

Synthesis and thermal evaluation of novel monoand bis-adamantylated resorcinol-based phthalonitrile resins with enhanced solubility

Ajit Shankar Singh¹ · S. K. Shukla¹ · Preeti Mishra¹ · A. K. Pandey¹

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Abstract

Phthalonitrile (PN) resins are high-temperature-resistant thermosetting polymers which find applications in military as well as aerospace owing to their outstanding performance. At present, most of the PN resins are melt-processed and cured at high temperature via resin transfer moulding owing to their poor solubility in common organic solvents. In the present, embodiment efforts have been made to change the PN resin backbone with adamantane as potential functionality. Mono- and novel bis-adamantylated resorcinols **1a** and **1b** have been synthesized via Amberlyst-15 solid acid resin-catalysed Friedel–Crafts alkylation reaction, as precursor material for the synthesis of novel phthalonitrile (PN) resin monomers **2a** and **2b**, respectively. The study includes structural and thermal characterization of resin monomers **2a** and **2b** along with their solubility in common organic solvents. These resins when cured to their thermosets have demonstrated thermal stability ~ 723 K (5% mass loss) with no glass transition temperature (Tg) up to 673 K. The resin monomers show very good solubility in industry-friendly organic solvents like acetone, ethyl acetate, methyl ethyl ketone and methyl isobutyl ketone.

Keywords Adamantane · Amberlyst-15 · Polymers · Phthalonitrile · Antioxidant

Introduction

PN resins are currently the most researched high-temperature-resistant thermosetting polymers on account of their excellent thermal, mechanical, thermo-mechanical and dielectric properties [1]. Naval research laboratory, Washington, is the premier in this field and has synthesized various types of PN resins, like biphenyl-based phthalonitrile (**BPN**), resorcinol-based phthalonitrile (**RPN**) and bisphenol A-based phthalonitrile (**BAPN**), and evaluated their structure–property relationship (Fig. 1).

One of the serious drawbacks associated with these resins is that the monomers and pre-polymers have poor solubility in common organic solvents leading to their restricted use for the solvent-based coating for composite applications such as hand layup and prepregging.

Ajit Shankar Singh acdri2005@gmail.com In order to improve the solubility and processibility, many substituted bisphthalonitrile resins have been synthesized having flexible hinge groups like ether, thioether, sulphones, phosphine oxides, imides and ether ketones that have shown better processing properties [2, 3]. Researchers have even incorporated other crosslinking groups like benzoxazine [4], propargyl [5], cyanate ester [6] and vinyl [7] self-curing [8] groups to improve processing parameters.

Adamantane group is one of the most versatile groups that has been used extensively not only in basic polymer research but also in medicinal [9–13], optical [14–16], optoelectronic [17] lithographic [18, 19], explosive detector [20], flame retardant [21], water vapour sorption [22] and nano-electronics [23, 24] field, in order to modulate the properties of the materials. Adamantane molecule on account of positive log P (hydrophobicity factor) value (2.83) [25–27] and condensed structure shows excellent hydrophobic nature and dissolves easily in common low boiling organic solvents like benzene, acetone, chloroform, dichloromethane, diethyl ether, etc. It has been observed that adamantane substituent casts multifold effect on polymer backbone owing to its special molecular arrangement [28]. Studies in polymer chemistry have revealed

¹ The Defence Materials and Stores Research Development Establishment, G.T. Road, Kanpur 208013, India



Fig. 1 Commercially available phthalonitrile resin monomers

that the introduction of adamantane groups in polymer backbone improves the solubility, wherein the bulkiness of the adamantane substituents tends to inhibit the packing of polymer chains and in this process decreases their crystallinity and increases their solubility [29]. Glass transition temperature and thermal stability have also been shown to get increased with introduction of adamantane groups on account of their highly rigid and compact aliphatic structure [30, 31]. Adamantane groups have been incorporated in different polymers which include polyimides [29, 31, 32], polyether ether ketones [33, 34], polyether ether sulphones [34], acrylates [35, 36], phenolics [37], polyolefins [38], polyphenylenes [39], acetylenic polymers [40], epoxy [41, 42], polyphosphazenes [43, 44], maleimides [45] and polyamides [46, 47] that have shown improved properties.

Till date no one has reported the structure-property relationship of adamantane group in phthalonitrile resin backbone and its consequences on thermal stability and solubility. In the present study, we report synthesis and characterization of adamantane substituted phthalonitrile (PN) resin monomers **2a** and **2b** together with their corresponding mechanistic crosslinking to polymers **3a** and **3b**. The work also provides a glimpse of their structure and thermal property relationship [48].

Experimental

Materials

Resorcinol, Amberlyst-15, 1-adamantanol, Pd/C, hydrazine hydrate, dry DMSO, dry DMAc and 4-nitro phthalonitrile and meta-bis-(amino phenoxy) diphenyl sulphone (m-BAPS) were purchased from Sigma-Aldrich, USA, and were used as received without further purification except resorcinol which was recrystallized in hot benzene. Anhydrous ethanol, K_2CO_3 and silica gel were purchased from Merck, India, and were used as such. Benzene, hexane and EtOAc were purchased from Spectrochem, India. All apparatus were oven-dried prior to use.

Characterization tools

The ¹H NMR and ¹³C NMR spectra were recorded using Bruker Supercon Magnet DRX-400 spectrometer (operating at 400 MHz for ¹H and 100 MHz for ¹³C) and Bruker Avance III-300 MHz Bruker, Switzerland (operating at 300 MHz for ¹H and 75 MHz for ¹³C), using CDCl₃ and CD_3OD as solvents. Tetramethylsilane ($\delta 0.00$ ppm) served as an internal standard in ¹H NMR. Mass analysis was carried out on PerkinElmer's Qsight triple quadrupole LC-MS/ MS mass spectroscope in ESI mode. Infrared spectra were recorded on a PerkinElmer FT-IR RXI spectrophotometer. Glass transition temperatures (T_{o}) and curing temperatures were obtained using differential scanning calorimetry using TA Instruments, USA (Model No. DSC Q200) at a heating rate of 283 K min⁻¹ under N₂ atmosphere. The degradation temperatures (T_d) were recorded using Mettler Toledo instrument (Model No. SDTA 851) at a heating rate of 293 K min⁻¹ under N₂ atmosphere. Elemental analysis was made on a Vario-EL Elemental (CHNSO) Analyzer.

Synthetic Procedure Considering the ensuing advantages of adamantane moiety, in the present embodiment, a mono-[4-(1-adamantyl) resorcinol], **1a**, and a novel bisadamantylated resorcinol [4, 6-bis(1-adamantyl) resorcinol], **1b**, have been synthesized, respectively, via modified Friedel–Crafts alkylation reaction using Amberlyst-15 resincatalysed solid support reaction by varying the moles of 1 adamantanol, in 96% and 93% yields, respectively (Fig. 2). The adamantylated resorcinol **1a** has already been used as a precursor material in both polymers [34, 48] and medicinal compounds [49, 50], but the bis-adamantylated resorcinol **1b** has not been reported so far and has a vast potential for utilization in field of applied chemistry.

Both electrophilic [50] and nucleophilic [34] substitution reactions have been reported for the synthesis of **1a**, but formation of **1b** during the course of reaction has not been reported.

For the synthesis of **1a** and **1b** reactions, other acid media apart from Amberlyst-15 were also tried initially like methane sulphonic acid, conc H_2SO_4 , benzene sulphonic acid, p-toluene sulphonic acid, camphor sulphonic acid and dodecyl benzene sulphonic acid using benzene as solvent. In all the cases, **1a** was obtained in comparative yields from 90–95%, within 24 h but **1b** could not be isolated except in case of Amberlyst-15.

Since for the synthesis of **1b** the reactions for longer period (>24 h) were required, as there is double nucleophilic addition, by varying the mole percentage of 1-adamantanol, in all the cases initially the TLC did show formation of **1b**



Fig.2 Synthesis of compound 1a-b, 2a-b and crosslinked polymers 3a-b

but it was very difficult to isolate it from the complex mixture of non-polar products, and in all the above cases **1a** was the major product as the reaction never led to completion. When the reaction was carried out for longer period, the TLC showed more decomposition/side products.

The Amberlyst-15-catalysed reaction initially showed formation of both **1a** and **1b**, but as the reactions progressed **1a** disappeared and **1b** was obtained as sole product. The predominant formation of **1b** in case of solid resin-catalysed reaction could be attributed to the efficient and restricted catalysis on solid support where in **1a** molecules formed during course of reaction apart from adsorption/desorption phenomenon undergo a hydrogen bonding interaction with the sulphonic acid groups of resin forming a cluster of hydrogen bonded molecules on solid surface, thereby preventing it from getting decomposed by excess of free acid catalyst in case of liquid phase reactions [51, 52].

In order to utilize the unique properties of adamantane substituent, the adamantylated resorcinols **1a** and **1b** have been used as precursor material for the synthesis of corresponding phthalonitrile resin monomers **2a** and **2b** having one and two adamantane moieties, respectively (Fig. 2). The synthesized resins monomers **2a** and **2b** have been cured to their corresponding crosslinked polymers **3a** and **3b**, respectively, via catalytic curing with 5% m-BAPS and evaluated for their curing profile and thermal properties.

Synthesis of mono-adamantane substituted resorcinol **1a**, bis-phthalonitrile resin **2a** and its corresponding polymer **3a** involved following steps:

(i) Synthesis of compound 1a (6-(1'-adamantyl) resorcinol): To a refluxing solution of resorcinol (11.0 g, 100 mmol) in dry benzene (250 mL) fitted with a Dean Stark assembly under N₂ atmosphere was added Amberlyst-15 (solid supported acid resin catalyst) resin (2.0 g) and then 1-adamantanol (15.2 g, 100 mmol) in dry benzene (50 mL) was added gradually via dropping funnel for a period of 1 h and the reaction was allowed to reflux at the same temperature for 6 h. The reaction was then cooled to room temperature and filtered through sintered funnel, and the filtrate was dried via rotary evaporator to furnish crude product which was then purified by column chromatography using silica gel (60-120 mesh) and 20% ethyl acetate//hexane as eluent to furnish pure 1a as white solid (23.5 g, 96.3% yield). M.p by DSC: 519 K, FT-IR (KBr, cm⁻¹) 799, 985, 1163, 1230, 1440, 1597, 1614, 2851, 2903, 3391, 3487. ¹H NMR (400 MHz, CDCl₂) δ 1.61–2.08 (m, 15H) 5.35 (s, 1H, -OH), 5.46 (s, 1H, -OH), 6.23 (s, 1H), 6.35 (d, 1H, J = 8.0 Hz), 7.02 (d, 1H, J = 8.0 Hz), ¹³C NMR (100 MHz, CD₃OD) δ 29.3 (3×CH), 35.8 (C), 36.9 (3×CH₂), 40.6 (3×CH₂), 103.5 (CH), 105.5 (CH), 126.4 (CH) 128.1 (C), 155.5 (C), 156.9 (C).; ESI-MS: 245 $[M+1]^+$; Analysis Calculated for C₁₆H₂₀O₂: C; 78.65, H; 8.25. Found: C; 78.62, H; 8.29.

(ii) Synthesis of compound 2a [4,4'-(4-(1"-adamantyl)-1,3-phenylene) bis(oxy) diphthalonitrile]: A mixture of 4-adamantyl resorcinol, 1a (4.88 g, 20 mmol), 4-nitrophthalonitrile (7.92 g, 40 mmol) and potassium carbonate (8.28 g, 60 mmol) in anhydrous DMSO (50 mL) under N₂ atmosphere at room temperature was stirred for 24 h. The reaction mixture was poured in distilled water (200 mL) to obtain white precipitate which was filtered and washed firstly with water $(3 \times 100 \text{ mL})$ and then with isopropanol $(3 \times 100 \text{ mL})$. The residue was then dried under vacuum oven at 100 °C to obtain compound 2a as white powder (9.71 g, 97.8% yield). M.p by DSC: 388 K, FT-IR (KBr, cm⁻¹) 1240, 1252, 1280, 1486, 1594, 2232, 2852, 2906. ¹H NMR (400 MHz, CDCl₃) δ 1.62–2.62 (m, 15H), 6.57 (s, 1H), 6.96 (d, 1H, J=8 Hz), 7.26–7.28 (m, 5H), 7.52 (d, 1H, J = 8.0 Hz), 7.75 (d, 1H, J = 8.0 Hz), 7.79 (d, 1H, J = 8.0 Hz), ¹³C NMR (100 MHz, CDCl₃) δ 28.7 (3×CH), 36.6 (3×CH₂), 36.9 (C), 41.3 (3×CH₂), 109.4 (C), 109.6 (C), 113.3 (CH), 114.9 (C), 115.2 (C), 117.6 (CH), 117.8 (C), 118.0 (C), 121.6 (CH), 121.8 (CH), 122.2 (CH), 122.3 (CH), 130.2 (CH), 135.6 (CH), 135.8 (CH), 140.4 (C), 152.6(C), 154.4 (C), 161.0 (C), 161.10 (C).; ESI-MS: 497 [M+1]⁺; Analysis Calculated for C₃₂H₂₄ N₄O₂: C; 77.40, H; 4.87, N; 11.28. Found: C; 77.45, H; 4.90, N; 11.32.

(iii) Preparation of crosslinked polymer 3a: Compound 2a (5 g) was grinded well with m-BAPS (0.025 g, 5% w/w) using mortar and pestle and kept in vacuum oven firstly at 453 K for 2 h and then at 473 K for another 1 h. The mixture was then kept at 523 K and 275 °C for 1 h each and then at 573 K and 598 K for 2 h each and then post-curing at 623 K and 648 K for 2 h each to form thermosetting crosslinked polymeric network **3a**.

Crosslinked films were cased in form of 33-mm (diameter) circular disc in aluminium petri dishes on account of ease of removal of hard and brittle films. Casting films on glass petri dishes was not possible as it often led to removal of glass piece from the petri dish which remain attached to the sample. The films were casted by dissolving 5 g of monomer **2a** in 10 mL of acetone, dioxane and DMF, respectively, and then heated firstly at 10 °C below the boiling points of respective solvents and then via process reported above.

Synthesis of di-adamantane substituted resorcinol **1b**, bis-phthalonitrile resin **2b** and its corresponding polymer **3b** involved following steps:

(i) Synthesis of compound 1b (4, 6-diadamantyl resorcinol): To a refluxing solution of resorcinol (11.0 g, 100 mmol) in dry benzene (250 mL) fitted with a Dean Stark assembly, under Ar atmosphere was added Amberlyst-15 resin (2.0 g) and then 1-adamantanol (30.4 g, 200 mmol) in dry benzene (50 mL) was added gradually via dropping funnel for a period of 1 h and the reaction was allowed to reflux at the same temperature for 48 h. The reaction was then cooled to room temperature and filtered through sintered funnel, and the filtrate was dried via rotary evaporator to furnish crude product which was then purified by column chromatography using silica gel (60–120 mesh) and 5% ethyl acetate/hexane as eluent to furnish pure 1b as white solid. (35.2 g, 93.1% yield). M.p by DSC: 543 K, FT-IR (KBr, cm⁻¹) 826, 977, 1100, 1134, 1216, 1398, 1450, 1513, 1612, 2848, 2903, 3553. ¹H NMR (400 MHz, CDCl₃) δ 1.76-2.18 (m, 30H), 5.43 (s, 2H, OH), 6.09 (s, 1H), 7.00 (s, 1H), ¹³C NMR (100 MHz, CD₃OD) δ 33.3 (6×CH), 40.1 (2×C), 40.9 (6×CH₂), 44.7 (6×CH₂), 108.9 (CH), 127.6 (CH), 130.6 (2×C), 158.0 (2×C).; ESI–MS: 379 $[M+1]^+$; Analysis Calculated for $C_{26}H_{34}O_2$: C; 82.49, H; 9.05. Found: C; 82.46, H; 9.09.

(ii) Synthesis of compound 2b [4,4"-(4,6 diadamantyl 1,3-bis-oxyphenyl) diphthalonitrile]: A mixture of 4,6-diadanmantyl resorcinol **1b** (3.78 g, 10 mmol), 4-nitrophthalonitrile (3.46 g, 20 mmol) and potassium carbonate (5.52 g, 40 mmol) in anhydrous DMSO (50 mL) under N₂ atmosphere at room temperature was stirred for 24 h. The reaction mixture was poured in distilled water (200 mL) to obtain white precipitate which was filtered and washed firstly with water (3 × 100 mL) and then with isopropanol (3 × 100 mL). The residue was then dried under vacuum oven at 373 K to obtain compound **2b** as white powder (5.85 g, 92.9% yield). M.p by DSC: 567 K, FT-IR (KBr, cm⁻¹) 1252, 1284, 1310, 1452, 1624, 2230, 2850, 2906. ¹H NMR (400 MHz, CDCl₃) δ 1.72–2.07 (m, 30H), 6.28 (s, 1H), 7.22–7.25 (m, 4H), 7.48 (s, 1H), 7.75 (m, 2H), ¹³C NMR (100 MHz, CDCl₃) δ 28.8 (6×CH), 36.7 (6×CH₂), 37.2 (2×C), 41.3 (6×CH₂), 109.3 (CH), 114.4 (2×C), 114.9 (2×C), 115.2 (2×C), 117.9 (2×C), 121.8 (4×CH), 128.1 (CH) 135.7 (2×CH), 139.8 (2×C), 151.4 (2×C), 161.4 (2×C).; ESI–MS: 631 [M+1]⁺ Analysis Calculated for C₄₂H₃₈ N₄O₂: C; 79.97, H; 6.07, N; 8.88. Found: C; 79.95, H; 6.09, N; 9.02.

(iii) *Preparation of polymer 3b*: Compound **2b** (5 g) was grinded well with m-BAPS (0.025 g, 5% w/w) using mortar and pestle and kept in vacuum oven firstly at 453 K for 2 h and then at 473 K for another 1 h. The mixture was then kept at 523 K and 548 K for 1 h each and then at 573 K and 598 K for 2 h each and then post-curing at 623 K and 648 K for 2 h each to form thermosetting crosslinked polymeric network **3b**.

Crosslinked films of **3a** were casted in the similar way as that of **2a**.

¹H and ¹³C NMR analysis of compound **1a**, **1b**, **2a** and **2b**:

The ¹H NMR analysis of **1a** showed merged multiplet from δ 1.61–2.08 corresponding to 15 adamantyl (H_{Ad}) protons. Singlets at 5.35 and 5.46 correspond to two hydroxy groups labelled as H_c and H_e, respectively. An upfield singlet at 6.23 corresponds to H_d proton due to electron pairdonating effect of hydroxy groups. Doublets at 6.35 and 7.02 correspond to two ortho-coupled protons H_b and H_a with coupling constant of 8 Hz, respectively (Table 1).

The ¹³C NMR of **1a** showed 10 peaks out of which peaks at δ 29.3, 35.8, 36.9 and 40.6 correspond to aliphatic adamantyl carbons. Upfield peak at 103.5 corresponds to C_d carbon due to electron pair-donating effect of hydroxy groups. Peaks at 105.5 and 126.4 correspond to aromatic CH carbons. Peak at 128.1 was due to aromatic quaternery carbon attached to adamantyl group. Downfield peaks at 155.5 and 156.9 correspond to aromatic quaternery carbons attached with negative inductive effect creating hydroxy groups (Table 1).

The ¹H NMR analysis of **1b** showed merged multiplet from δ 1.76–2.18 corresponding to 30 adamantyl (H_{Ad}) protons. A singlet at 5.43 corresponds to two hydroxy groups labelled as H_c. An upfield singlet at 6.09 corresponds to H_b proton due to electron pair-donating effect of hydroxy groups. Peak at 7.02 corresponds proton H_a (Table 1).

The ¹³C NMR of **1b** showed 8 peaks due to highly symmetrical structure out of which peaks at δ 33.3, 40.1, 40.9 and 44.7 correspond to aliphatic adamantyl carbons. Upfield peak at 108.9 corresponds to C_d carbon due to electron pairdonating effect of hydroxy groups. Peak 127.6 corresponds

Table 1 Detailed labelling of ¹H and ¹³C NMR values of compounds 1a-b and 2a-b

Structure and ¹H NMR values





5.46 (H_e, s, 1H, -OH), 6.23 (H_d, s, 1H), 6.35 (H_b, 103.5 (C_d), 105.5 (C_b), 126.4 (C_a) 128.1 (C_f), d, 1H, J = 8.0 Hz), 7.02 (H_a, d, 1H, J = 8.0 Hz).



1b







 δ 33.3 (Cg), 40.1 (Ce), 40.9 (Ch), 44.7 (Cf), δ 1.76-2.18 (H_{Ad}, m, 30H), 5.43 (H_c, s, 2OH,), 108.9 (C_d), 127.6 (C_a), 130.6 (C_b), 158.0 (C_c) 6.09 (H_b, s, 1H), 7.00 (H_a, s, 1H),



 δ 1.62-2.62 (H_{Ad}, m, 15H), 6.57 (H_c, s, 1H), 6.96 $(H_b, d, 1H, J = 8.0 Hz), 7.26-7.28 (H_d, H_i, m, 4H), \delta 28.7 (C_y), 36.6 (C_z), 36.9 (C_w), 41.3 (C_x), \delta 28.7 (C_y), 36.6 (C_z), 36.9 (C_w), 41.3 (C_x), \delta 28.7 (C_y), \delta 28.7 (C_y),$ 7.52 (H_a, d, 1H, J = 8.0 Hz), 7.75 (H_f, d, 1H, J =8.0 Hz), 7.79 (H_g, d, 1H, J = 8.0 Hz)

2H)





109.4 (C_j), 109.6 (C_r), 113.3 (C_d), 114.9 (C_n), 115.2 (C_u), 117.6 (C_b), 117.8 (C_m), 118.0 (C_v), 121.6 (C_h, C_P), 121.8 (C_l, C_t), 122.2 (C_i), 122.3 (Cs), 130.2 (Ca), 135.6 (Ck), 135.8 (Cq), 140.4 (Cf), 152.6(Ce), 154.4 (Cc), 161.0 (Cg), 161.10 (C_o)

> O ď

> > CN



 $\delta \; 1.72 - 2.07 \; (H_{Ad}, \; m, \; 30H), \; 6.28 \; (H_b, \; s, \; 1H), \; 7.22 - \\ \delta \; 28.8 \; (C_o), \; 36.7 \; (C_p), \; 37.2 \; (C_m), \; 41.3 \; (C_n), \; 41.3 \; (C_$ $7.25 \; (\mathrm{H_{e},\,H_{e},\,m,\,4H}), \; 7.48 \; (\mathrm{H_{a},\,s,\,1H}), \; 7.75 \; (\mathrm{H_{d},\,d}, \quad 109.3 \; (\mathrm{C_{i}}), \; 114.4 \; (\mathrm{C_{d}}), \; 114.9 \; (\mathrm{C_{i}}), \; 115.2 \; (\mathrm{C_{k}}), \;$ 117.9 (C_i), 121.8 (C_f, C_g), 128.1 (C_a) 135.7 (C_h) , 139.8 (C_b) , 151.4 (C_c) , 161.4 (C_e)

2b

to aromatic CH carbon. Peak at 130.6 was due to aromatic quaternery carbon attached to adamantyl group. Downfield peak at 158.0 corresponds to aromatic quaternery carbons attached with negative inductive effect creating hydroxy groups (Table 1).

The ¹H NMR analysis of **2a** showed merged multiplet from δ 1.76–2.18 corresponding to 15 adamantyl (H_{Ad}) protons. An upfield singlet at 6.57 corresponds to H_c proton due to electron pair-donating effect of hydroxy groups. Doublets at 6.96 and 7.52 correspond to ortho-coupled proton H_b and H_a with coupling constant of 8 Hz, respectively. Multiplet at 7.26–7.28 corresponds to H_d and H_i protons. Downfield doublet at 7.75 corresponds to H_f proton which is ortho-coupled to H_d via a coupling constant of 8 Hz due to electron-withdrawing effect of nitrile group which was also visible in H_g proton whose peak appeared at 7.79 which is ortho-coupled with H_i proton via a coupling constant of 8 Hz (Table 1).

The ¹³C NMR of **2a** showed 24 peaks due to highly unsymmetrical structure out of which few peaks at merged due to same chemical shift values. Peaks at δ 28.7, 36.6, 36.9 and 41.3 correspond to aliphatic adamantyl carbons. Upfield peaks at 109.4 and 109.6 correspond to C_i and C_r carbon due to para electron pair-donating effect of hydroxy groups. Peaks at 113.3 (C_d), 114.9 (C_n), 115.2 (C_u), 117.6 (C_b), 117.8 (C_m), 118.0 (C_v), 121.6 (C_h, C_P), 121.8 (C_l, C_t), 122.2 (C_i), 122.3 (C_s), 130.2 (C_a), 135.6 (C_k), 135.8 (C_q) correspond to various aromatic carbons as shown in Table 1. Peak at 140.4 was due to aromatic quaternery carbon, C_f attached to adamantyl group. Downfield peaks at 152.6 (C_e) , 154.4 (C_c) correspond to aromatic quaternery carbons attached with negative inductive effect creating hydroxy groups. Further downfield peaks at 161.0 (C_{o}), 161.10 (C_{o}) correspond to aromatic quaternery carbons attached with phthalonitrile benzene ring having negative inductive effect created hydroxy groups and electron-withdrawing effect created through mesomeric effect by nitrile groups (Table 1).

The ¹H NMR analysis of **2b** showed merged multiplet from δ 1.72–2.07 corresponding to 30 adamantyl (H_{Ad}) protons. An upfield singlet at 6.28 corresponds to H_c proton due to electron pair-donating effect of hydroxy groups. A multiplet from 7.22–7.25 corresponds to H_c and H_e protons. A singlet at 7.48 correspond to H_a proton sandwiched between two adamantyl groups. A doublet at 7.75 correspond to H_d proton ortho-coupled with H_e proton via coupling constant of 8 Hz (Table 1).

The ¹³C NMR of **2b** showed only 15 peaks due to highly symmetrical structure. Peaks at δ 28.8 (C_o), 36.7 (C_p), 37.2 (C_m), 41.3 (C_n) correspond to aliphatic adamantyl carbons. Upfield peak at 109.3 corresponds to C_i carbon due to para electron pair-donating effect of hydroxy groups. Peak at 114.9 corresponds to C_d carbon. Peaks at 114.9 (C₁) and 115.2 (C_k) correspond to two nitrile groups. Peak at 117.9 corresponds to C_i carbon attached to nitrile group. Both C_f



Fig. 3 FT-IR spectra of 2a and 2b

and C_g carbons came at same chemical shift value of 121.8 due to highly symmetrical nature of molecule. Peak at 128.1 came due to sandwiched carbon C_a between two adamantyl groups. Peak at 135.7 corresponds to C_h carbon attached with phthalonitrile benzene ring. Peak at 139.8 corresponds to aromatic quaternery carbons attached with adamantyl group. Downfield peak at 151.4 corresponds to aromatic quaternery carbons C_c attached directly with oxygen via aromatic ether linkage. Further downfield peak at 161.4 corresponds to aromatic quaternery carbons C_e attached directly with oxygen via aromatic ether linkage in phthalonitrile benzene ring having negative inductive effect that



Fig. 4 Expanded FT-IR spectra of 3a and 3b

created hydroxy groups and electron-withdrawing effect that created through mesomeric effect by nitrile groups (Table 1).

Results and discussion

FT-IR Analysis for curing of 2a and 2b

The FT-IR analysis of **2a** and **2b** as shown in Fig. 3 showed characteristic peaks at 2232 cm⁻¹ and 2230 cm⁻¹, respectively, corresponding to the $-C\equiv N$ linkage which upon curing diminished in case of cured samples **3a** and **3b** (Fig. 4). The FT-IR spectrum of cured resins could not resolve properly due to highly crosslinked structure. The increase in the intensity of broad merged peaks at form 1500–1750 in case of cured resins showed formation of highly aromatic

ring system corresponding to -C = N linkage of triazine at 1530 cm⁻¹ and 1595 cm⁻¹ due to isoindoline moiety along with -C = C stretching bands at 1610–1650 cm⁻¹. The appearance of peak at 1010 cm⁻¹ indicated formation of dehydrophthalocyanine functionality as well. The broad peak from 500 to 800 cm⁻¹ also gave information about formation of isoindoline skeleton [53] (Fig. 4). The plausible mechanism of curing based on FT-IR results for the formation of triazine, isoindoline and dehydrophthalocyanine skeletons is shown in Fig. 5 i-iv.

Mechanism of Crosslinking and formation of various backbones based on FT-IR.

The formation of triazine can be explained on the basis of trimerization cyclization reaction in which three nitrile





Dehydrophthalocyanine skeleton

Table 2 DSC analysis of bis-phthalonitrile resin monomers 2a, 2b and their corresponding polymeric thermosets 3a, 3b

Sample Name (Uncured)	T _m /K	T _{ons} /K	T _{max} /K	T _{end} / K	Processing Win- dow (T _{ons} -T _m) K	Curing window (T _{ons} -T _{end}) K	Enthalpy of curing(J/g)	Sample Name (Cured)	Tg/K (Cured)
2a	388	465	514	560	77	95	54.3	3a	>673
2b	567	578	589	598	09	20	10.5	3b	>673



Fig. 6 DSC curves of uncured resins 2a and 2b



Fig. 7 DSC curves of cured resins 3a and 3b

Table 3 TG analysis of bis-phthalonitrile thermosets 3a and 3b

Sample Name (Cured)	Td _{ons} /K	Td _{max} /K	Char Yield at 1073 K (%)	LOI (Calcu- lated)
3a	721	778	65	43.1
3b	738	818	70	45.5



Fig. 8 TG analysis of bis-phthalonitrile resin polymers 3a and 3b

groups cyclize via addition reaction resulting in formation of aromatic triazine ring system under thermal treatment as shown in Fig. 5i. In this case there is no role of catalyst so the process is slow and often takes long time with inefficient curing as phthlonitrile resins can be cured without curing catalyst.

The formation of isoindoline skeleton as shown in Fig. 5II has been explained on the basis of nucleophilic attack of diamine on the nitrile group followed by tandem polymerization leading to formation of isoindoline backbone-based crosslinked network as shown in Fig. 3iv. Further tetramerization, cyclization and aromatization of isoindoline skeleton lead to the formation of dehydrophthalocyanine-based crosslinked structure as shown in Fig. 5iii and iv.

Differential scanning calorimetric (DSC) analysis of monomers **2a**, **2b** and polymers **3a** and **3b**.

Differential scanning calorimetry (DSC) analysis of PN resin monomer **2a** showed melting (T_m) at 388 K with onset of curing (T_{ons}) at 465 K along with maximum rate of curing (T_{max}) at 514 K and endset of curing (T_{end}) at 560 K. The processing window for curing calculated from formula (T_{ons} - T_m) was found to be 77 K, while the curing window calculated from the formula (T_{ons} - T_{end}) came 95 K. The DSC scan of its corresponding thermoset polymer **3a** showed

no glass transition temperature (T_g) up to 673 K (Table 2, Figs. 6, 7).

The DSC scan of PN resin monomer **2b** showed melting at 567 K which is expected due to presence of highly rigid bis-adamantylated structure, with onset of curing (T_{ons}) at 578 K with maximum rate of curing (T_{max}) at 589 K and endset of curing (T_{end}) at 598 K with a processing window of 09 K and curing window of 20 K, respectively. The DSC scan of its corresponding thermoset polymer **3b** showed no glass transition temperature (T_g) up to 673 K (Table 2, Figs. 6, 7).

A large processing window in case of **2b** offered better diffusion of resin and wetting of reinforcement material during processing and ample time for removal of base solvent during fabrication of composites. A large curing window ensured that latent curing can be achieved with this resin system which can result in high crosslinking density due to slow curing process [53]. High enthalpy of curing also insured better curing reaction. The low processing and curing window coupled with low heat of enthalpy in case of **3b** indicated processing complexity associated with this resin but with an ensuing advantage of ease of solvent processing.

Thermogravimetric analysis (TG) of thermosets **3a** and **3b**.

Both the cured polymers 3a and 3b were then investigated for thermo-degradation analysis using thermogravimetric analyser under N₂ atmosphere (Table 3, Fig. 8).

The thermogravimetric (TG) analysis of the cured monoadamantly-based polymer **3a** showed approx 5% mass loss up to 721 K (Td_{ons}), with maximum rate of decomposition (Td_{max}) at 778 K along with char yield of 65% at 1073 K. The limiting oxygen index (LOI) calculated from TG results using Krevelen's equation [54] showed value of 43.5%.

[Krevelen's Equation, (LOI) = $17.5 + 0.4(\sigma)$, where σ is the % char yield at 1073 K.]

The TG analysis of the cured bis-adamantly-based polymer resin **3b** showed approximately 5% mass loss up to 738 K (Td_{ons}) with maximum rate of decomposition (Td_{max}) at 818 K along with char yield of 70% at 1073 K. The LOI was found to be 45.5%. The TG analysis of adamantanebased bisphthalonitrile resin polymers showed high degradation temperature of > 673 K and high LOI values of > 40%, thereby ensuring these materials can be used as high-temperature flame-retardant resin. The high thermal stability and char yield of these resins can be attributed to the formation of graphitic structure upon thermal treatment of aromatic backbone structures like phthalocyanine, triazine and isoindoline in the crosslinked polymer [53].

Solubility of monomers 2a and 2b in common solvents.

Both mono- and bis-adamantylated monomers 2a and 2b showed excellent solubility in most of the common organic solvents in comparison to commercial PN resin monomers **BPN** and **RPN** having Log *P* values of 6.92 and 5.24,

Table 4 Solubility of monomers 2a and 2b in various solvents and their comparative analysis with commercially available materials BPN and RPN

Serial No	Solvents	Boiling points at atmos-	Solubility in various solvents				
		pheric pressure/K	2a Log <i>P</i> 7.69	2b Log <i>P</i> 10.14	BPN Log <i>P</i> 6.92	RPN Log <i>P</i> 5.24	
1	n-Hexane	342	_	_	_	_	
2	Benzene	353	-	-	-	_	
3	p-Xylene	411	+	+ +	-	_	
4	CHCl ₃	334	+ + +	+ + +	-	-	
5	CH ₂ Cl ₂	313	+ + +	+ + +	-	-	
6	1,4-Dioxane	373–375	+++	+++	-	-	
7	Diethyl ether	308	+++	+++	-	-	
8	THF	338-240	+++	+ + +	-	-	
9	Ethyl acetate*	350	+ + +	+++	-	_	
10	Acetone*	329	+++	+++	-	-	
11	MEK*	353	+++	+++	-	-	
12	MIBK*	390–391	+ + +	+ + +	-	_	
13	Ethanol*	329	++	+	-	-	
14	Methanol	338	+	-	-	-	
15	DMF	338	+++	+++	+ + +	+ + +	
16	DMAc	438	+ + +	+ + +	+++	+ + +	
17	DMSO	462	+++	+ + +	+ + +	+ + +	
18	NMP	477	+ + +	+ + +	+++	+++	
19	H_2O^*	373	-	-	-	-	

+ + + Soluble at room temperature (301–305 K) \geq 50 mg mL⁻¹

+ + Sparingly soluble at room temp but soluble upon heating

+ Insoluble at room temp but soluble upon heating

_ Insoluble at room temp but partially soluble upon heating

____ Insoluble both at room temp and upon heating

*Common industry-friendly solvents

Table 5 Isothermal ageing of cured samples for 300 h at 573 K

Entry No	Sample Name	Mass loss after 100 h /%	Mass loss after 200 h /%	Mass loss after 300 h /%
1	3a	2.5	2.9	3.2
2	3b	2.7	3.2	3.5

respectively, owing to their high positive Log P values of 7.69 and 10.14, respectively, as shown in Table 4.

The high degree of solubility in common low boiling point solvents provided an additional advantage for these resins over other class of PN resins in terms of solution processing for composite fabrication like hand layup and prepregging as removal of high boiling solvents for PN resins like DMF, and DMAc is very difficult and often inflict deleterious effects on final products in terms of unwanted voids and gaps.

The very reason for high solubility of adamantane substituted molecules in most of the industry friendly organic solvents is due to their highly aliphatic condensed structure implicated by the adamantane moiety having ten carbon groups arranged in a specific conformation within a very confined space. [26–28].

Isothermal Ageing

The isothermal ageing in air of cured **3a** and **3b** was carried out by keeping their samples in a glass Petri dish at 573 K weighing them at 0 h, 100 h, 200 h and 300 h on a microbalance after each thermal operation. The % mass loss for n^{th} hr was calculated from following equation.

Mass loss (%) = $(W_0 - W_n) 100 / W$

where W_0 is initial mass of sample at 0 h and Wn is the mass at n^{th} hr.

The isothermal ageing of **3a** showed 7.7, 8.2 and 8.5% mass loss when measured after 100 h, 200 h and 300 h respectively at 573 K, while **3b** showed 7.2, 7.8 and 8.1% mass loss, respectively, after similar intervals when kept at 573 K. These results indicated that in both the cases initial mass loss for first 100 h was substantial in comparison to mass loss after 200 h and 300 h. The mass loss between 200 to 300 h was minimal. The initial higher mass loss both the cases was probably due to some decomposition of curing agent component of cured matrix or some uncured monomers. The decrease in mass loss with respect to time was probably due to stabilization of matrix by initial loss of volatile degradation products and formation of graphitic structure on the surface of the samples which thereby stopped further oxidation of the samples. The similar pattern of the mass loss for both 3a and 3b could be attributed to same degree of crosslinking of bonds in the matrix (Table 5).

Water uptake properties of 3a and 3b

The % water absorption by cured samples **3a** and **3b** was measured by immersing their casted films on a glass Petri dish into deionised water for 48 h at room temperature (\sim 303 K). The films coated on glass Petri dish were then taken out wiped with tissue paper and quickly weighted on a microbalance. The water uptake of these glass coated films was calculated from the following equation:

Water uptake (%) = $(W_{48} - W_0) 100 / W_0$

where W_0 is initial mass of sample at 0 h and W_{48} is the mass at 48 h.

The water uptake of **3a** was 0.14% which was relatively low due to presence of highly hydrophobic adamantane group along with aromatic content in polymer skeleton comprising of phenyl and hetero-aromatic ring systems like triazine, dehydrophthalocyanine and isoindoline. The water uptake by **3b** was found to be 0.12% which was slightly less in comparison to **3a** probably due to the presence of two hydrophobic adamantane groups in the matrix. Only slight decrease in water absorption also suggested that once the saturation is achieved, further increase in hydrophobicity parameter from (Log P = 7.69 for **3a**) to (Log P = 10.14for **3b**) by incorporating hydrophobic alkyl groups has little effect on water absorption properties (Fig. 2).

Conclusions

- 1. Adamantylated resorcinols **1a** and **1b** have been synthesized via solid acid resin catalysis.
- 2. Bis adamantylated resorcinol **1b**, have been reported first time.
- Adamantylated resorcinols 1a and 1b have been converted to their corresponding PN resin monomers 2a and 2b which have been thermally cured to their corresponding crosslinked polymers 3a and 3b.
- 4. The curing phenomenon of **2a** and **2b** has been studied via FT-IR and DSC.
- 5. The resin monomer **2a** showed much better curing profile via DSC in comparison to **2b** with large processing (77 K) and curing (95 K) window.
- The TGA results of cured resins 3a and 3b showed high thermal stability of ≈ 723 K. (5% mass loss) and char yield of ≥ 65%.
- Both the resins showed excellent solubility in common industry friendly solvents like acetone, ethyl acetate, MEK and MIBK, used for fabrication of fabric reinforced laminates probably due to the presence of highly condense and aliphatic adamantane moiety.
- Cured resins have also been evaluated for their isothermal ageing and water uptake properties taking into account of their end-use application as matrix material for fabrication of composites.

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