

Synthesis and Characterization of Dicyanate Monomers Containing Methylene Spacers

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ABSTRACT: The bisphenols containing methylene spacer were prepared by treating eugenol/2-allyl phenol with 2,6-dimethyl phenol/guaiacol/*o*-cresol in the presence of AlCl₃. All the bisphenols were converted to their respective cyanate esters by treating with CNBr. The structural confirmation was done by FTIR, ¹H NMR, ¹³C NMR spectral methods, and elemental analysis. Thermal characterization was done by DSC and TGA. DSC transition shows that the *T_g* is in the range of 208–239°C. The *T_g* is highest for the cyanate ester Cy(b) with symmetric structure. The *T_g* of the cured network depends on the length

and symmetry of the monomer, *T_g* being higher for shorter and the para-substituted monomers. The *T₁₀* values are in the range of 364–381°C. The char yield is in the range of 47–53%. From the char yield, the limiting oxygen index (LOI) value was determined, which is used to confirm the flame retardancy of the cyanate ester resins. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 938–944, 2008

Key words: cyanate esters; methylene spacer; toughness; symmetry-high *T_g*; thermal stability

INTRODUCTION

Cyanate ester resins are an important class of polymers that have been under intense investigation and development in the past few years because of their unique properties such as low curing temperatures and high thermal stability, which give them a distinct advantage over other resin systems.¹ Cyanate ester resins are used for a variety of electronics and microelectronics applications.² Presently, the bulk of cyanate ester resins are consumed by the high-speed electronics industry, which was once dominated by epoxy resins.³ Cyanate esters differ from multifunctional epoxies and bismaleimides in at least two major aspects. The cyanate esters often have a lower crosslink density and an increase in the flexibility due to the high percentage of oxygen linkages (67% rotational freedom).⁴ This characteristic may allow for high fracture toughness and lower modulus values relative to the epoxy and bismaleimide counterparts.⁵ In addition, reactive thermoplastic toughening has been successfully applied to cyanate systems.

Cyanate esters possess attractive features like high *T_g*, built-in toughness, radar transparency, good flame resistance, absence of strong dipoles, and hence low moisture absorption and dielectric properties.⁶ For example, monomers ranging from high melting crystalline solids to low viscosity liquids have been reported, which are a function of their molecular structure. Hence, the aim of this research was the synthesis of new dicyanate monomers that may improve some of the beforementioned properties. On this basis, dicyanate monomers with methylene spacer on the polymer backbone have been synthesized. It was expected that the incorporation of flexible aliphatic methylene spacer between the reactive end units could afford a moderate improvement in toughness and decrease in dielectric properties. Increasing bulkiness of the hydrocarbon bridging units [e.g., methylene < isopropylene < dicyclopentadiene < *meta*-diisopropenylbenzene (RTX-366)] progressively lowers dielectric constant by diluting dipole concentrations and decreasing electronegativity of the substituted benzene rings.⁷ A chemical modification, *ortho*-methylation also significantly lowers dielectric constant by shielding and weakening the C—O, C—N, and C=N dipoles. *Ortho*-alkyl substituents may also depress dielectric constant (*D_k*) values by contributing increased free volume (*D_k* of air is 1.00). This study deals with the synthesis of cyanate esters with methylene units. Their structural characterization and thermal properties are also discussed.

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EXPERIMENTAL

Materials

Eugenol (4-allyl-2-methoxy phenol) and 2-allyl phenol were purchased from Lancaster (Chennai, India). Guaiacol, *o*-cresol, toluene, dichloromethane, and 2,6-dimethyl phenol were purchased from SRL, Mumbai, India. Cyanogen bromide (CNBr, *toxic!*), triethyl amine, and anhydrous aluminum chloride were purchased from Spectrochem (Mumbai, India). All reagents were used as received, except triethyl amine which was distilled from CaH₂ prior to use.

Measurements

Fourier transform infrared (FTIR) spectra were recorded in a Nicolet impact 400 spectrometer using KBr pellet. ¹H and ¹³C nuclear magnetic resonance spectrometer measurements were carried out with a Jeol Ex-400 spectrometer (500 MHz). Samples were prepared in CDCl₃ solution and spectra were acquired at 298 K using tetramethyl silane (TMS) as the internal standard. Elemental analysis was performed using a Carlo Erbra EA 1108 elemental analyzer. Differential scanning calorimetric analysis (DSC) was carried out using a TA instruments Q10 model at a heating rate of 10°C/min. Measurements were made under flowing N₂ (60 mL/min) using sealed, crimped, aluminum pans. Thermogravimetric analysis (TGA) was performed using a TA instruments Q 600 model at a heating rate of 20°C/min under flowing N₂ between 25 and 800°C.

Synthesis of bisphenols containing methylene units

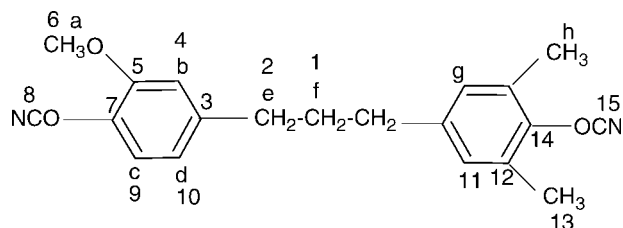
To a three-necked round bottomed flask equipped with a stirrer and condenser, 0.12 mol (15.8 g) of guaiacol and 2 wt % AlCl₃ (based on Eugenol; 0.04 g) were added. The reaction mixture was gradually heated to 80°C, and 0.018 mol (3 g) of eugenol was added in drops over a period of 45 min. The same temperature was maintained for another 1.5 h. After the reaction was completed, 0.01 mol of 20 wt % NaOH(aq) was added and the mixture was stirred for 0.5 h. The reaction mixture was filtered and the filtrate was extracted with water three times. The organic phase was then distilled to remove excess guaiacol. The crude product was dissolved in toluene and extracted with water several times. Then the organic phase was distilled for the removal of toluene and water.⁸ The liquid product was obtained with an yield of 87%. The structure of the product was confirmed by FTIR spectroscopy. The bands observed for the bisphenols with methylene spacer are O—H stretching vibration at 3375–3490 cm⁻¹, asymmetric and symmetric stretching vibration of

—CH₂ around 2900 and 2800 cm⁻¹, respectively, and absence of bands due to allyl CH=CH stretching vibration at 1640 cm⁻¹. All the other bisphenols were prepared by following the same procedure.

Synthesis of cyanate ester monomers

To a 250-mL three-necked round bottomed flask fitted with an overhead stirrer, nitrogen inlet, and dropping funnel, 75 mL of acetone (dried over fresh 4 Å molecular sieves for 1 day) was added. After cooling to -10°C, 0.1 mol (11 g) of CNBr was added and the solution was further cooled to -15°C. A solution of 0.05 mol (14.85 g) of bisphenol(a) and 0.05 mol (7.2 mL) of triethyl amine in 25 mL of acetone was prepared, transferred to a dropping funnel, and added dropwise with rapid stirring over a period of 1.5 h while maintaining the reaction temperature at -15°C. When the mixture had warmed to -2°C it was rapidly filtered and the white ammonium bromide salt (Et₃N·HBr) was removed.⁹ The cold filtrate and wash was diluted with 100 mL of cold dichloromethane and rapidly extracted with 100 mL of cold distilled water and twice with 50 mL of cold 1% aqueous NaCl solution. The clear CH₂Cl₂ solution was then vacuum-distilled to yield resinous mass. All other prepared bisphenols were converted into the corresponding dicyanate ester monomers in a similar way.

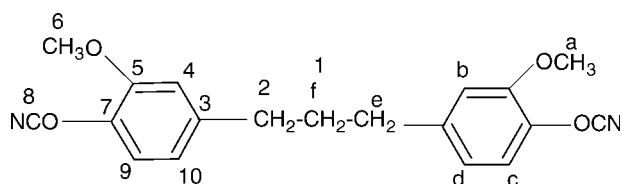
Cy(a): FTIR (KBr, cm⁻¹): 2232, 2259 (ν_{-OCN}), 2959 (asym ν_{C-H}), 2860 (sym ν_{C-H}), absence of O—H band at 3300–3500 cm⁻¹. ¹H NMR (CDCl₃, ppm): 3.73 (3H, s, H_a); 7.15 (1H, s, H_b), 6.94 (1H, d, H_c); 6.75 (1H, d, H_d); 2.55 (4H, t, H_e); 1.95 (2H, q, H_f); 6.87 (2H, s, H_g); 2.35 (6H, s, H_h). ¹³C NMR (CDCl₃, ppm): C₁ = 28.8, C₂ = 35.9, C₃ = 131.7, C₄ = 112.7, C₅ = 154.5, C₆ = 56.2, C₇ = 152.7, C₈ = 109.3, C₉ = 117.0, C₁₀ = 121.9, C₁₁ = 124.6, C₁₂ = 122.9, C₁₃ = 14.7, C₁₄ = 152.9, C₁₅ = 109.5.



Cy(a)

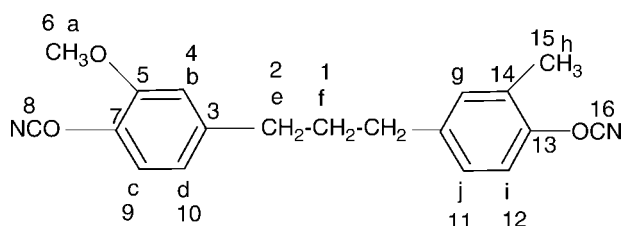
Cy(b): FTIR (KBr, cm⁻¹): 2235, 2270 (ν_{-OCN}), 2981 (asym ν_{C-H}), 2856 (sym ν_{C-H}), absence of O—H band at 3300–3500 cm⁻¹. ¹H NMR (CDCl₃, ppm): 3.81 (6H, s, H_a); 6.89 (2H, s, H_b), 6.87 (2H, d, H_c); 6.78 (2H, d, H_d); 2.61 (4H, t, H_e); 1.92 (2H, q, H_f). ¹³C NMR (CDCl₃, ppm): C₁ = 28.9, C₂ = 36.0, C₃

= 132.4, C₄ = 114.9, C₅ = 155.7, C₆ = 55.7, C₇ = 152.5, C₈ = 109.8, C₉ = 117.1, C₁₀ = 123.1.



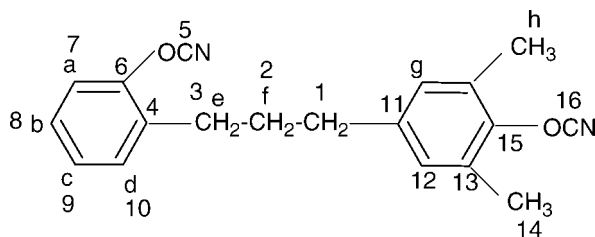
Cy(b)

Cy(c): FTIR (KBr, cm⁻¹): 2234, 2266 (ν_{-OCN}), 2979 (asym ν_{C-H}), 2852 (sym ν_{C-H}), absence of O—H band at 3300–3500 cm⁻¹. ¹H NMR (CDCl₃, ppm): 3.81 (3H, s, H_a); 7.18 (1H, s, H_b), 7.21 (1H, d, H_c); 7.11 (1H, d, H_d); 2.57 (4H, t, H_e); 1.89 (2H, q, H_f); 6.77 (1H, d, H_g); 2.40 (3H, s, H_h); 6.85 (1H, d, H_i); 6.77 (1H, d, H_j). ¹³C NMR (CDCl₃, ppm): C₁ = 28.8, C₂ = 35.9, C₃ = 132.6, C₄ = 114.8, C₅ = 154.6, C₆ = 56.0, C₇ = 152.9, C₈ = 109.7, C₉ = 117.8, C₁₀ = 123.4, C₁₁ = 127.8, C₁₂ = 116.0, C₁₃ = 152.5, C₁₄ = 126.3, C₁₅ = 14.1, C₁₆ = 109.5.



Cy(c)

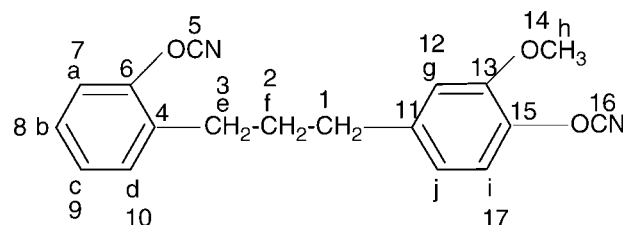
Cy(d): FTIR (KBr, cm⁻¹): 2234, 2268 (ν_{-OCN}), 2954 (asym ν_{C-H}), 2866 (sym ν_{C-H}), absence of O—H band at 3300–3500 cm⁻¹. ¹H NMR (CDCl₃, ppm): 7.02 (1H, d, H_a); 6.96 (1H, t, H_b), 6.87 (1H, t, H_c); 6.81 (1H, d, H_d); 2.57 (4H, t, H_e); 1.88 (2H, q, H_f); 6.76 (2H, s, H_g); 2.29 (6H, s, H_h). ¹³C NMR (CDCl₃, ppm): C₁ = 36.2, C₂ = 29.3, C₃ = 24.9, C₄ = 126.1, C₅ = 109.4, C₆ = 152.3, C₇ = 116.2, C₈ = 128.7, C₉ = 127.9, C₁₀ = 130.8, C₁₁ = 136.9, C₁₂ = 129.6, C₁₃ = 126.2, C₁₄ = 14.2, C₁₅ = 152.1, C₁₆ = 109.7.



Cy(d)

Cy(e): FTIR (KBr, cm⁻¹): 2229, 2258 (ν_{-OCN}), 2952 (asym ν_{C-H}), 2872 (sym ν_{C-H}), absence of O—H band at 3300–3500 cm⁻¹. ¹H NMR (CDCl₃, ppm):

7.06 (1H, d, H_a); 6.94 (1H, t, H_b), 6.83 (1H, t, H_c); 6.81 (1H, d, H_d); 2.54 (4H, t, H_e); 1.93 (2H, q, H_f); 6.79 (1H, s, H_g); 3.72 (3H, s, H_h); 6.84 (1H, d, H_i); 6.75 (1H, d, H_j). ¹³C NMR (CDCl₃, ppm): C₁ = 35.9, C₂ = 29.1, C₃ = 24.9, C₄ = 126.2, C₅ = 109.5, C₆ = 152.4, C₇ = 116.7, C₈ = 128.8, C₉ = 128.0, C₁₀ = 131.0, C₁₁ = 137.1, C₁₂ = 114.8, C₁₃ = 155.6, C₁₄ = 56.2, C₁₅ = 152.2, C₁₆ = 109.8, C₁₇ = 117.1.



Cy(e)

Homopolymerization of cyanate esters

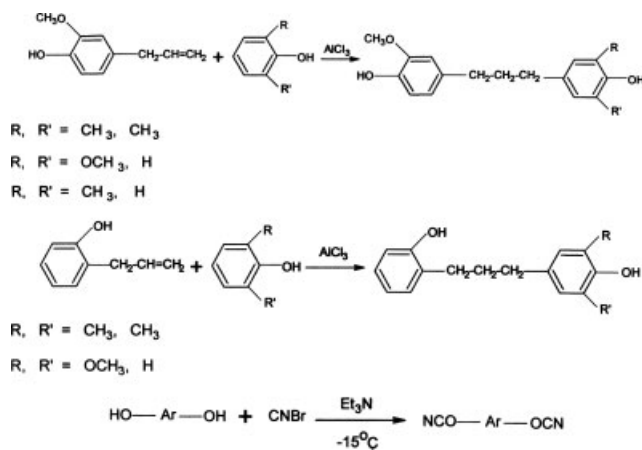
All the cyanate esters were trimerized by thermal curing according to the following cure schedule: 100°C (30 min) → 150°C (30 min) → 200°C (60 min) → 250°C (3 h).^{10,11} Reactant consumption and product formation were monitored using infrared spectroscopy. The absorption bands for the reactive cyanate ester functionality appear at 2270 cm⁻¹. The triazine ring shows a strong absorption at 1565 cm⁻¹. These bands were monitored to indicate the completion of the cure.¹²

RESULTS AND DISCUSSION

The bisphenols with aliphatic chain between the two phenolic groups were prepared by treating eugenol/2-allyl phenol with 2,6-dimethyl phenol/guaiacol/*o*-cresol in the presence of AlCl₃.⁸ The temperature of the reaction was maintained at 80°C. The compound was extracted with dichloromethane and the proposed structure was confirmed by spectroscopic methods. All the bisphenols were treated with CNBr and converted to their respective cyanate esters. The synthesis of dicyanate monomers with methylene spacer is shown in Scheme 1.⁹

FTIR was used to confirm the formation of cyanate ester group. Figure 1 shows the FTIR spectra of dicyanate esters. The band at 2236 and 2272 cm⁻¹ corresponds to the —OCN group. The band at around 2952 and 2861 cm⁻¹ corresponds to the asymmetric and symmetric C—H stretching vibration of —CH₂— group. The absence of band at 3400–3500 cm⁻¹ for —OH band shows the completion of the reaction.

Figure 2 shows the ¹H NMR spectra of the prepared cyanate esters. The Ar—CH₂ protons appear as



Scheme 1 Synthesis of cyanate esters with aliphatic chain between the two phenolic groups.

triplet at 2.55 ppm. The Aliph-CH₂ protons appear as pentet at 1.95 ppm. The aromatic protons appear in the range of 6.75–7.06 ppm. Methoxy protons appear as a singlet at around 3.7–3.81 ppm. The methyl group appears as doublet at around 2.29–

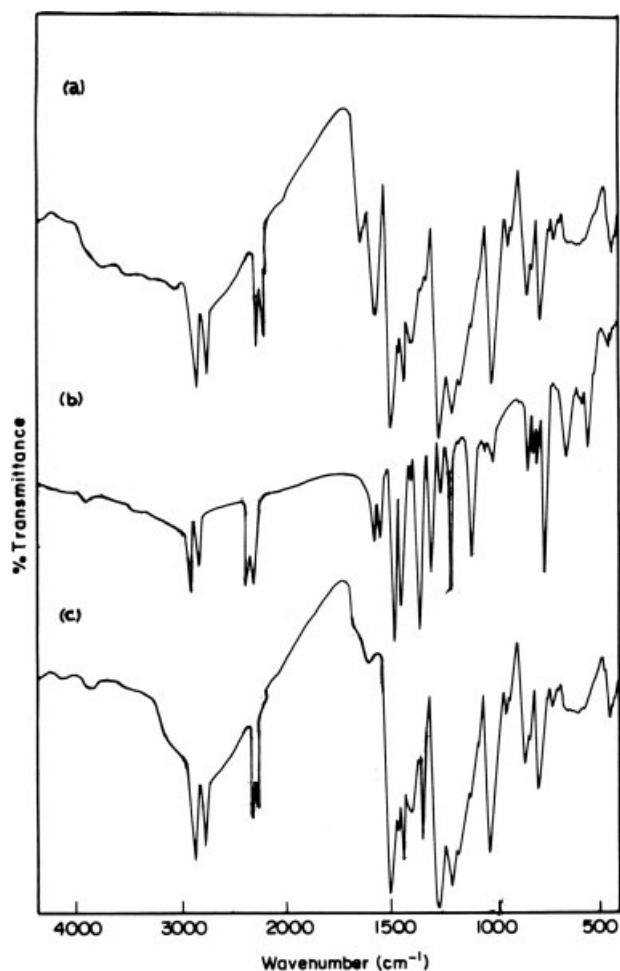


Figure 1 FTIR spectra of dicyanate monomers.

2.40 ppm. The absence of hydroxyl protons at 9.0–10.5 ppm and allyl —CH=CH₂ protons at 5.25–6.03 ppm proves the formation of the dicyanate esters.

The ¹³C NMR spectra of dicyanate monomers is shown in Figure 3. Methylene carbons appear at around 28–36 ppm. The characteristic carbon of the cyanate functionality is found at around 109.5 ppm. Aromatic carbons appear in the range of 124.6–155.7 ppm. The methyl carbon appears at 14.3 ppm. The signal at around 56.2 ppm corresponds to methoxy carbon. The elemental analysis values are given in Table I. The calculated and experimental values of elemental analysis data are in good agreement. Hence, the proposed structure of the dicyanate is confirmed.

Thermal characterization of dicyanate monomers

DSC analysis

Cyanates react simply by heating via a highly selective cyclotrimerization reaction to produce (aryloxy)-1,3,5-triazines (ether ketone). No secondary reactions take place or only to a very small extent, and thus, in the case of dicyanate esters, highly crosslinked polymers (so-called polycyanurates) with a very reg-

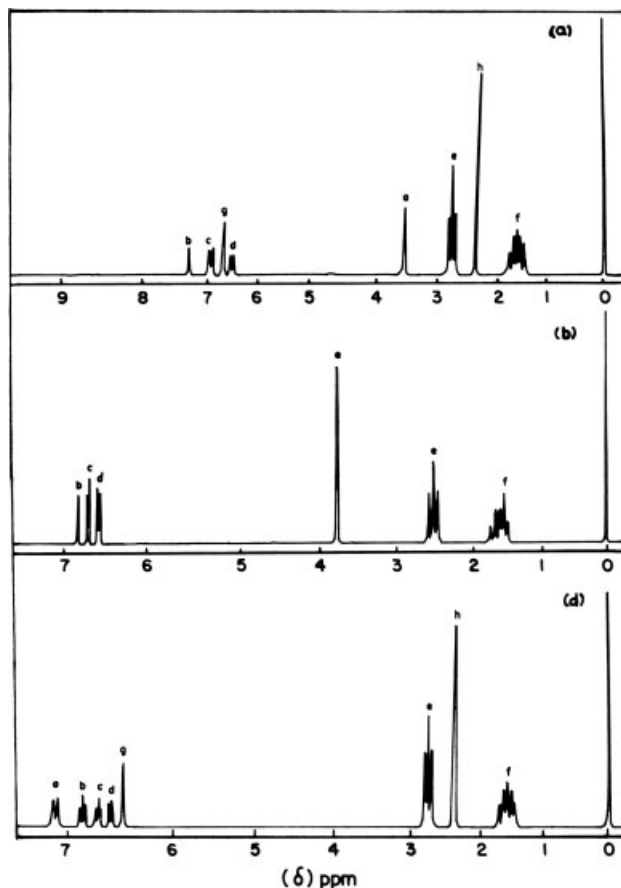


Figure 2 ¹H NMR spectra of dicyanate monomers.

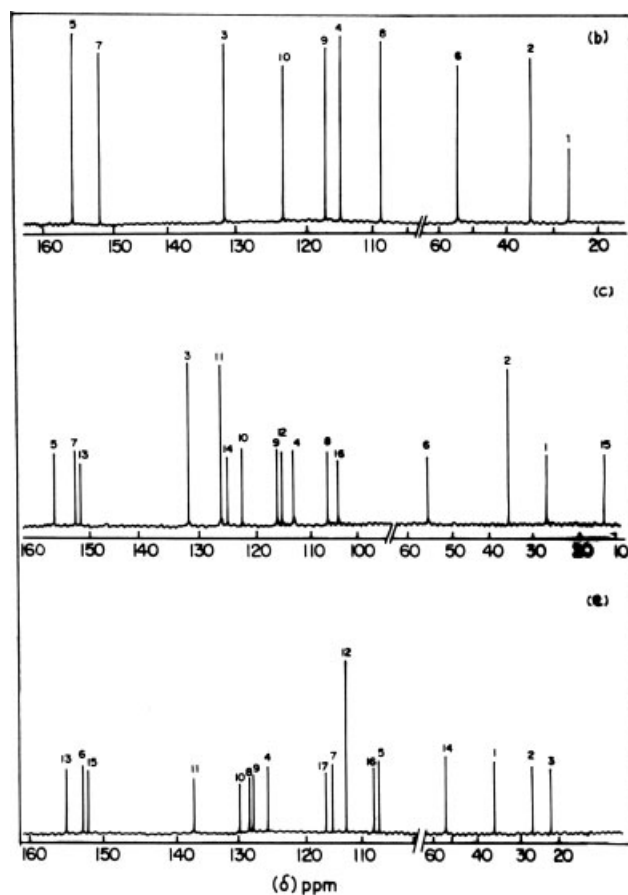


Figure 3 ^{13}C NMR spectra of dicyanate monomers.

ular chemical structure are obtained.¹³ The thermal behavior of the dicyanate esters were characterized by DSC. Figure 4 represents the DSC scan of dicyanate esters and the data are given in Table II. The T_i , the cure onset temperature, T_{max} , the maximum cure temperature, and T_{end} , the cure-end temperature are reported. The glass transition temperature was obtained by cooling the sample and re-run of the same sample was carried out. The glass transition temperature is in the range of 208–239°C. The T_g is

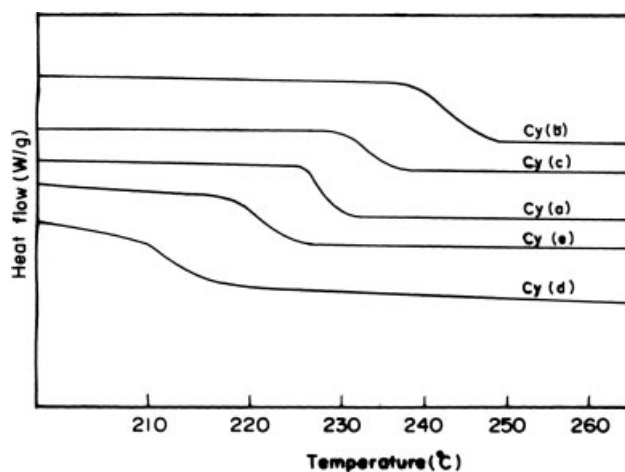


Figure 4 Glass transition temperature of methylene-bridged cyanate esters.

highest for the cyanate ester Cy(b). This can be explained by the centrosymmetric dimeric structure of the monomer. Unsymmetrical attachment of the ring depresses the T_g of the resulting networks. The next higher T_g was observed in the cyanate ester Cy(c). The T_g of the cured network depends on the length and symmetry of the monomer, T_g being higher for monomers containing shorter and the para-substituted rings. Rigidity of the shorter chain was found to retard the cure reaction.³ The Cy(a) cyanate ester has T_g of 227°C. The next lower T_g was observed in the cyanate ester Cy(e). The cyanate ester Cy(d) has the lowest T_g , which may be attributed to its asymmetric nature. We can expect these effects to reduce effective chain packing and interchain forces resulting in reduction of the transition temperatures and possibly even the crosslink density.

Thermogravimetric analysis

The thermal degradation of the cured cyanate esters were studied by TGA and the thermograms are shown in Figure 5. Table III gives initial decomposi-

TABLE I
Yield and Elemental Analysis Data of Dicyanate Monomers

Monomer code	Molecular formula	Yield (%)	Elemental analysis (wt %)		
			Carbon	Hydrogen	Nitrogen
Cy(a)	$\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$	85	C 71.42	C 5.99	C 8.33
			F 71.34	F 5.81	F 8.19
Cy(b)	$\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_4$	83	C 67.45	C 5.36	C 8.28
			F 67.48	F 5.28	F 8.17
Cy(c)	$\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_3$	92	C 70.80	C 5.63	C 8.69
			F 70.69	F 5.49	F 8.72
Cy(d)	$\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2$	84	C 74.50	C 5.92	C 9.14
			F 74.36	F 5.81	F 9.05
Cy(e)	$\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3$	89	C 70.12	C 5.23	C 9.08
			F 70.04	F 5.11	F 9.12

TABLE II
Thermal Transitions of Cyanate Esters by DSC

Monomer code	T_i (°C)	T_{max} (°C)	T_{end} (°C)	T_g (°C)
Cy(a)	151	197	249	227
Cy(b)	148	198	242	239
Cy(c)	143	195	212	230
Cy(d)	171	219	252	208
Cy(e)	151	197	231	219

tion (T_i), 10% weight loss (T_{10}), char remaining at 800°C, limiting oxygen index (LOI) of the polycyanurates. The 10% weight loss is in the range of 364–381°C. Among the cyanate esters prepared, the initial degradation temperature is comparatively higher for Cy(b) cyanate ester. This may be due to its higher crosslink density derived from its symmetrical network. The cyanate ester Cy(d) shows the least stability due to its asymmetric structure, which leads to more free volume fraction. The thermal stability follows the same trend as discussed in glass transition temperature.

$$\text{Cy(b)} > \text{Cy(c)} > \text{Cy(a)} > \text{Cy(e)} > \text{Cy(d)}$$

The other cyanate esters occupy the intermediate position according to the symmetric nature of their structures.

The char yield at 800°C shows some variations according to the different substituents. The flame retardancy of the cured cyanate ester resins was evaluated from their 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.¹⁴ The LOI value was calculated by using Krevelen's equation.¹⁵

$$\text{LOI} = 17.5 + 0.4(\sigma)$$

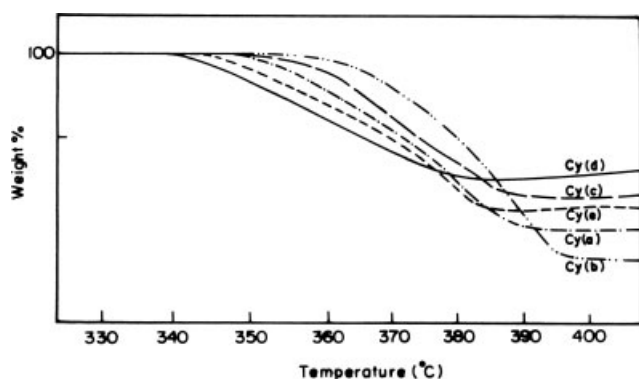


Figure 5 Thermograms of methylene-bridged polycyanurates.

TABLE III
Thermal Stability of Cyanate Ester Resins

Cured monomer code	T_i (°C)	T_{10} (°C)	Char yield at 800°C (%)	LOI value
Cy(a)	351	372	53	38.7
Cy(b)	362	381	47	36.3
Cy(c)	358	375	51	37.9
Cy(d)	342	364	48	36.7
Cy(e)	347	371	52	38.3

where σ is the percentage of char yield. The LOI was found to be in the range of 36.3–38.7. The char formation at the polymer surface reduces flammability by acting as a barrier (principally carbonaceous) to inhibit gaseous products from diffusing to the flame and to shield the polymer surface. Thus, the developed cyanurate can be considered as a better flame-retardant material.

CONCLUSIONS

Several dicyanate monomers/cured resins bearing methylene units were synthesized and characterized by spectroscopic, thermal, and elemental analysis. Spectroscopic techniques and elemental analysis data are in accordance with the proposed structure of the prepared dicyanate esters. The thermal property decreases in the order $\text{Cy(b)} > \text{Cy(c)} > \text{Cy(a)} > \text{Cy(e)} > \text{Cy(d)}$. This can be explained by the symmetric structure of the monomers. The T_g of the cured network depends on the length and symmetry of the monomer, being higher for those with shorter and the para-substituted rings. Rigidity of the shorter chain was found to retard the cure reaction. A similar trend was observed for the thermal stability by TGA in which the symmetry is directly correlated to its crosslink density. The flame retardancy of the cured resins was found by calculating LOI value. The LOI was found in the range of 36.3–38.7 indicating that the prepared polycyanurates are thermally stable.

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