvent and subsequently converted into the corresponding dianhydrides by using acetic anhydride (Scheme 2) (21). The characteristric bands of tetraacid were observed (Figure 1; IIIa) around 1758 cm^{-1} (C=O strecting) and in the region of 3400–3550 cm^{-1}(O—H strecting). The disappearance of the characteristric stretching band due to the cyano (C≡N) group in the FT-IR spectrum confirms the completion of hydrolysis. The FT-IR spectrum of the dianhydride (Fig. 1; IVa) exhibits two characteristic cyclic anhydride absorptions near 1845 and 1785 cm^{-1}, attributed to the asymmetric and

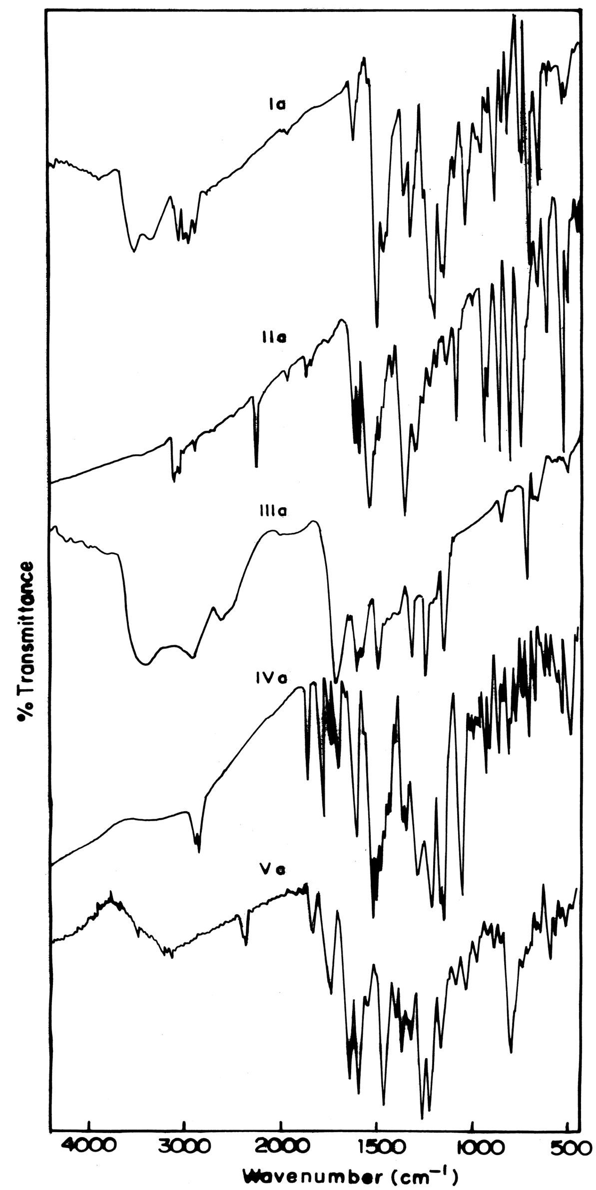
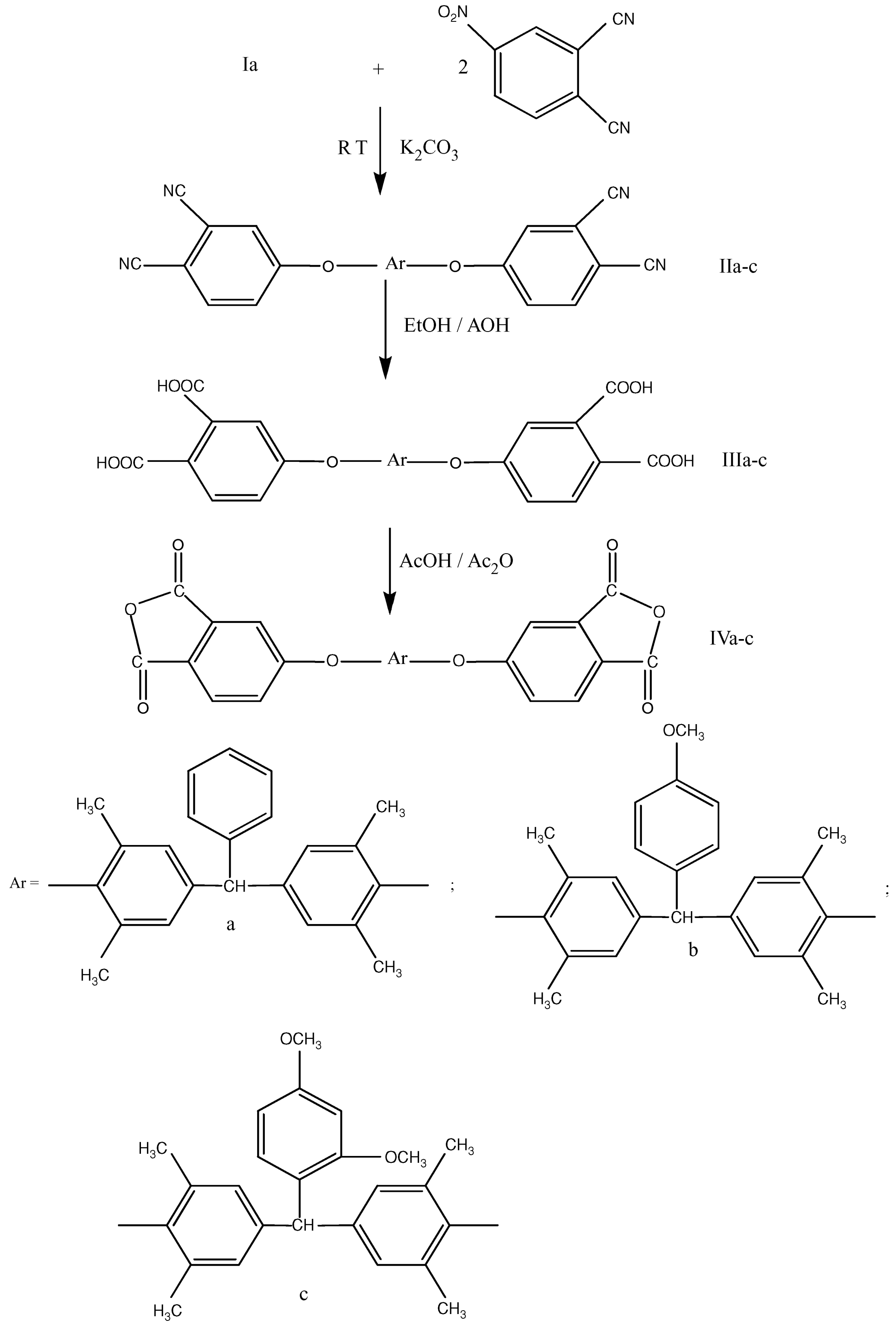


Fig. 1. FT IR Spectra of monomers **Ia–Va**.



Sch. 2. Synthesis of dianhydride compounds IVa–c.

symmetric stretching vibrations of C=O. The ^{1}H NMR spectrum of the dianhydride **IVa** (Fig. 4) shows a singlet at 2.25 and 5.52 ppm due to the methyl protons and methine proton respectively.

The aromatic proton signals appear in the range between 6.71–8.30 ppm. The end capping reagent 4-(4′-aminophenoxy)phthalonitrile was synthesized by the nucleophilic nitro-displacement reaction of

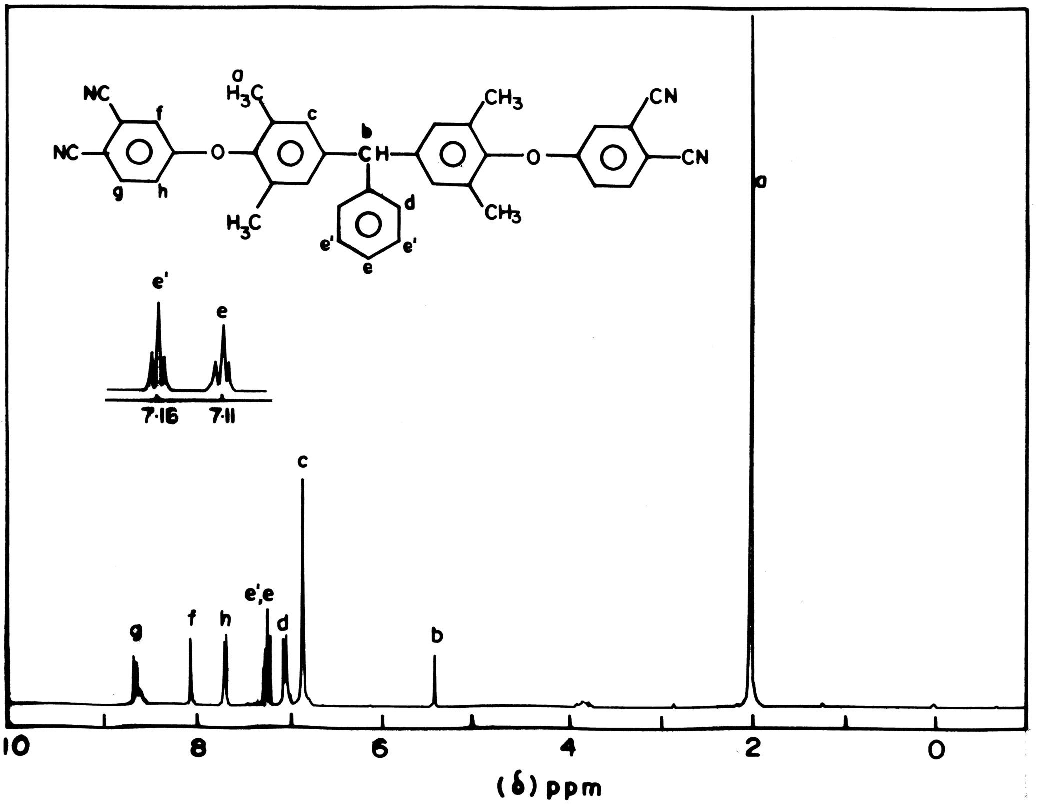


Fig. 2. ^{1}H-NMR Spectrum of monomer **IIa**.

4-nitrophthalonitrile and p-aminophenol in NMP in the presence of potassium carbonate at room temperature. The FT-IR spectrum of APPH observed a band at 2235 cm^{-1} due to the cyano group (C≡N) and the band due to hydroxyl (O—H) stretching is absent. But a sharp band appears in the region of 1253 and 1053 cm^{-1} due to the formation of C—O—C linkage. Two characteristic bands at 3375 and 3457 cm^{-1} are due to the symmetrical and asymmetrical stretching vibration of the amino group. The ^{1}H-NMR spectrum of 4-(4′-aminophenoxy)phthalonitrile observed a broad singlet at 5.2 ppm due to the two amino protons. The five aromatic protons show four doublets and one singlet in the aromatic region, 6–8 ppm.

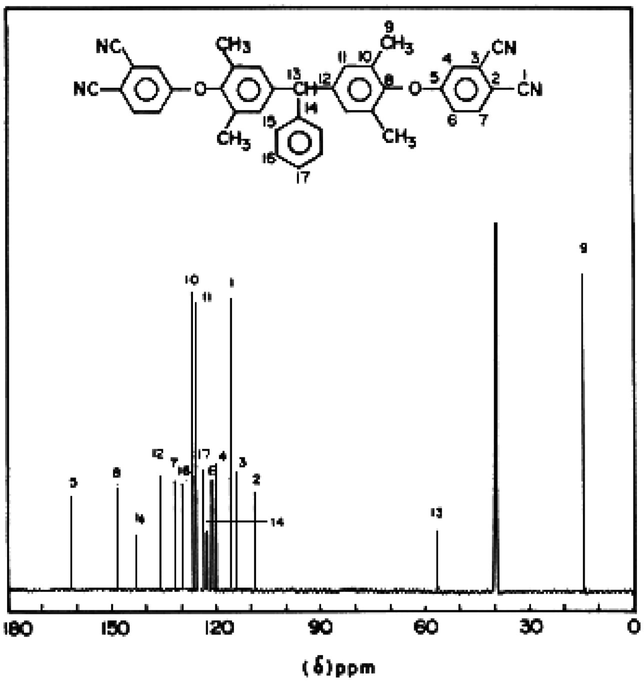
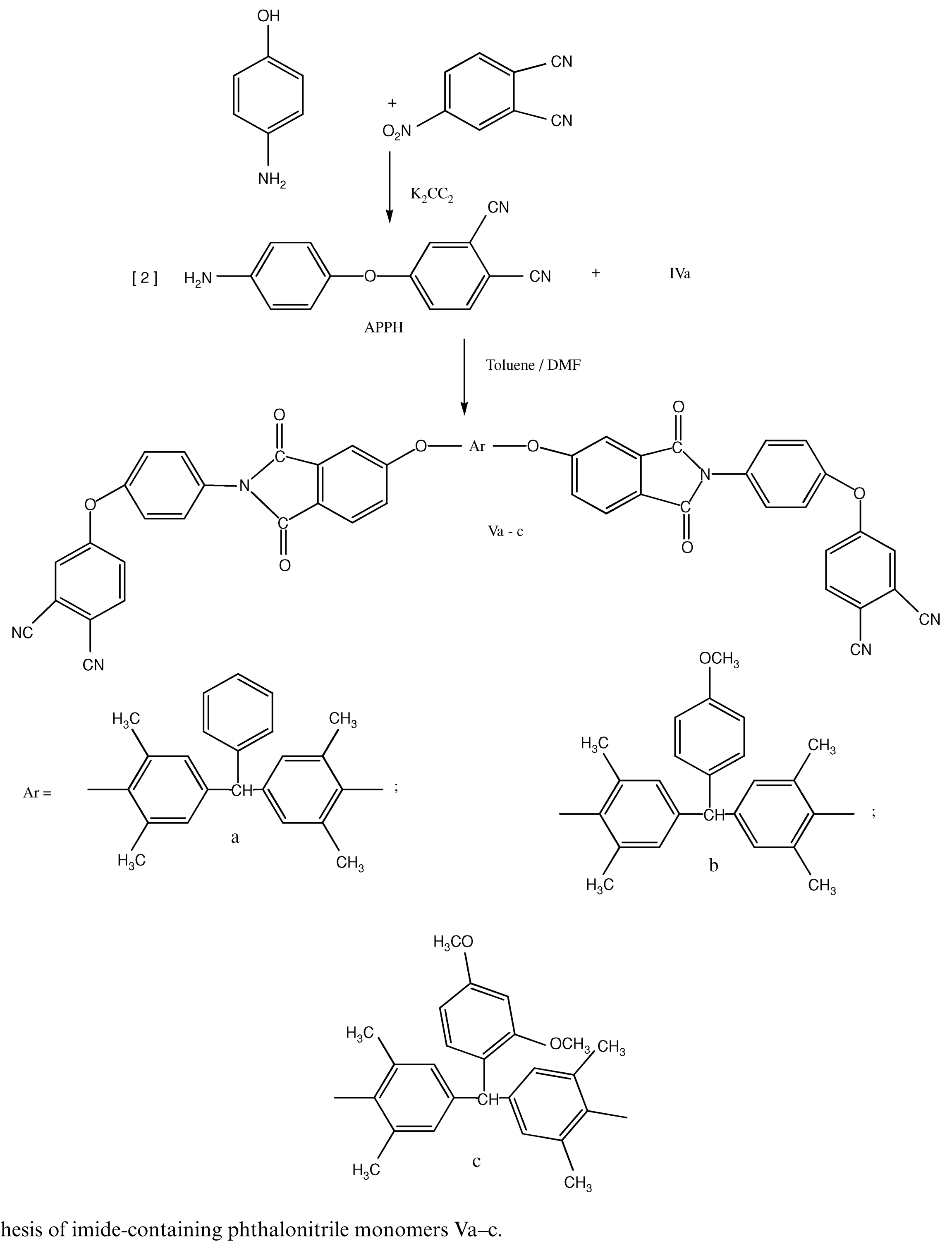


Fig. 3. ^{13}C-NMR Spectrum of bisphthalonitrile **IIa**.

3.2 Synthesis of Imide-Containing Phthalonitrile Monomers, Va–c

The new imide-containing phthalonitrile monomers (ICPHs) were prepared by condensation of the dianhydride monomer (DDBD) with phthalonitrile end-capping reagent 4-(4′-aminophenoxy)phthalonitrile through a two step method by chemical imidization (Scheme 3) (1). All the imide containing phthalonitrile monomers were obtained in high yields, and elemental analysis data show that the proposed structures are correct since the calculated and observed values agree well with each other (Tables 1 and 2). Figure 1**(Va)** shows the FT-IR spectrum of ICPH monomer Va. The formation of imide linkage was confirmed by the characteristic imide absorption bands at 1776 (asymmetrical C=O stretch), 1726 cm^{-1} (symmetrical C=O stretch), 1357 (C-N stretch), 1141, and 786 cm^{-1} (imide ring deformation). Figure 5 shows the ^{1}H-NMR spectrum



Sch. 3. Synthesis of imide-containing phthalonitrile monomers Va–c.

of ICPH (Va). The singlet appearing at 2.20 ppm is due to the methyl protons and that at 5.36 ppm corresponds to the methine proton. The aromatic proton signals appear in the range between 6.63–8.10 ppm. The results show that the ICPH monomer had formed and its structure is confirmed. The structure of all intermediate compounds and the monomers were also confirmed by elemental analysis, which are in good agreement with calculated values, as reported in Tables 1 and 2.

3.3 Prepolymer and Polymer Synthesis

The synthesized monomers **Va–c** were washed with sodium hydroxide solution to remove residual impurities, dried,

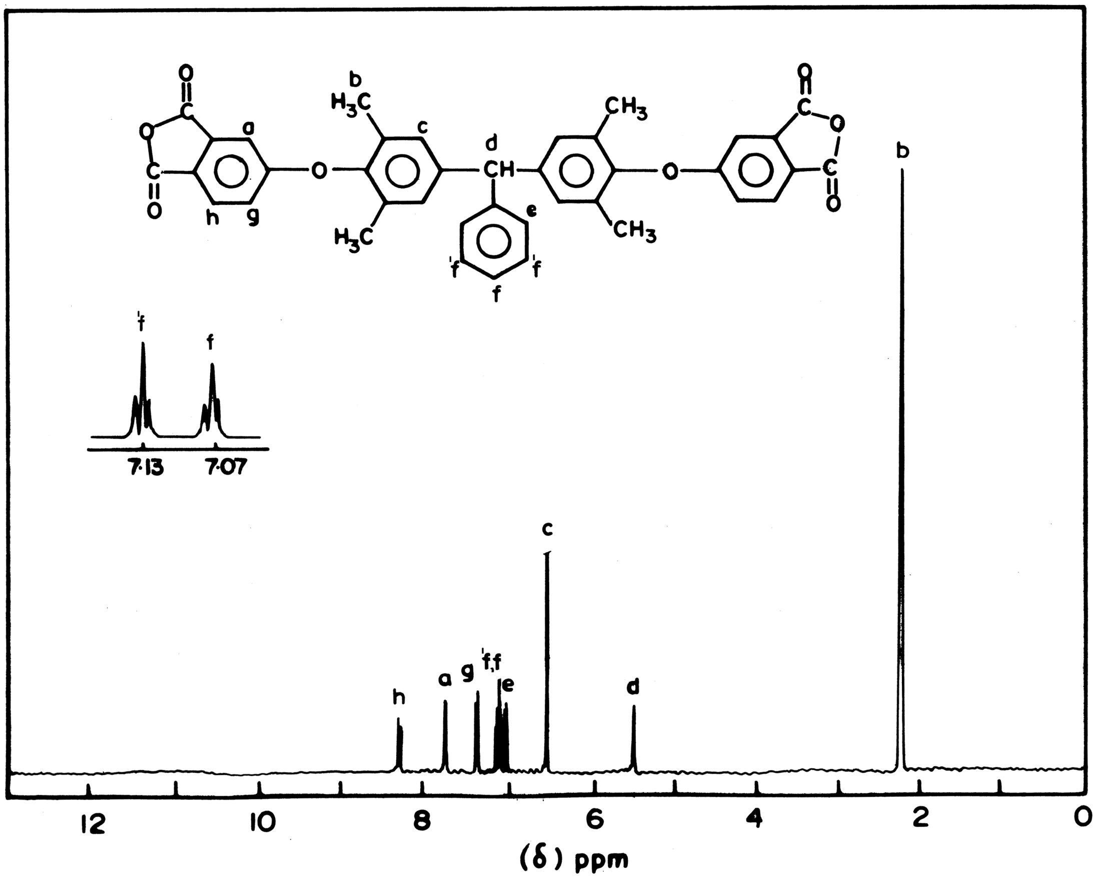


Fig. 4. ^{1}H-NMR Spectrum of dianhydride **IVa**.

washed with isopropanol and dried in a vacuum oven at 100°C overnight prior to use. The melting point range is 242–246°C for **Va**, 251–254°C for **Vb** and 256–261°C for **Vc** monomers. Polymerization of phthalonitrile monomers into crosslinked network involves two steps. In the first step, phthalonitrile monomer (Vc) was mixed with 4,4′-diaminodiphenylsulphone (DDS) in the molten state to prepare the prepolymer mixture (B-stage resin). The FT

Table 1. Elemental analysis results of monomers Ib–Vb

Code	*Elemental analysis (%)* C	H	N
Ib			
Calculated	79.55	7.18	—
Found	79.68	7.13	—
IIb			
Calculated	78.17	4.88	9.12
Found	78.72	5.01	9.05
IIIb			
Calculated	69.12	5.03	—
Found	69.56	4.92	—
IVb			
Calculated	73.39	4.58	—
Found	73.58	4.96	—
Vb			
Calculated	75.0	4.04	7.72
Found	74.82	4.16	7.86

Table 2. Elemental analysis results of monomers Ic–Vc

Monomer code	*Elemental analysis (%)* C	H	N
Ic			
Calculated	76.53	7.14	—
Found	76.98	7.21	—
IIc			
Calculated	76.39	4.96	8.69
Found	76.38	5.04	8.58
IIIc			
Calculated	68.33	5.0	—
Found	68.98	4.96	—
IVc			
Calculated	71.92	4.67	—
Found	72.03	4.87	—
Vc			
Calculated	74.06	4.11	7.51
Found	74.28	4.18	7.56

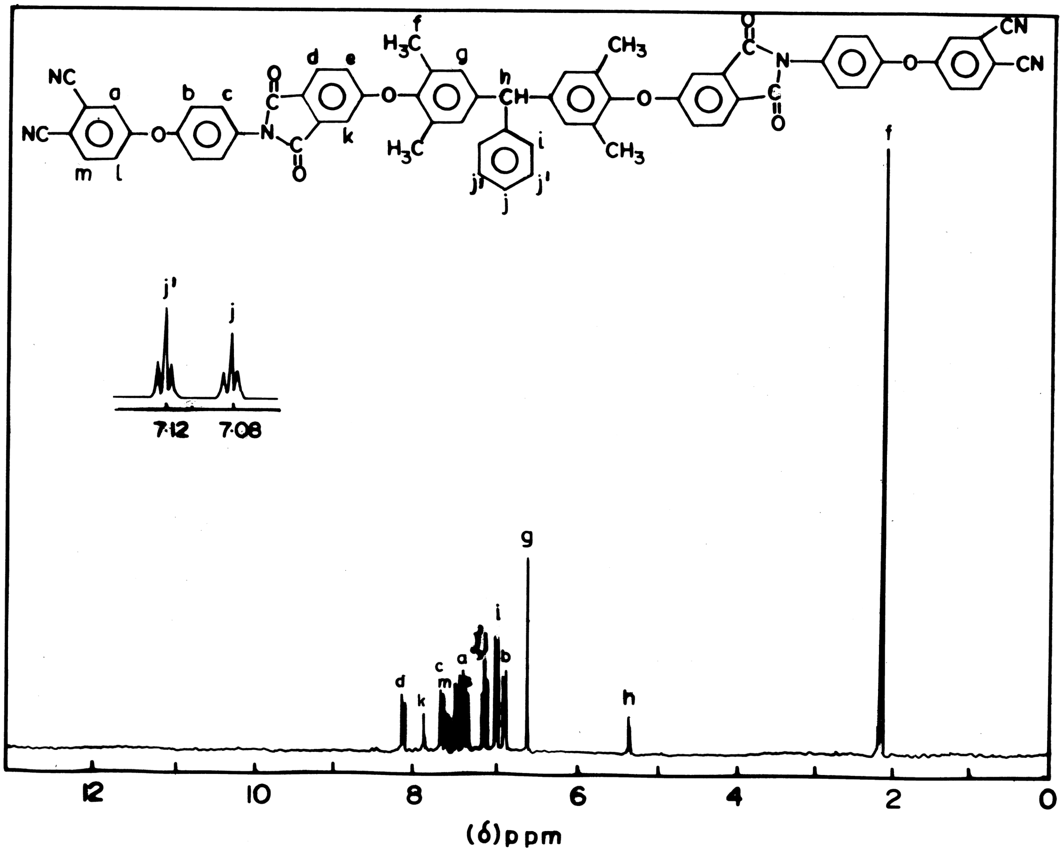


Fig. 5. ^{1}H-NMR Spectrum of monomer **Va**.

IR spectra of the prepolymers are found to be very much similar to that of the monomer except that very weak bands at 1510 and 1342 cm^{-1} due to the triazine rings formed. The second step involves the polymerization of B-stage resin in air oven by heating at various temperatures and extended period of time. During this curing reaction, more and more of nitrile groups trimerize to form triazine rings. 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 (4).

3.4 Cure Cycle Determination

3.4.1. *Rheometric studies*

Rheometric studies on phthalonitrile prepolymers were performed with three different concentrations of curing agents (2.5, 3.0 and 3.5 wt %) to monitor the melt viscosity during polymerization. An isothermal analysis was conducted to determine the amine concentration needed for curing reaction. Viscosity increases as a function of time due to crosslinking, which depends upon the concentration and reactivity of the curing agent. During the crosslinking process, the cyano groups react in the presence of diamine to form triazine ring structures (5, 22). A plot of viscosity change vs. time at 290°C as a function of temperature for phthalonitrile prepolymers containing 2.5% to 3.5% by weight of DDS is shown in Figure 6. It was observed that the viscosity increases more gradually over one hour for the prepolymers containing the initial concentration of 2.50 and 3.0 wt% of amine. At a higher amine concentration (3.5 wt%) viscosity increases at a faster rate. Based on these observations, 3.5 wt% of amine content was considered as optimum level of curing agent concentration for polymerization.

3.4.2. *DSC analysis*

The polymerizations of monomers Va–Vc were studied by DSC analysis. The DSC thermogram of the monomers with 3.5 wt% diamine mixtures is shown in Figure 7. The DSC scan exhibits a small endotherm around 155°C and a large endotherm between 255–263°C, corresponding to the diamine and monomer melting transitions, respectively. A broad exotherm immediately after the melting peak of the monomer is observed for all three monomers **Va–Vc**. This exotherm corresponds to the reaction of the nitrile group of the monomer in the presence of the aromatic diamine. The cure reaction was initiated at 285°C and the exotherm completed at 302°C.

From the rheometric and DSC analysis results, a new cure cycle has been developed for the polymerization of

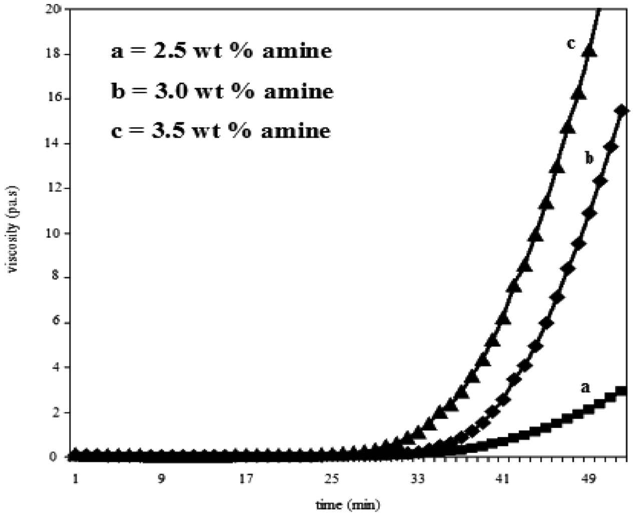


Fig. 6. Rehometric studies on phthalonitrile monomer **Va** at 290°C (a) with 2.5 wt% diamine (DDS) (b) with 3.0 wt% DDS (c) with 3.5 wt% DDS.

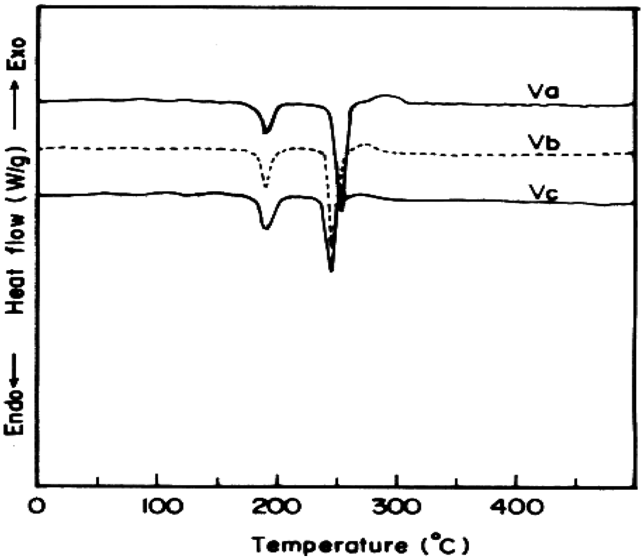


Fig. 7. DSC cure scans of **Va, Vb** and **Vc** with 3.5 wt% diamine (DDS).

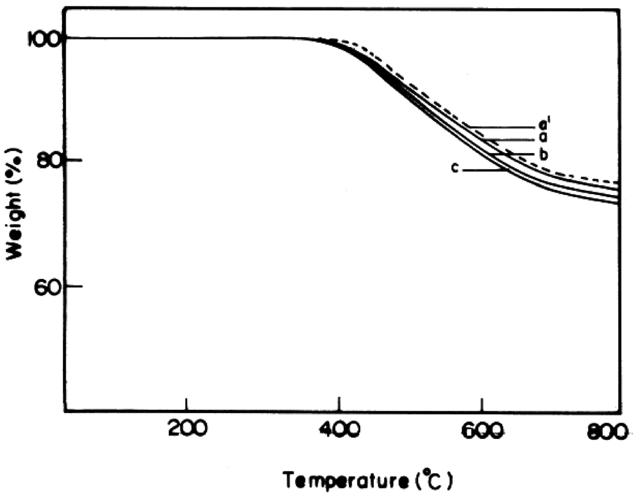


Fig. 8. TGA thermogram of Polymers **Va, Vb** and **Vc** in nitrogen atmosphere.

phthalonitrile monomers. Initially the monomer Va–Vc were heated at 255–260°C and degassed under reduced pressure to remove residual solvent. The temperature was reduced and 3.5 wt % of diamine was added with stirring. After homogeneity occurred the samples had been cured at 250°C for 4 h, 280°C for 6 h, 320°C for 10 h and post-cured at 340°C for 5 h and 370°C for10 h, respectively.

3.5 Thermal Properties

The thermal and oxidative properties of Va-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 resins are summarized in Table 3. Figure 8 shows the thermal stability of Va-c in nitrogen atmosphere. All three polymers show good thermal stability up to 430°C and begin to lose weight at higher temperatures and 60–72% of char yield remaining at 800°C. The temperature at 5% and 10% weight loss are in the range of 433–440, 482–492°C, respectively. As the temperature exposure was increased from 340 to 370°C (curve a') for an additional 5 h, an improvement in the thermal stability

Table 3. Thermal properties of polymers

		(TGA)^{b}in N$_2$		*(TGA)^c in air*		*Char yield (%)^{d,e}*	
Monomer Code	*(DSC)^a T_{cure} (°C)^a*	*T_5(°C)*	*T_{10}(°C)*	*T_5(°C)*	*T_{10}(°C)*	*N$_2$*	*Air*
Va	285–305	433	482	424	467	76	48
Vb	278–296	429	476	421	462	74	45
Vc	280–302	428	474	416	457	73	43
Va^1	—	440	492	434	478	76	51

[a] DSC measurements conducted at a heating rate of 10°C min^{-1} (DSC); [b] Temperature at 5, 10% weight loss in N$_2$ and air determined by TGA at a heating rate of 20°C min^{-1} (TGA), [c] (TGA); [d,e] Char yield (%) at 800°C in N$_2$ and air: 5 h additional post cured at 370°C (Va^1).

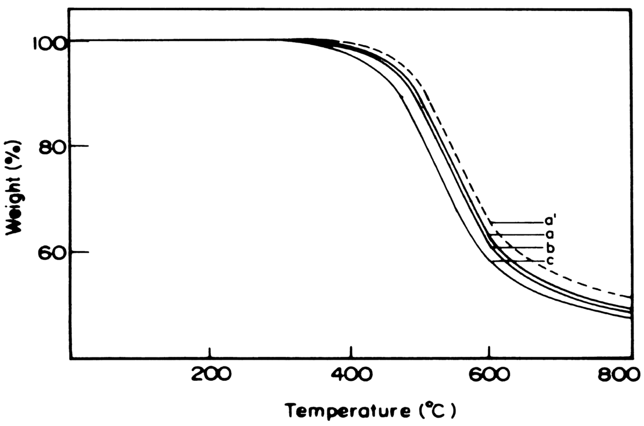


Fig. 9. TGA thermogram of Polymers **Va**, **Vb** and **Vc** in air atmosphere.

was observed. Therefore, the polymeric stability was found to be dependant on cure cycle and post cure temperatures (13).

Figure 9 shows the thermo-oxidative stability of Va–c in air atmosphere. All three polymers did not exhibit obvious weight loss before the scanning temperature reached 420°C in air atmosphere, indicating that no thermal decomposition occurred. The temperature at 5 and 10% weight loss was in the range of 424–431, 467–478°C, respectively. In addition, on further heating to 800°C, the residual weight retentions were found to be 30.2–42.7%, implying that these polymers possess good thermo-oxidative stability. When the post cure temperature of **Va** was increased from 340 to 370°C for an additional 5 h, the onset degradation temperature increased to 430°C and showed improvement in oxidative stability and the char yield. Once the degradation process commences, the catastrophic breakdown occurs. From these results, it is obvious that the polymers have high thermal stability that could be attributed to the incorporation of imide units, phenyl groups in the backbone and triazine rings.

4 Conclusions

A series of imide linkage containing phthalonitrile monomers were prepared in high yield from dianhydrides (IVa–c) and 4-(4′-aminophenoxy)phthalonitrile. Since the imide linkage was formed before the curing, this resin system can be fabricated as void-free composite materials. DSC scans exhibit the polymerization reaction occurs at 283–302°C. There was no Tg observed up to 450°C, proving that there is no viscoelastic transition. Based on the rheometric curves, monomers were cured with 3.5 wt% of diamine (DDS). The rate of polymerization can be controlled and optimized by the amount of curing additive added. TGA results exhibits excellent thermal stability upto 450°C in N_2 atmosphere with very high char yield (60–72%). Good thermo-oxidative stability observed up to 440°C in air atmosphere with 30.2–42.7% char yield. As the post-cure temperature was increased to 370°C, enhancement of thermal stability was observed.

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