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Synthesis and Characterization of Novel Betti Type Cyanate Esters

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Summary

Several aromatic diols bearing amino benzyl linkage in the main chain have been synthesized through high yield Betti reaction, which involves the reaction of an aldehyde with p-amino phenol and 8-hydroxy quinoline. Five different aldehydes have been used to prepare five new bisphenols. These bisphenols were converted to their corresponding cyanate esters by the treatment of cyanogen bromide in the presence of triethyl amine. The structures of the diols and dicyanate esters were confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR spectral studies and elemental analysis. The cyclotrimerization reactions of cyanate esters have been studied by differential scanning calorimetry (DSC). The maximum curing temperatures of these cyanate esters are in the range of 186-201°C. T_g values of the polycyanurate networks are above 270°C. Thermogravimetric analysis (TGA) shows that the 10% weight loss of all the cured cyanate esters is above 400°C in N_2 atmosphere. The char yield is in the range of 66-73%. The flame retardancy of the cyanate ester resins have been studied using Limiting Oxygen Index (LOI) value which is in the range of 43.9-46.7% at 700°C.

Introduction

The modern technology development needs reliable high performance composite materials of light weight with excellent thermal and mechanical properties. The Betti reaction is a chemical reaction of aldehydes, primary aromatic amines and phenols producing α-aminobenzyl phenols [1,2]. Cyanate esters have drawn a great deal of attention as one of the high performance thermosets, comparable to epoxies and polyimides [3,4]. Polycyanurates are addition cured thermoset polymers [5] which are formed when three cyanate ester monomers containing the –OCN functional group undergo a thermally initiated cyclotrimerization reaction to form a six membered oxygen-linked cyanurate ring [6]. It can also be cured in the presence of co-ordination metal catalysts and an active hydrogen initiator. The unique chemistry of –OCN functionality and the aryl polycyanurate network formed after cure creates distinctive features, which can be further enhanced by altering the polyphenol backbone structures [7].

Common characteristics associated with cyanate ester resin systems are low molecular weight (Generally dicyanate monomers are small molecules of low molecular weight), melting point, viscosity, easy processing, aromaticity increasing with cure, weak dipoles, high T_g and disruption of crystallinity by non-symmetric bisphenol linkages [8]. The absence of strong dipoles, attributed to the symmetrical arrangement of electronegative oxygen and nitrogen atoms around an electropositive carbon atom, may explain the characteristically low dielectric loss and moisture absorption properties of polycyanaurates [9]. However, their widespread use is unfortunately limited in many applications by their inherent brittle behaviour [10]. To improve the toughness of a cured cyanate ester resin, approaches such as the preparation of flexibilized cyanate resins, the incorporation of monocyanates, the utilization of rubber toughening technologies and the preparation of semi-interpenetrating networks (SIPNs) have proven useful methods [11,12]. But toughening usually occurs at the expense of other characteristics like thermal stability of the cyanate ester resin [13]. These brittle thermosets may be toughened by altering the structure of dicyanate esters by incorporation of bulky pendant groups as modifiers. With this approach we intended to have crosslinked polymer with high thermal stability and free volume fraction, thereby having widespread aromaticity than tightly packed crosslinked networks (obtained from cyanate esters without bulky group). This paper reports the synthesis of a series of new cyanate esters having different pendant groups by Betti type reaction. Their structural confirmation, thermal properties, and flame retardancy are discussed in this paper.

Experimental

Materials

Anisaldehyde, benzaldehyde, 4-chlorobenzaldehyde, 9-anthraldehyde, napththaldehyde, ethanol, triethylamine, cyanogen bromide (CNBr) and 8-hydroxy quinoline (8-quinolinol) were received from Spectrochem, India. p-Amino phenol was purchased from Lancaster, India. Triethyl amine was distilled from CaH_2 prior to use. Ethanol was refluxed with CaO for six hours and distilled. All other chemicals were used as received unless otherwise mentioned.

Measurements

Fourier transform infrared (FTIR) spectra were recorded in a Nicolet Impact 400 FT-IR spectrometer using KBr pellet. ^1H and ^{13}C nuclear magnetic resonance spectrometer measurements were carried out with a Jeol Ex-400 spectrometer (500 MHz). Samples were prepared in DMSO-d_6 solution and spectra were acquired at 298K using tetramethyl silane (TMS) as the internal standard. Elemental analysis was performed using a Carlo Erbra EA 1108 elemental analyzer. Melting temperatures were determined on an electrothermal melting point apparatus IA 6304 using capillary tubes at a heating rate of 4K/min and are uncorrected. Differential Scanning Calorimeteric analysis (DSC) was carried out using a TA instruments Q10 model at a heating rate of 10°C/ min. Measurements were made under flowing N_2 ($60 mm^3$/min) using sealed, crimped, aluminum pans. Thermogravimetric analysis (TGA) was performed using a TA instruments Q600 model at a heating rate of 20°C/min under flowing N_2 between 25°C and 700°C.

Preparation of bisphenols

In a 100 ml round bottomed flask, 50 ml of ethanol, 2.80g (0.02 mole) of anisaldehyde and 2.24g (0.02 mole) of p-amino phenol were taken. The mixture was stirred at room temperature for 24 hrs. 3.0 g (0.02 mole) of 8-hydroxy quinoline was then added and again stirred for 24 hrs at room temperature. The compound was removed by filtration and recrystalized from ethanol. The solid which separates on cooling was collected and dried at 100°C. M.Pt.155°C; Yield: 82%. The same procedure was adopted for the preparation of other bisphenols.

Spot Test: Test was performed by adding a drop of an ethanol solution of the compound to 1% aqueous ferric chloride solution. All the compounds gave green colour with ferric chloride solution.

Preparation of dicyanates

The dicyanates were prepared as shown in Scheme 1. To a 250 ml three necked flask equipped with an overhead stirrer, thermometer and dropping funnel were added 75 ml of acetone (dried over fresh 4 Å molecular sieves for one day). After cooling to -10°C, 5.99 g (0.05 mol) of BrCN (caution: toxic!) were added and the solution was further cooled to -15°C. A solution of 10.53 g (0.02 mol) of diphenol and 2.86 g (0.02 mol) of triethylamine in 25 ml of acetone was prepared, transferred into a dropping funnel, and added dropwise with rapid stirring over a 40 min period while maintaining the reaction temperature at -15°C [14]. When the mixture had warmed to -2°C it was rapidly filtered and the white coloured ammonium bromide salt ($Et_3N.HBr$) was removed. The filtrate was poured into water. The precipitated product was removed by filtration and recrystallized from chloroform. The solid which separates on cooling was collected and dried at 100°C. The acronym, yield, melting point and elemental analysis of the cyanates are given in Table 1.

[7-(α-cyanato anilino benzyl)-8-cyanato quinoline] (Cy 1) FT-IR (KBr cm^{-1}) 2237, 2273 (ν_{-OCN}), 2852 (ν_{C-H}), 3136 (ν_{N-H}), absence of O-H band at 3300-3500 cm^{-1}. ^{1}H-NMR (DMSO- d_6, ppm): 7.48 (2H, d, H_a); 7.39 (2H, d, H_b); 3.52 (1H, d, H_c); 5.46 (1H, d, H_d); 6.79 (2H, d, H_e); 6.98 (2H, t, H_f); 6.85 (1H, t, H_g); 7.02-7.12 (4H, m, H_{h-k}); 8.39 (1H, d, H_l). ^{13}C-NMR (DMSO-d_6, ppm): C_1- 108.9, C_2- 148.3, C_3- 116.6, C_4- 118.4, C_5- 147.2, C_6- 46.8, C_7- 138.2, C_8- 128.9, C_9- 128.6, C_{10}- 125.8, C_{11}- 118.9, C_{12}- 126.4, C_{13}- 120.6, C_{14}- 127.4, C_{15}- 135.2, C_{16}- 121.5, C_{17}- 151.4, C_{18}- 148.1, C_{19}- 154.5, C_{20}- 109.3.

[7-(α-cyanato anilino chloro benzyl)-8-cyanato quinoline] (Cy 2)

FT-IR (KBr cm^{-1}): 2234, 2269 (ν_{-OCN}), 2866 (ν_{C-H}), 3236 (ν_{N-H}), absence of O-H band at 3300-3500 cm^{-1}. ^{1}H-NMR (DMSO- d_6, ppm): 7.45 (2H, d, H_a); 7.36 (2H, d, H_b); 3.69 (1H, d, H_c); 5.68 (1H, d, H_d); 7.39 (2H, d, H_e); 7.54 (2H, d, H_f); 6.98-7.34 (4H, m, H_{g-j}); 8.47 (1H, d, H_k). ^{13}C-NMR (DMSO- d_6, ppm): C_1- 109.7, C_2- 152.5, C_3- 116.8, C_4- 118.9, C_5- 147.4, C_6- 47.1, C_7- 136.7, C_8- 130.5, C_9- 128.8, C_{10}- 131.3, C_{11}-112.3, C_{12}- 126.9, C_{13}- 121.0, C_{14}- 129.5, C_{15}- 136.0, C_{16}- 122.0, C_{17}- 150.3, C_{18}- 137.7, C_{19}- 152.7, C_{20}- 109.7.

[7-(α-cyanato anilino anisyl)-8-cyanato quinoline] (Cy 3)

FT-IR (KBr cm^{-1}): 2235, 2270 (ν_{-OCN}), 2848 (ν_{C-H}), 3227 (ν_{N-H}), absence of O-H band at 3300-3500 cm^{-1}. ^{1}H-NMR (DMSO- d_6, ppm): 7.78 (2H, d, H_a); 7.45 (2H, d, H_b); 3.06 (1H, d, H_c); 5.32 (1H, d, H_d); 6.91 (2H, d, H_e); 7.12 (2H, d, H_f); 3.81 (3H, s, H_g); 7.29-7.38 (4H, m, H_{h-k}); 8.82 (1H, d, H_l). ^{13}C-NMR (DMSO-d_6, ppm): C_1- 109.8, C_2- 151.8, C_3- 116.1, C_4- 118.2, C_5- 147.7, C_6- 46.2, C_7- 137.8, C_8- 129.2, C_9- 114.9,

C_{10}- 159.9, C_{11}- 54.1, C_{12}- 113.1, C_{13}- 126.1, C_{14}- 122.0, C_{15}- 128.4, C_{16}- 135.9, C_{17}- 123.9, C_{18}- 150.2, C_{19}- 135.7, C_{20}- 152.7, C_{21}-109.8.

[7-(α-cyanato anilino naphthyl)-8-cyanato quinoline] (Cy 4)

FT-IR (KBr cm^{-1}): 2236, 2268 (ν_{-OCN}), 2881 (ν_{C-H}), 3254 (ν_{N-H}), absence of O-H band at 3300-3500 cm^{-1}. ^{1}H-NMR (DMSO- d_6, ppm): 7.81 (2H, d, H_a); 7.58 (2H, d, H_b); 3.78 (1H, d, H_c); 5.33 (1H, d, H_d); 7.51 (2H, d, $H_{e,h}$); 7.46 (2H, t, $H_{f,g}$); 7.48 (1H, s, H_i); 7.32 (1H, t, H_j); 7.30 (1H, d, H_k); 6.97-7.12 (4H, m, H_{l-o}); 8.59 (1H, d, H_p). ^{13}C-NMR (DMSO-d_6, ppm): C_1- 109.2, C_2- 154.1, C_3- 133.1, C_4- 114.2, C_5- 149.3, C_6- 48.5, C_7- 133.9, C_8- 124.6, C_9- 126.9, C_{10}- 126.5, C_{11}- 133.5, C_{12}- 128.6, C_{13}-125.6, C_{14}- 125.2, C_{15}- 124.2, C_{16}- 132.6, C_{17}- 112.9, C_{18}- 125.8, C_{19}- 121.6, C_{20}- 128.2, C_{21}- 135.4, C_{22}- 124.0, C_{23}- 151.2, C_{24}- 134.9, C_{25}- 154.1, C_{26}- 109.6.

Table 1: Acronym, yield, melting point and elemental analysis of dicyanates

S.No.	Cyanate ester code	Yield (%)	M.Pt. (°C)	Elemental Analysis		
				C	H	N
1.	Cy 1 M.F. $C_{24}H_{16}N_4O_2$ M.Wt. 392.35	79	116	C 73.46 F 73.12	C 4.11 F 4.02	C 14.27 F 14.09
2.	Cy 2 M.F. $C_{24}H_{15}N_4O_2Cl$ M.Wt.426.79	75	112	C 67.54 F 67.19	C 3.54 F 3.29	C 13.12 F 12.98
3.	Cy 3 M.F. $C_{25}H_{18}N_4O_3$ M.Wt. 422.36	86	96	C 71.09 F 70.89	C 4.29 F 4.08	C 13.26 F 13.18
4.	Cy 4 M.F. $C_{28}H_{18}N_4O_2$ M.Wt. 442.40	81	118	C 76.01 F 75.93	C 4.10 F 3.99	C 12.66 F 12.54
5.	Cy 5 M.F. $C_{32}H_{20}N_4O_2$ M.Wt. 492.46	83	124	C 78.04 F 77.91	C 4.09 F 3.97	C 11.37 F 11.22

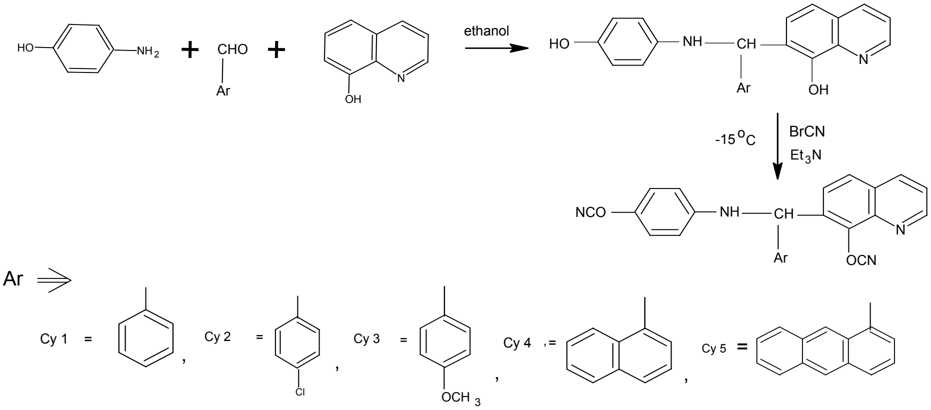
M.F. Molecular formula, M.Wt. Molecular weight, C: calculated value, F: Found value

[7-(α-cyanato anilino anthryl)-8-cyanato quinoline] (Cy 5)

FT-IR (KBr cm^{-1}): 2234, 2272 (ν_{-OCN}), 2872 (ν_{C-H}), 3239 (ν_{N-H}), absence of O-H band at 3300-3500 cm^{-1}. ^{1}H-NMR (DMSO- d_6, ppm): 7.81 (2H, d, H_a); 7.51 (2H, d, H_b); 3.66 (1H, d, H_c); 5.42 (1H, d, H_d); 7.61 (4H, d, $H_{e,h}$); 7.39 (4H, t, $H_{f,g}$); 7.44 (1H, s, H_i), 7.72-7.80 (4H, m, H_{j-m}); 8.50 (1H, d, H_n). ^{13}C-NMR (DMSO- d_6, ppm): C_1- 108.5, C_2- 153.9, C_3- 132.4, C_4- 116.5, C_5- 148.8, C_6- 48.2, C_7- 134.1, C_8- 129.5, C_9- 130.0, C_{10}- 137.4, C_{11}- 127.4, C_{12}- 126.2, C_{13}- 126.9, C_{14}- 127.0, C_{15}- 119.2, C_{16}- 129.1, C_{17}- 119.1, C_{18}- 126.4, C_{19}- 136.2, C_{20}- 122.9, C_{21}- 154.1, C_{22}- 145.8, C_{23}- 155.1, C_{24}- 109.3.

Synthesis of Cyanurate networks

All the cyanate esters were trimerized by thermal curing according to the cure schedule:100°C (30 min) → 150°C (30 min) → 200°C (60 min) → 250°C (3hr). The curing reaction was conducted in hot air oven. Thermal properties of these cured dicyanate esters have been studied.



Scheme 1. General preparation of bisphenols and dicyanates

Results and discussion

The bisphenol reaction was performed by mixing equimolar amounts of amine and aldehyde in a sufficient amount of ethanol to dissolve the Schiff base that is usually formed and subsequent adding of 8-hydroxy quinoline. It may be that the reaction involves the addition of 8-quinolinol to a Schiff base. The new amino benzyl linkage formed, was confirmed by spot test. The spot test will not answer for the either of the reactants or for the Schiff base formed as the intermediate. It only answers (gives green colour) for the amino benzyl linkage formed after the reaction with 8-hydroxy quinoline. Hence we can confirm the linkage formation. All the bisphenols gave a green colour with aqueous ferric chloride solution and characteristic colours with sulphuric (red colour) and nitric acid (yellow or violet). All the three tests were not answered by the reagents alone or by the Schiff bases which were tested at the first 24 hrs of the reaction.

Spectral characterizations

FT-IR spectroscopy: The prepared bisphenols were treated with BrCN in the presence of a base at low temperatures (-15° to -5°C) to give the corresponding dicyanate esters. Figure 1 shows the FT-IR spectrum of dicyanate esters. The bands at 2235 and 2270 cm^{-1} are characteristic of –OCN stretching vibration. The band at 2891cm^{-1} is due to the presence of aldehydic C-H stretching vibration. A weak absorption was observed at 3385 cm^{-1} due to the presence of secondary amine. The disappearance of broad O-H band at 3400-3500 cm^{-1} shows the completion of the reaction.

^{1}H-NMR spectroscopy: Furthermore ^{1}H-NMR supports the confirmation of the dicyanate esters structure (scheme 2). The $-OCH_3$ protons appear at 3.8-3.9 ppm. Aromatic protons appear in the range of 6.8-8.5 ppm. The proton of a secondary amine appears as a doublet at 3-4 ppm. The doublet of aldehydic –CH appears at 5-6 ppm. The absence of hydroxyl protons at 9-10 ppm proves the formation of the dicyanate esters.

^{13}C-NMR spectroscopy: The carbon of the cyanate group is found at 108-109 ppm. Aromatic carbons appear in the wide range of 112-158 ppm. The aldehydic carbon appears in the range of 46-48 ppm. The carbons ortho to -OCN group appears in the

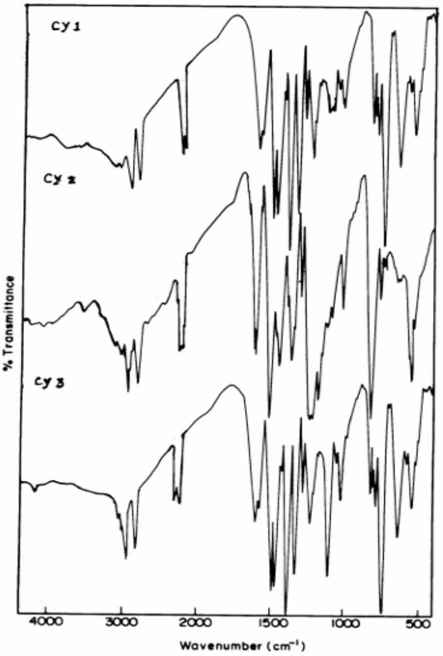
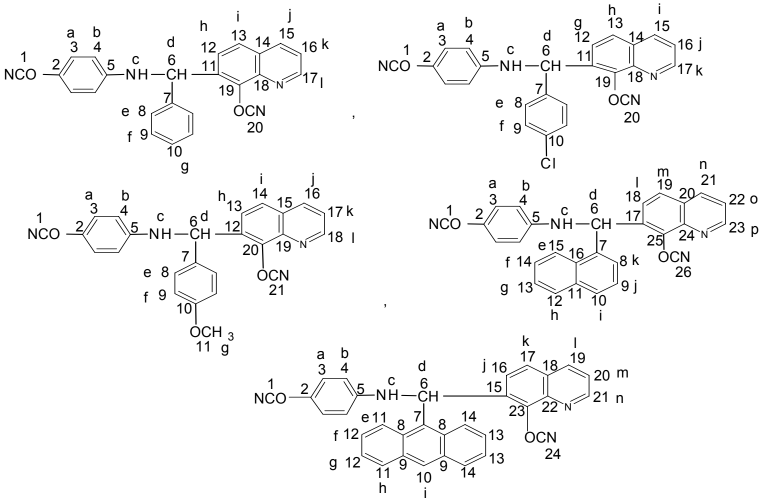


Figure 1. FT-IR spectra of dicyanate esters



Scheme 2. Naming for NMR interpretation

range of 148-155 ppm. The signal at 54.1 ppm corresponds to $-OCH_3$ carbon. The carbon ortho to quinoline nitrogen appears at around 152 ppm.

DSC Analysis

The thermal properties of the dicyanate esters were characterized by DSC. Figure 2 represents the DSC scan of dicyanate esters and the data are presented in Table 2.

The melting point of the cyanate esters is indicated as a sharp peak indicated its high purity. All the dicyanates show an onset of cure at around 150°C and the maximum curing temperature of these cyanate esters are in the range of 186°C-201°C without addition of catalyst. The percentage conversion is in the range of 81-90% for all the dicyanate esters prepared. The reactivity of cyanate ester bonded to the phenol and cyanate ester bonded to the quinoline may differ. But the cure behaviour obtained from DSC shows single exotherm only. The cured anthraldehyde dicyanate ester shows highest glass transition temperature. This may be attributed to its restricted molecular mobility due to its bulky nature. Similar explanation can be offered for naphthaldehyde dicyanate ester. But benzaldehyde based dicyanate ester having smaller pendant group shows lower glass transition. On comparing chlorobenzaldehyde and anisaldehyde, anisyl dicyanate ester having electron releasing –OCH_3 is likely to have weak van der waals forces with the adjacent polymer cyanurate ring [15,16]. Hence, this cyanate shows higher T_g value. Whereas the chlorobenzaldehye dicyanate ester having electron withdrawing –Cl group has lower T_g. From the above results it is understood that as the size of the pendant ring (benzaldehyde, naphthaldehyde, anthraldehyde) increases, its T_g also increases due to its bulky and rigid structures [17]. From the view point of substituted benzaldehydes (anisaldehyde, chlorobenzaldehye), the electron releasing anisyl group has higher T_g than electron withdrawing chloro group.

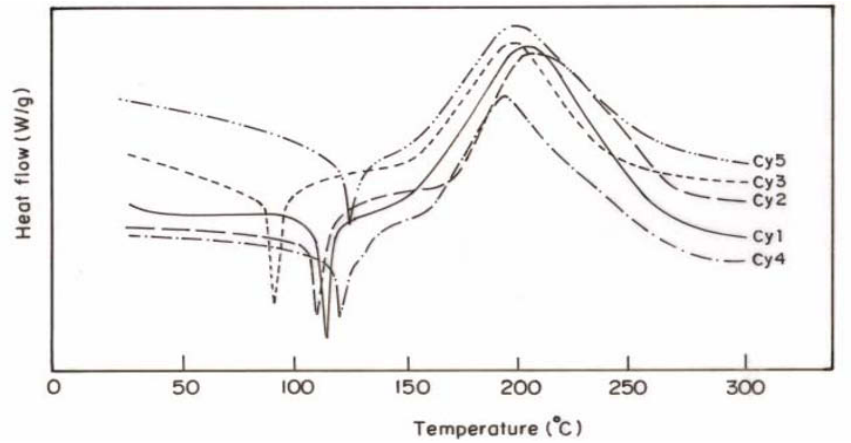


Figure 2. DSC scan of dicyanate esters

Table 2: Thermal Behaviour of cured dicyanate esters

Sample code	M.pt (°C)	Onset of cure (°C)	Maximum cure (°C)	End of cure (°C)	T_g (°C)	Processing window	ΔH (J/g)
Cy 1	116	168	201	271	271	52	193.1
Cy 2	112	149	192	273	273	37	207.3
Cy 3	96	148	187	280	277	52	204.6
Cy 4	118	155	186	276	280	37	190.3
Cy 5	124	133	201	282	282	9	224.6

Thermal stability

Cyanate esters are well known for their good thermal stability due to their aromatic ring and cyanurate ring, which are formed by thermal/catalytic cyclotrimerization during cure [18]. The thermal degradation of the cured cyanate esters were studied by TGA and the thermograms are shown in Figure 3. Among the dicyanate esters prepared, the anthraldehyde dicyanate ester shows highest thermal stability. This may be due to its bulky nature which acts as pendant, makes larger free volume fraction in the polycyanurate network. The free volume fraction (air) is responsible for the low coefficient of thermal expansion and low dielectric loss [19]. This factor may be attributed to the high thermal stability of the dicyanate ester. From the same view point (bulky nature), the naphthaldehyde dicyanate ester shows the initial decomposition at 392°C comparatively lower than that of anthraldehyde dicyanate ester. The reverse reason holds good for benzaldehyde. Because, being shorter and smaller pendant, the benzaldehyde dicyanate shows least thermal stability of 382°C. In the substituted benzaldehydes, the anisaldehyde dicyanate shows higher thermal stability which may be due to their rigid structure and weak Van der Waals forces between the polymer chains. Chlorobenzaldehyde shows less thermal stability due to its electron withdrawing nature. The 10% weight loss values are in the range of 402-427°C. The T10 values also follow the same trend as initial decomposition of dicyanate esters. The char yield for the prepared polymers is in the range of 66-73%. Hence, these dicyanate esters have significant flame retardant property.

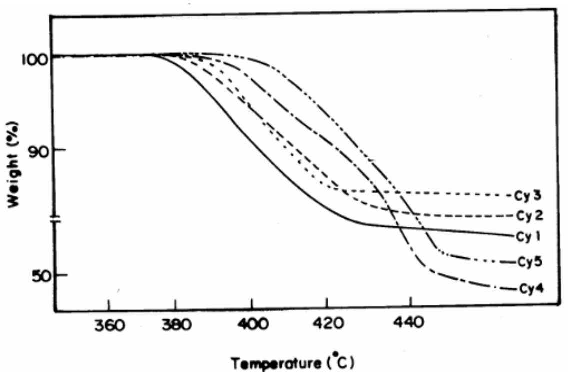


Figure 3. Thermograms of dicyanate esters

Table 3: Thermal stability of cured dicyanate esters

Sample code	T_i (°C)	T_{10} (°C)	Char Yield (%)	LOI Value
Cy 1	382	402	70	45.5
Cy 2	384	414	71	45.9
Cy 3	386	408	73	46.7
Cy 4	392	421	66	43.9
Cy 5	403	427	69	45.1

T_i : Initial decomposition; T_{10} : 10% weight loss; LOI : Limiting oxygen index

Flame retardancy

Polycyanurates exhibit good [20] to outstanding [21] fire resistance [22,23] and high char yield. Increasing char formation could limit the production of combustible gases, decrease the exothermicity of the pyrolysis reaction and decrease the thermal conductivity of the resin consequently to limit the resin's flammability. The char yield of the cured resins (Cy 1 to 5) are found to be in the range of 66-73% indicating the good flame retardancy of the resin (Table 3). The flame retardancy of this cured cyanate ester resin was confirmed by their limiting oxygen index (LOI) value. The LOI values of the polymer systems should be above the threshold value of 26, to render them self-extinguishing and for their qualification for many applications requiring good flame resistance. The LOI value was calculated by using Krevelen's equation, LOI = $17.5 + 0.4 (\sigma)$ where σ is the percentage of char yield. It was found that the LOI values of these polymers are consistently >40, indicating good flame retardancy [21]. The gist is that the introduction of a flexible phenyl (or naphthyl) group into the rigid aromatic polymer would enhance the flame retardancy and improve the solubility of the polymer in organic solvents without sacrificing its inherent thermal stability [24]. Since, all the substituents on cyanate ester backbone are introduced as pendant groups only a marginal difference (43-45) was observed in the LOI value.

Conclusions

A series of dicyanates and their bisphenol precursors with pendant aldehydic group have been prepared by Betti type reaction. Their structures have been confirmed by FT-IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis. It was found that the cured dicyanate esters have high (271-282°C) glass transition temperature. The thermograms of dicyanate esters show single stage decomposition in the range of 382-403°C. The T_{10} for all the cyanate esters are in the range of 402-427°C. The char yield is above 65%. The LOI value which is calculated from char yield is in the range of 43.9-46.7% at 700°C. From the above results it is understood that as the size of the pendant ring (benzaldehyde, naphthaldehyde, anthraldehyde) increases, its thermal properties also increases due to its bulky and rigid structures. From the view point of substituted benzaldehydes (anisaldehyde, chlorobenzaldehye), the electron releasing anisyl group incorporates higher thermal properties than electron withdrawing chloro group.

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