

Rigid-Rod Thermosets Based on 1,3,5-Triazine-Linked Aromatic Ester Segments

G. G. Barclay,[†] C. K. Ober,^{*,†} K. I. Papathomas,[‡] and D. W. Wang[†]

Department of Materials Science and Engineering, Bard Hall, Cornell University, Ithaca, New York 14853-1501, and Systems Technology Division, IBM Corporation, Endicott, New York 13760-0553

Received June 21, 1991; Revised Manuscript Received February 4, 1992

ABSTRACT: Liquid-crystalline (LC) thermosets were prepared by the thermal cyclotrimerization of dicyanate compounds of ring-substituted bis(4-hydroxyphenyl) terephthalates. The resulting triazine networks formed a mesophase as the curing reaction proceeded, thereby enabling alignment in applied fields. Alignment of the LC phase during the curing process under the influence of a magnetic field produced oriented triazine networks with a smecticlike molecular organization. The effect of this anisotropy on the properties of these networks was investigated by both wide-angle X-ray diffraction and by measuring the coefficient of thermal expansion parallel and perpendicular to the direction of alignment. Remarkably well-oriented triazine networks were obtained ($f \sim 0.50$) with low values of the coefficient of thermal expansion observed (17 ppm/°C) in the direction of the applied field. The triazine networks have glass transition temperatures of ~ 190 °C and show little decomposition until ~ 440 °C. The alignment of the LC triazine networks induced by curing in magnetic fields was found to be thermally stable until at least 100 °C above the glass transition temperature.

Introduction

Recently there has been a growing interest in the preparation and characterization of rigid-rod thermosets.¹⁻³ The rigid-rod nature of the molecules used to prepare such networks has resulted in some of these networks having a liquid crystalline (LC) molecular organization.⁴ The main impetus for this research has been the growing interest in both the theoretical aspects and the technical applications of rigid-rod networks. If both the rigid-rod segment and the cross-linking functions possess high thermal stability, then such materials will have potential applications ranging from matrix materials for advanced composites to thin-film, low-dielectric materials in electronics packaging. The use of thermally stable, oriented networks is also being explored in recent studies of thermosets designed for nonlinear optical applications.⁵

Some of the first liquid crystalline polymers were thermosets prepared by thermally polymerizing diacrylate Schiff base monomers to give a cross-linked network.⁶ Further work on the polymerization of similar diacrylate Schiff bases from the nematic state in a 4.5-kG magnetic field resulted in a well-oriented cross-linked network, as shown by X-ray diffraction.⁷ Polymeric networks prepared from liquid crystalline diacrylate precursors have also been extensively described in the patent literature.⁸⁻¹² The use of liquid crystalline diglycidyl compounds and diisocyanate compounds in the preparation of structured networks has also been reported.^{13,14} The polyaddition or polycondensation process described in these patents was claimed as having been carried out within the mesophase temperature range of the polyfunctional unit possessing a liquid crystalline character.

Rigid-rod molecules end-capped with maleimide, nadimide, and methyladimide groups have been recently used to prepare liquid crystalline thermosets.^{4,15} However, a variety of cross-link sites are formed during the curing reaction of these reactive groups. The resulting networks have a characteristic LC texture upon cross-linking when examined by polarized-light microscopy which leads to the conclusion that the molecular organization of the LC

state appears to be "frozen" into the cross-linked network. In our studies of LC networks, we have also investigated the formation, characterization, and alignment of networks prepared from glycidyl end-capped thermotropic oligoethers.¹⁶

The formation of networks via the cyclotrimerization of the cyanate group to the 1,3,5-triazine cross-link site is unique, because the reaction forming the triazine ring undergoes very few side reactions.¹⁷ Triazine networks should therefore prove to be good model systems for the investigation of rigid-rod networks, since only one cross-link structure is possible. It has also been claimed that triazine systems based on 2,4,6-tris[4-[(4-aminophenyl)alkoxy]benzylidene]-1,3,5-triazines form a discotic liquid crystalline phase.¹⁸ This report made the investigation of such networks of even more interest.

The work reported here describes the preparation of new liquid crystalline 1,3,5-triazine networks from dicyanate compounds of substituted bis(4-hydroxyphenyl) terephthalate, a preliminary report of which was described elsewhere.¹⁹ The thermal and mechanical properties of these networks are also reported. Furthermore, we have prepared novel, highly anisotropic triazine networks resulting from the magnetic field induced alignment of the liquid crystalline phase during the curing reaction. In view of the potential use of these thermosets in thin-film applications, the effect of anisotropy was measured by determining the coefficient of thermal expansion (CTE) of these networks parallel and perpendicular to the direction of alignment and by studying their wide-angle X-ray diffraction (WAXD) behavior.

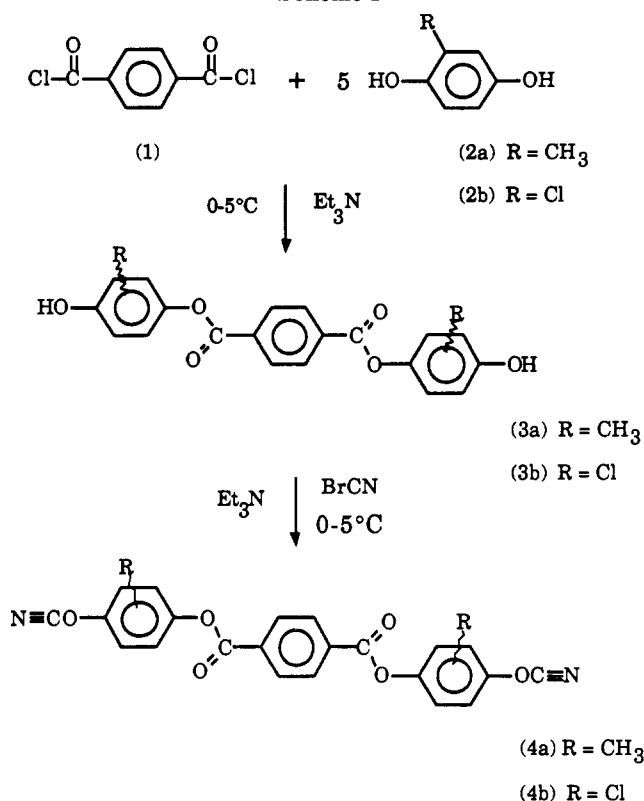
Experimental Section

Materials. Methylhydroquinone (99%), hydroquinone (99+%), terephthaloyl chloride (99+%), 4-butoxybenzoyl chloride (99%), cyanogen bromide (97%), and phosphorus pentachloride were used as obtained (Aldrich). Chlorohydroquinone (technical grade; Aldrich) was recrystallized twice from chloroform prior to use. Triethylamine and pyridine were distilled from barium oxide; tetrahydrofuran (THF) was distilled from a mixture of Na metal and benzophenone; acetone was distilled from Drierite, and carbon tetrachloride was distilled from phosphorus pentoxide prior to use. Zinc(II) stearate, copper(II) acetate, and cobalt(III) acetylacetonate (AcAc) catalysts were supplied by IBM, Systems Technology Division, Endicott NY.

[†] Cornell University.

[‡] IBM Corp.

Scheme I



Preparation of Bis(4-hydroxymethylphenyl) Terephthalate (3a). The general procedure for the preparation of the bisphenols and dicyanates is shown in Scheme I. Methylhydroquinone (2a; 15.27 g, 0.123 mol) was dissolved in 25 mL of pyridine and 75 mL of THF under nitrogen. This solution was then cooled to 5 °C in an ice bath, and a solution of terephthaloyl chloride (1; 5.00 g, 0.025 mol) in 25 mL of THF was added dropwise over 4 h at 5 °C. The reaction mixture was stirred at room temperature overnight. The mixture was washed with 2 N HCl (NaCl added to aid separation) and water. The THF phase was precipitated into 3500 mL of water at 65–70 °C, and the resulting solid was filtered. The crude product was dissolved in a minimum amount of warm acetone, filtered, and reprecipitated in water at 65–70 °C. The purified yellow precipitate was dried in a vacuum oven at 50 °C overnight, yield 6.88 g (73%). Thin-layer chromatography on silica gel, using ethyl acetate as eluent, showed one spot ($R_f = 0.55$). DSC (10 °C/min) showed two melting points at 192 and 209 °C due to a mixture of isomers. ¹H NMR (acetone-*d*₆): δ 2.15, 2.22, and 2.30 (6 H, s, CH₃, a mixture of isomers depending upon the position of the methyl group on the phenyl ring); 2.89 (2 H, br s, OH); 6.70–7.09 (6 H, complex m, aromatic); 8.32, 8.35, and 8.38 (4 H, s, aromatic). IR (KBr disk, cm⁻¹): 3424 (OH stretch); 2961, 2949, and 2928 (CH stretch); 1736 and 1713 (C=O stretch); 1510 (C=C aromatic stretch).

Preparation of Bis(4-hydroxychlorophenyl) Terephthalate (3b). Using the experimental procedure described in the example above, bis(4-hydroxychlorophenyl) terephthalate (3b) was prepared using the following reactants: chlorohydroquinone (2b; 14.24 g, 0.310 mol), terephthaloyl chloride (1; 4.00 g, 0.020 mol), pyridine (25 mL), and anhydrous THF (100 mL) as solvent. After purification, thin-layer chromatography on silica gel, using ethyl acetate as eluent showed one spot ($R_f = 0.69$), yield 5.59 g (69%). DSC (10 °C/min) showed two melting endotherms at 216 and 231 °C due to the mixture of isomers. ¹H NMR (acetone-*d*₆): δ 6.86–7.60 (6 H, complex m, aromatic, a mixture of isomers depending upon the position of the chlorine on the phenyl ring); 8.34, 8.36, and 8.40 (4 H, s, aromatic); 9.00 (2 H, br s, OH). IR (KBr disk, cm⁻¹): 3401 (OH stretch); 1738 and 1713 (C=O stretch); 1499 (C=C aromatic stretch).

Preparation of the Dicyanate of Bis(4-hydroxymethylphenyl) Terephthalate (4a). Bis(4-hydroxymethylphenyl) terephthalate (3a; 3.00 g, 0.0079 mol) and cyanogen bromide

Table I
Thermal Behavior of Dicyanate Precursors

dicyanate	T_m , ^a °C	T_n , ^b °C	T_{ex} , ^c °C	T_{cat} , ^d °C
4a	151, 162, 181	230	323	180
4b	165, 187	206	275	179

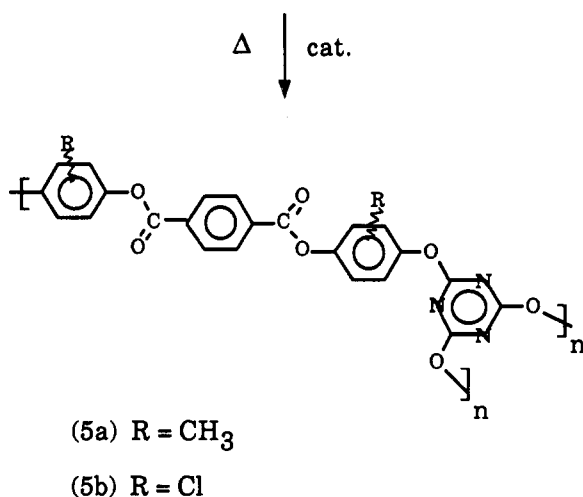
^a Polymorphic melting behavior due to mixture of isomers. ^b Temperature at which nematic droplets appear due to the cyclotrimerization reaction as shown by hot-stage optical microscopy at a heating rate of 10 °C/min. ^c Uncatalyzed cyclotrimerization reaction exotherm. ^d Zinc stearate catalyzed cyclotrimerization reaction temperature.

(2.00 g, 0.019 mol) were dissolved in anhydrous acetone. Then under nitrogen at 0–5 °C, triethylamine (1.92 g, 0.019 mol) dissolved in acetone was added dropwise with stirring. The reaction mixture was stirred for a further 40 min at 0–5 °C. The mixture was then poured into ice/water and the resultant precipitate filtered off, washed with water, and dried in vacuo. Thin-layer chromatography on silica gel with chloroform as eluent showed the crude reaction product to consist of a major product ($R_f = 0.57$) and a minor product ($R_f = 0.19$). The product was purified twice by fractional reprecipitation from chloroform into hexanes, the latter fraction being kept and dried in vacuo. The precipitate consisted of solely the major product, yield 2.04 g (65%). DSC showed polymorphic melting behavior due to the mixed isomers; see Table I. ¹H NMR (chloroform-*d*): δ 2.31 and 2.37 (6 H, 2 s, CH₃, a mixture of isomers depending upon the position of the methyl group on the phenyl ring); 7.15–7.30 (4 H, complex m, aromatic); 7.50–7.54 (2 H, complex m, aromatic); 8.31 and 8.34 (4 H, 2 s, aromatic). IR (KBr disk, cm⁻¹): 2266 (CN stretch); 1738 (C=O stretch); 1491 (C=C aromatic stretch). ¹³C NMR (chloroform-*d*, selected peaks): δ 15.51 and 16.50 (CH₃); 108.78 (OCN); 163.90 and 163.53 (C=O, ester).

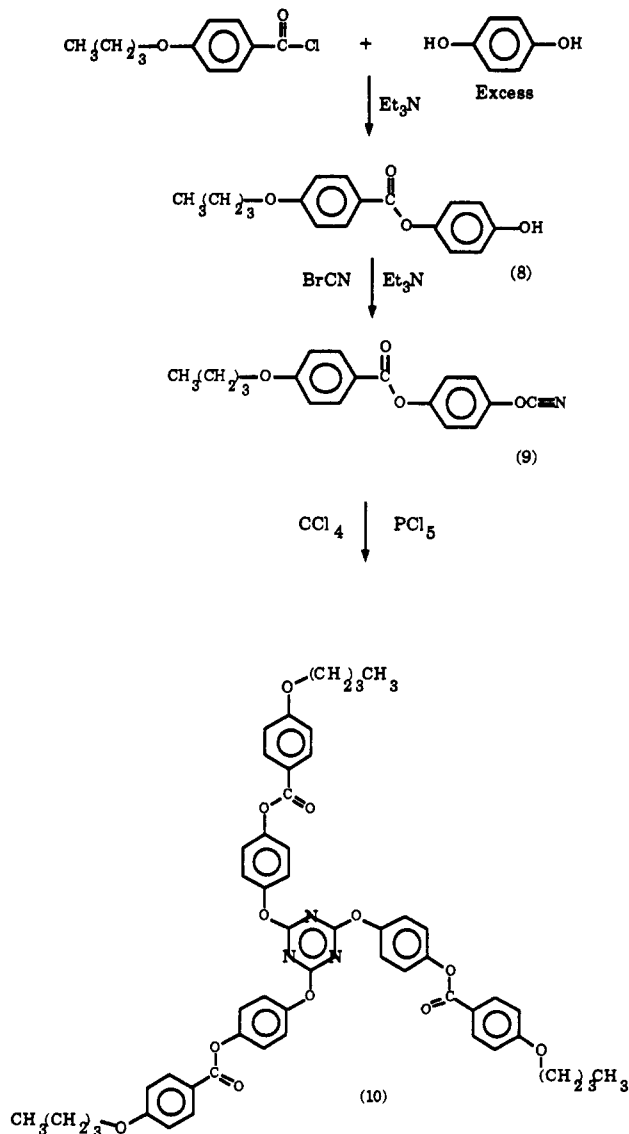
Preparation of the Dicyanate of Bis(4-hydroxychlorophenyl) Terephthalate (4b). Using the experimental procedure described in the example above, the dicyanate of bis(4-hydroxychlorophenyl) terephthalate (3b) was prepared using the following reactants: bis(4-hydroxychlorophenyl) terephthalate (3.00 g, 0.0072 mol), cyanogen bromide (1.83 g, 0.0173 mol), triethylamine (1.75 g, 0.0173 mol), and anhydrous acetone as solvent. The crude product was fractionally precipitated twice from ethyl acetate into hexanes, the latter fraction being kept, yield 1.59 g (47%). Thin-layer chromatography on silica gel with chloroform as eluent showed one spot ($R_f = 0.81$). DSC showed polymorphic melting behavior due to the formation of mixed isomers; see Table I. ¹H NMR (DMSO-*d*₆): δ 7.53–7.92 (complex m, aromatic); 8.14 (d, aromatic); 8.32, 8.35, and 8.38 (3 s, aromatic). IR (KBr disk, cm⁻¹): 2260 and 2245 (CN stretch); 1740 (C=O stretch); 1480 (C=C aromatic stretch). ¹³C NMR (chloroform-*d*, selected peaks): δ 107.83 (OCN); 162.83 and 164.57 (C=O, ester).

Preparation of 1,3,5-Triazine Networks (5a and 5b). The catalytic thermal cyclotrimerization of dicyanates of 4a and 4b was carried out using 2 mol % of the transition metal in the form of zinc(II) stearate, copper(II) acetate, or cobalt(III) acetylacetonate. The general reaction is given in Scheme II. The catalyst and dicyanate were mixed in acetone, and then the acetone was removed under high vacuum. Samples of the thermoset were prepared by placing the powdered mixture of the dicyanate and catalyst into an aluminum mould (25 mm × 7 mm × 1 mm) between PTFE sheets. The mould was placed into a hot press at the appropriate temperature (175 °C for the methyl-substituted dicyanate (4a) and at 190 °C for the chloro-substituted dicyanate (4b)). A pressure of 2000 psi was then applied and the curing reaction allowed to proceed under these conditions for 1 h. The temperature was increased to 230 °C after which the sample was allowed to cool to room temperature. The extent of the cyclotrimerization reaction was followed by infrared spectroscopy. Using the above curing cycle, infrared spectroscopy indicated the removal of the nitrile stretching absorption at 2260 cm⁻¹ of the dicyanate compound and the appearance of triazine stretching absorptions at 1560 and 1370 cm⁻¹.

Preparation of the Cyanate of 4-Hydroxyphenyl 4-Butoxybenzoate (9). The reaction used for the preparation of the triazine model compound is given in Scheme III. 4-Hydroxyphenyl 4-butoxybenzoate was prepared as described in the

Scheme II
(4a or 4b)

Scheme III



literature.²⁰ 4-Hydroxyphenyl 4-butoxybenzoate (8; 0.50 g, 1.75 mmol) and cyanogen bromide (0.22 g, 2.1 mmol) were dissolved in 20 mL of anhydrous acetone. Then under nitrogen at 0–5 °C, triethylamine (0.21 g, 2.10 mmol) dissolved in acetone was added

dropwise with stirring. The reaction mixture was further stirred for 1 h at 0–5 °C. The mixture was poured into ice/water and the resultant precipitate filtered off, washed with water, and dried in vacuo. Thin-layer chromatography (TLC) on silica gel with chloroform as eluent showed the crude reaction product to consist of a major product (*R_f* = 0.73) and a minor product (*R_f* = 0.20). The product was purified by recrystallization twice from ethanol/water. The purified product consisted solely of the cyanate (9), yield 0.38 g (70% of theory). Mp (uncorrected): 82 °C. ¹H NMR (chloroform-*d*): δ 1.00 (3 H, t, CH₃); 1.50 (2 H, sextet, CH₂); 1.8 (2 H, quintet, CH₂); 4.05 (2 H, CH₂); 6.95 (2 H, d, aromatic); 7.32 (4 H, d, aromatic); 8.10 (2 H, d, aromatic). IR (KBr disk, cm⁻¹): 2220 and 2180 (CN stretch); 1730 (C=O stretch); 1610, 1520, and 1500 (C=C aromatic stretch).

Preparation of 2,4,6-Tris[4-[(4-butoxybenzoyl)oxy]phenoxy]-1,3,5-triazine (10). 4-[(4-Butoxybenzoyl)oxy]phenyl cyanate 9; 0.100 g, 0.32 mmol) was dissolved in 10 mL of anhydrous carbon tetrachloride. To this solution was added a catalytic quantity of phosphorus pentachloride (0.005 g, 0.024 mmol). The reaction mixture was then stirred overnight at room temperature under N₂. The resulting white precipitate was filtered off, washed sequentially with carbon tetrachloride and distilled water, and then dried in vacuo. The crude product was recrystallized from pyridine, yield 0.09 g (90% of theory). Mp (uncorrected): 241 °C. ¹H NMR (pyridine-*d*₅ at 80 °C): δ 1.00 (3 H, t, CH₃); 1.50 (2 H, sextet, CH₂); 1.8 (2 H, quintet, CH₂); 4.06 (2 H, t, CH₂); 7.10 (2 H, d, aromatic); 7.45 (4 H, dd, aromatic); 8.28 (2 H, d, aromatic). IR (KBr disk, cm⁻¹): 1730 (C=O stretch); 1610 (C=C aromatic stretch); 1575 (C=N stretch triazine); 1520 and 1505 (C=C aromatic stretch); 1385 and 1370 (C=N stretch triazine). ¹³C NMR (pyridine-*d*₅ at 80 °C): δ 13.87 (CH₃); 19.53 (CH₂); 31.58 (CH₂); 68.68 (CH₂); 115.24, 122.46, 122.93, and 132.76 (aromatic carbons; note some aromatic carbons are obscured by pyridine signals); 164.32 and 164.89 (C=O); 174.55 (triazine). MS: *m/e* 934 (M⁺); six most intense peaks 307, 155, 154, 138, 137, and 136.

Preparation of Anisotropic 1,3,5-Triazine Rigid-Rod Networks. Orientation induced during the curing process was carried out at the MIT Bitter Magnet Laboratory using an Intermagnetics General Corp. superconducting magnet, at a field of 13.5 T. The mixture of the dicyanate of bis(4-hydroxymethylphenyl) terephthalate (4a) and the appropriate catalyst (2 mol % of transition metal in the form of zinc(II), stearate, copper(II) acetate, or cobalt(III) acetylacetonate) was packed into a thin-walled quartz vial (10 mm in length and 3 mm in diameter). The sample was then placed in a cylindrical graphite heater preheated at 175 °C in the magnetic bore under nitrogen. The sample was held at this temperature for 1 h. The temperature was then increased to 230 °C, after which the sample was allowed to cool to 30 °C before removal from the magnetic field.

Physical Characterization. Product compositions were determined using a Varian XL-200 ¹H and ¹³C NMR. Infrared spectroscopy was performed using a Mattson 2020 Galaxy Series FT/IR. Thermal transition temperatures were obtained on a Du Pont 9900 thermal analyzer at a heating rate of 20 °C/min. Liquid crystalline mesophases were examined using a Leitz polarizing optical microscope at 200× magnification equipped with a Mettler FP-52 hot stage heating at 10 °C/min and a Canon AE-1 35-mm camera. Wide-angle X-ray diffraction (WAXD) exposures were taken using a wavelength of 1.54 Å at the Cornell High Energy Synchrotron Source (CHESS). The coefficient of thermal expansion (CTE) was measured at 10 °C/min using a Du Pont 943 thermomechanical analyzer calibrated with aluminum standards. Thermal decomposition was measured at 10 °C/min using a Du Pont 951 thermogravimetric analyzer under a nitrogen atmosphere (flow rate 80 cm³/min) and under an air atmosphere (flow rate 80 cm³/min). Dynamic mechanical analysis was performed using a Polymer Laboratories DMTA at 1-Hz frequency (*strain* ×4 instrument setting) and heating rate of 5 °C/min. Computer modeling was performed using Alchemy II (Tripos Associates).

Results and Discussion

Synthesis of Rigid-Rod Dicyanate Precursors. In order to develop a rigid-rod network, both a rigid-rod

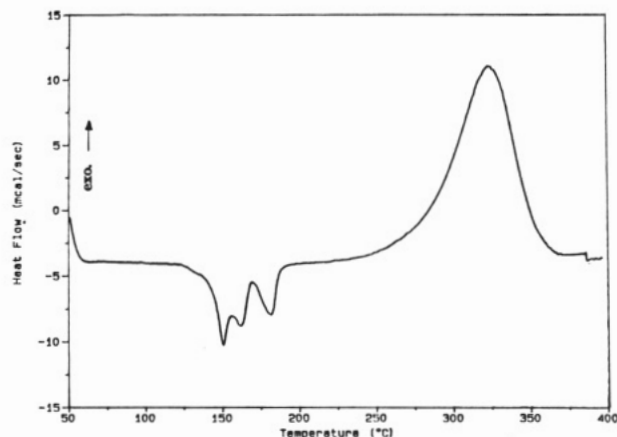


Figure 1. DSC of the methyl-substituted cyanate precursor (4a; scan rate 20 °C/min).

segment and a stiff cross-linking function were incorporated into a network structure. The selected triazine cross-link, produced by the cyclotrimerization of cyanate functions, was known to be thermally stable²¹ and as an aromatic ring was assumed to be rather inflexible. The bisphenol bridging group, bis(4-hydroxyphenyl) terephthalate, was chosen since this type of mesogenic structure has been used extensively in the preparation of liquid crystalline polymeric materials and as such has the rigidity required for the target networks.²² The dicyanate compounds of bis(4-hydroxyphenyl) terephthalate (4a and 4b) were previously unknown.

The synthesis of these dicyanate compounds (Scheme I) involved first reacting terephthaloyl chloride (1) with a large excess of the appropriately substituted ($R = \text{CH}_3$ or Cl) hydroquinone (2a or 2b) to form the bisphenols (3a and 3b). The unsubstituted bisphenol ($R = \text{H}$) was unprocessable, and therefore the more tractable substituted derivatives were used. The variety of arrangements possible for the substituents lead to a mixture of isomers which depended upon the position of the substituent on the hydroquinone moiety of these bisphenols (3a and 3b). No effort was made to isolate these isomers, and they were therefore used in successive reaction steps. The bisphenols were reacted with cyanogen bromide, in the presence of triethylamine, to give the dicyanates (4a and 4b).

Thermal Behavior of the Dicyanate Precursors. The thermal behavior of the resulting dicyanate monomers (4a and 4b) was complex due to the presence of mixed isomers, the thermal cyclotrimerization reaction (Scheme II), and the formation of a liquid crystalline phase during the cross-linking reaction (Table I). The mixture of isomers resulted in both types of dicyanate precursors (4a and 4b) having broad polymorphic melting transitions (Figure 1). After heating above the melting temperature (T_m), both dicyanates exhibited an exotherm for the cyclotrimerization reaction. The exotherm for the Cl-substituted precursor (4b) reached a maximum at a much lower temperature (275 °C) than the exotherm for the methyl derivative (4a; 323 °C). This observation is in agreement with the finding that electron-donating groups diminish the reactivity of the cyanate, while electron-withdrawing groups increase the reactivity of the cyanate toward cyclotrimerization.²³

Hot-stage polarized-light optical microscopy showed that these dicyanate monomers formed isotropic fluids just after melting. However, as the temperature was increased, birefringent droplets appeared (Figure 2a) which coalesced to form a continuous mesophase with a schlieren texture (Figure 2b). Initially the mesophase was mobile

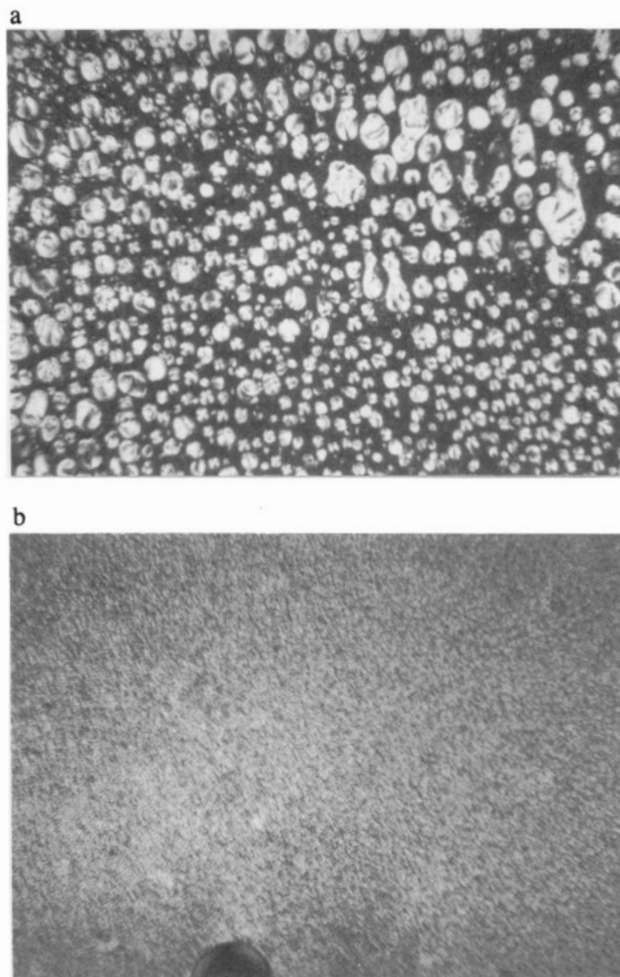


Figure 2. Cross-polarized optical microscopy of the curing reaction of precursor 4a: (a) birefringent droplets (230 °C); (b) schlieren texture of the cured network (magnification = 200 \times).

and stir-opalescent and could be sheared. The appearance of the droplets occurred at a lower temperature for the Cl derivative (206 °C) than for the methyl derivative (230 °C) due to the greater reactivity of the Cl-substituted precursor. As thermal cross-linking took place, the mesophase flowed less readily and was eventually "frozen" as the cross-linked network was formed.

Cyclotrimerization. The thermal cyclotrimerization of these dicyanates (4a and 4b) could be carried out using a transition-metal catalyst (e.g., Zn, Co, or Cu) to reduce the temperature at which the cross-linking reaction occurred. The reactivity of the transition-metal catalyst depended upon the choice of the coordination metal and the metal concentration.^{23,24} Transition-metal carboxylates (for example, zinc(II) stearate) have a high catalytic activity, while transition-metal chelates (for example, cobalt(III) acetylacetonate) are less reactive catalysts. The use of a catalyst facilitates the preparation of highly cross-linked samples at lower, more convenient temperatures.

Figure 3 shows the DSC trace of the cobalt(III) acetylacetonate catalyzed curing reaction of the methyl-substituted dicyanate (4a). The peak of the reaction exotherm for the catalyzed cyclotrimerization appeared at 176 °C immediately upon melting, a value much lower than 323 °C, the peak for the uncatalyzed reaction exotherm. As in the case of the uncatalyzed systems, a mobile liquid crystalline phase formed as the catalyzed curing reaction began and this mesophase was "frozen" into the networks as the cross-link density increased.

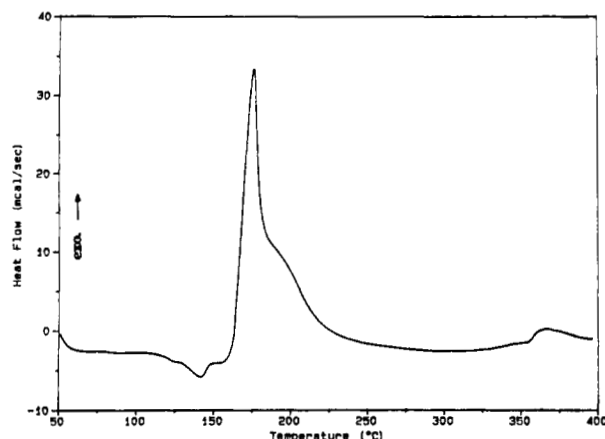


Figure 3. DSC of the Co^{III} AcAc catalyzed curing reaction of network precursor **4a** (scan rate $20\text{ }^{\circ}\text{C}/\text{min}$).

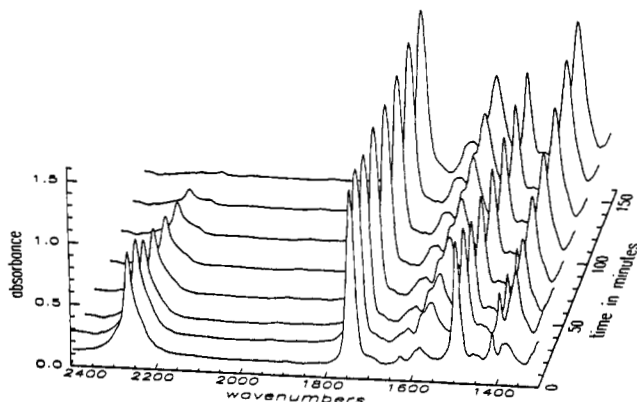


Figure 4. FT/IR of the uncatalyzed curing reaction of network precursor **4a** at $230\text{ }^{\circ}\text{C}$.

In order to establish optimal curing times and conditions, the extent of the cyclotrimerization reaction during curing was monitored by FT/IR. These results were compared with thermal data, and so by using both DSC and FT/IR analysis, reaction conditions were established. Figure 4 shows FT/IR spectra versus time for the uncatalyzed curing reaction of the methyl-substituted precursor (**4a**) at $230\text{ }^{\circ}\text{C}$. The reaction was followed by measuring the reduction in nitrile stretching absorption at 2260 cm^{-1} and the appearance of triazine $\text{C}=\text{N}$ stretching absorptions at 1564 and 1370 cm^{-1} . The carbonyl stretching absorption of the ester at 1740 cm^{-1} and the aromatic $\text{C}=\text{C}$ stretching absorption at 1493 cm^{-1} were used as internal references since they remain constant during the curing reaction. As can be seen from the removal of the nitrile absorption, the uncatalyzed reaction of the methyl-substituted precursor (**4a**) goes to completion after approximately 2.5 h.

The cyclotrimerization reaction formed new species that exhibited mesophase behavior over the temperature range in which the curing reaction was occurring. A possible structure capable of mesophase formation was the branched oligomer formed by chain extension during the curing reaction. This assumes that the resulting rigid rods have a sufficiently high axial ratio to form a liquid crystalline phase. Such an explanation has been put forward by Benicewicz and co-workers to account for the melting behavior of rigid-rod molecules end-capped with maleimide, nadimide, and methyladimide groups.¹⁵

The cyclotrimerization reaction of the cyanate group, however, is known to be highly selective,^{17,25} resulting in nearly quantitative triazine ring formation under the conditions used in the curing step. Therefore, it is unlikely that linear chain extension through the formation of

dimeric intermediate products could occur to any great extent. This selectivity occurs in contrast to the structurally analogous isocyanate group which is known to form dimeric species which do result in linear chain extension.²⁵ An alternative explanation for the formation of a liquid crystalline phase that also accounted for the selectivity of the reaction was that the disklike 2,4,6-substituted triazine cross-link site could form a discotic liquid crystal. The planar triazine ring can in principle act as the core of a molecule with 3-fold symmetry. It has been claimed that structurally similar triazine systems having 4-[(4-aminophenyl)alkoxy]benzylidene substituents formed a discotic liquid crystal.¹⁸ However, no data were reported to support this claim of LC behavior.

Mesophase Formation during Curing. To explore the possibility that 2,4,6-substituted triazine systems might exhibit discotic behavior, a readily synthesized triazine model compound (**10**) was prepared. This model system consisted of 2,4,6-tris[4-[(4-butoxybenzoyl)oxy]phenoxy]-1,3,5-triazine (**10**; Scheme III). The ester, 4-[(4-butoxybenzoyl)oxy]phenol (**8**), was synthesized by the Schotten-Baumann reaction of a large excess of hydroquinone (**6**) with 4-butoxybenzoyl chloride (**7**) according to the literature method.²⁰ The cyanate ester (**9**) of the phenol (**8**) was then prepared by reaction with cyanogen bromide in the presence of triethylamine. The compound 4-[(4-butoxybenzoyl)oxy]phenyl cyanate (**9**) was then cyclotrimerized in near quantitative yield in carbon tetrachloride using phosphorus pentachloride as catalyst to form the triazine model compound 2,4,6-tris[4-[(4-butoxybenzoyl)oxy]phenoxy]-1,3,5-triazine (**10**). This triazine model system (**10**) proved not to be liquid crystalline, melting to an isotropic liquid at $241\text{ }^{\circ}\text{C}$ on heating and crystallizing at $221\text{ }^{\circ}\text{C}$ on cooling.

It would seem therefore that the phenoxy-substituted triazine system with its flexible ether linkages between the rodlike substituents and the triazine ring does not necessarily induce formation of a discotic mesophase. One possible feature enabling mesophase formation was that the ether linkages connecting the bis(4-hydroxyphenyl) terephthalate units to the 2,4,6-positions of the triazine cross-link site were flexible enough to accommodate the formation of elongated rigid-rod species during the initial stages of the curing process. Such rigid-rod species, as previously suggested,¹⁵ have a sufficiently high length-to-diameter ratio to form a liquid crystalline phase. In the triazine networks, formation of these species would involve the rotation of rigid segments to lie parallel to one another so that the mesogenic group directors could adopt a common orientation. Such a rotation of mesogenic groups has been observed in many of the main chain/side chain LC polymers reported recently.²⁶ Usually, however, it has been assumed that a spacer is required so that the lateral mesogenic groups have the mobility needed to align with the main-chain mesogenic groups. This is not the case with the triazine networks, since no spacers are present.

Characterization of Mesomorphic Triazine Networks. Despite the lack of spacers in the resulting polymer network, X-ray diffraction investigations support the idea of rotation and subsequent colinearity of the mesogenic groups in the triazine networks. WAXD studies of these rigid-rod networks showed a diffuse ring at $5.2\text{ }\text{\AA}$ characteristic of a nematic mesophase (Figure 5a). A low-intensity inner ring at $19.6\text{ }\text{\AA}$ was also present in the diffraction pattern, suggesting a layered molecular organization of the triazine network. In view of the mesomorphic character of these networks, the possibility of

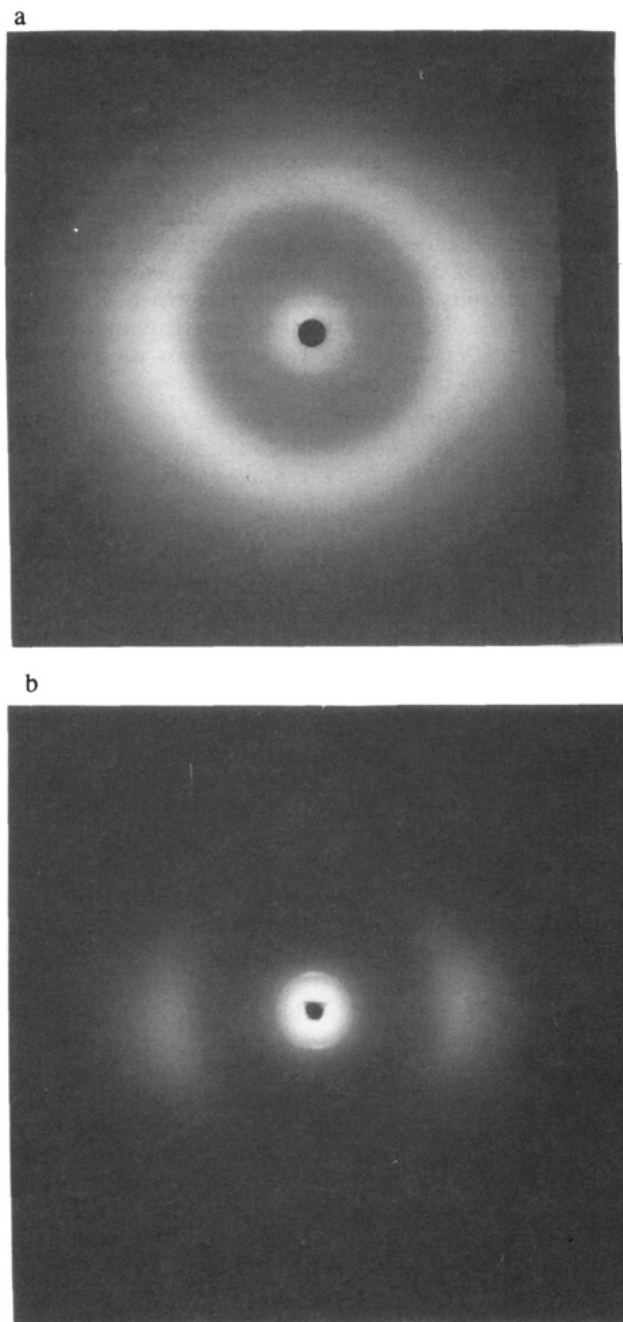


Figure 5. WAXD pictures of unaligned (a) and aligned (b) triazine networks prepared from precursor 4a.

aligning them in applied fields existed and will be described subsequently.

The resulting triazine, rigid-rod networks retained an extremely birefringent, liquid crystalline schlieren texture as shown by polarized-light microscopy (Figure 4b). If the triazine cross-link, due to its extremely bulky and planar nature, had disrupted the liquid crystalline phase during the final stages of curing, an isotropic polymer matrix would be anticipated. Hot-stage cross-polarized optical microscopy showed that the birefringence due to the molecular organization was "frozen" into the network until decomposition.

Dynamic mechanical analysis (Figure 6) of the unaligned LC triazine networks indicated that these networks possessed a high glass transition temperature (185 °C; $\tan \delta_{\max}$) and a reasonable modulus (Young's modulus, 0.8 GPa). This modulus was lower than those of epoxy-based LC thermosets we recently reported.¹⁶ Thermogravimet-

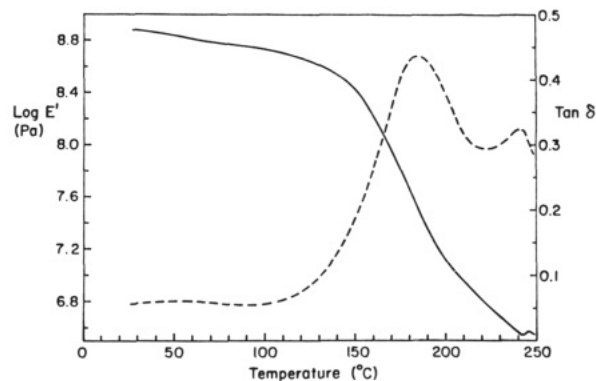


Figure 6. DMTA of unaligned triazine network 5a (scan rate 5 °C/min).

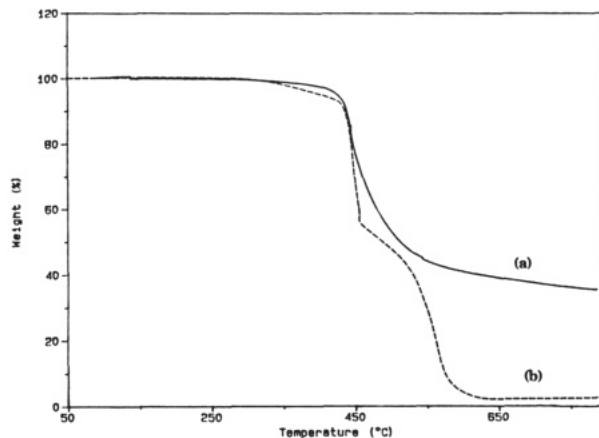


Figure 7. TGA of triazine network 5a in N₂ (a) and in air (b) (scan rate 10 °C/min).

ric analysis indicated that these materials possessed good thermal stability, 10% decomposition occurring at approximately 440 °C in both air and nitrogen (Figure 7). Triazine thermosets are known to exhibit good thermal stability due to the aromatic nature of the triazine ring, the stability of which is close to that of benzene.²⁵

Magnetic Alignment. An attempt was made to prepare triazine rigid-rod networks with oriented structures, that is, polymeric networks with a distinct directional orientation of the rigid-rod molecules within the cross-linked material. Highly cross-linked oriented networks are of interest because of the possibility of creating high T_g , anisotropic bulk, and thin-film specimens. The inherent anisotropy of these networks would be expected to increase the modulus and lower the CTE behavior of the thermoset in the direction of alignment. The process for orienting the molecules within these LC triazine thermosets involves the cross-linking of the rigid-rod species within the LC phase under the influence of a magnetic field (13.5 T).

Orientation was achieved in the triazine networks, thus suggesting that the formation of the bulky triazine cross-link did not hinder the ability of the liquid crystalline phase to align during the curing process. Wide-angle X-ray diffraction (WAXD) was used to measure the orientation of the rigid-rod species. For the unoriented network the diffracted intensity was azimuthally isotropic, while in the oriented network the diffracted X-ray intensity was limited to a specific range in azimuthal angle. WAXD of the aligned rigid-rod networks showed a layered molecular organization indicative of an aligned smecticlike network (Figure 5b). As well as equatorial arcs at 5.2 Å, meridional arcs at 19.6 Å could be seen. The former arcs are the result of diffraction from chains parallel to the

Table II
Properties of 1,3,5-Triazine Liquid Crystalline Networks

network	$T_g, ^\circ\text{C}$	CTE, ppm/ $^\circ\text{C}$				$N_2,^c\text{ }^\circ\text{C}$	residue, ^d %	air, ^c $^\circ\text{C}$	residue, ^d %
		unaligned		aligned ^b					
		\perp	\parallel	\perp	\parallel				
5a	177 ^a	61	70	94	17	440	35	436	3
5b	191 ^a	66	68	80	21	442	43	430	2

^a From DSC data. ^b Cured in the presence of a 13.5-T magnetic field. ^c Temperatures at 10% decomposition. ^d Residue at 800 $^\circ\text{C}$.

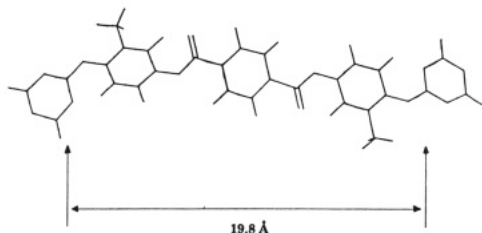


Figure 8. Computer projection of the rigid-rod unit between triazine cross-link sites.

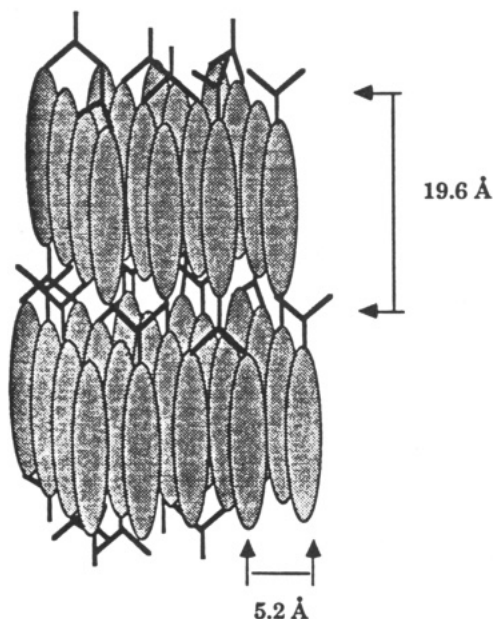


Figure 9. Schematic of the aligned triazine network with a layered structure.

applied field, while the latter arcs are the result of diffraction from layers perpendicular to the applied field. The dimensions derived from computer modeling of the rigid-rod mesogen between triazine cross-link sites (Figure 8) were in close agreement with the X-ray data for the layered structure. The distance between triazine cross-link sites calculated from molecular modeling was 19.8 Å which was consistent with the d -spacing measured for the meridional arcs (19.6 Å). The flexibility of the ether linkages connecting the mesogens to the triazine cross-link site as previously suggested must accommodate this highly organized layered network structure (Figure 9). The layering of the rigid groups as shown in Figure 9 is possible both as demonstrated with models and by looking at the strain energy computed with molecular modeling programs.

An orientation parameter f was calculated for the aligned triazine networks to determine the orientation of the chain directors relative to the direction of the applied field. This was based on Hermann's orientation parameter, defined as $f = (1/2) (3\langle \cos^2(\theta_z) \rangle - 1)$.²⁷ For an ideally oriented sample, $f = 1$, while for a randomly oriented sample $f = 0$. It was found that the degree of orientation of these

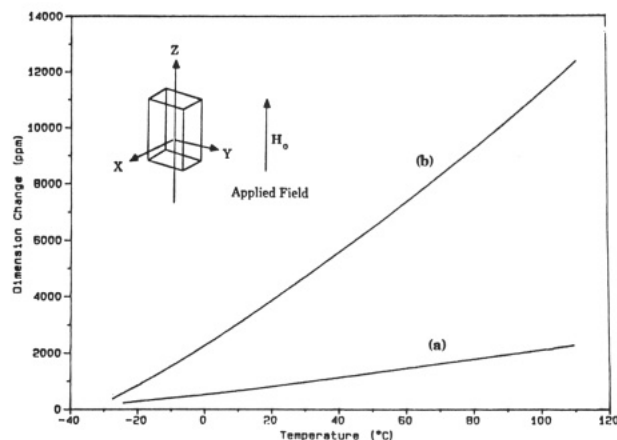


Figure 10. CTE measurements of aligned triazine network 5a parallel (a) and perpendicular (b) to the applied field (scan rate 10 $^\circ\text{C}/\text{min}$).

triazine networks could be influenced to some extent depending upon the type of catalyst used. For example, when highly active zinc(II) stearate was used, an orientation parameter of 0.42 was achieved. Using the less effective catalysts, cobalt(III) acetylacetonate and copper(II) acetate, higher orientation parameters of 0.46 and 0.54, respectively, were obtained. The orientation parameters ($f \sim 0.50$) achieved for these aligned triazine networks are comparable to orientation parameters reported for the magnetic field alignment of main-chain un-cross-linked LC polyesters.²⁸ Time-resolved, variable-temperature WAXD studies showed that the orientation that was "frozen in" during the curing process was stable to the highest temperature measured (280 $^\circ\text{C}$) for the aligned network prepared from precursor 4a using copper(II) acetate as catalyst.

The inherent anisotropy of the magnetically aligned rigid-rod networks prepared from the dicyanate of bis-(4-hydroxymethylphenyl) terephthalate (4a) is readily apparent from measurements of the coefficient of thermal expansion (CTE) parallel and perpendicular to the direction of the applied field (Figure 10). For the unoriented sample, the CTE values for the plane perpendicular to the applied field (X/Y directions) and the direction parallel to the applied field (Z direction) are comparable, ~ 60 – 70 ppm/ $^\circ\text{C}$. The oriented samples showed a considerable difference in CTE measurements between the X/Y and Z directions (Table II). In the oriented sample the CTE value parallel to the direction of the applied field (Z direction) was remarkably low (17 ppm/ $^\circ\text{C}$), whereas the CTE value perpendicular (X/Y directions) to the applied field was much greater (94 ppm/ $^\circ\text{C}$). Therefore, as suggested by these measurements and confirmed by X-ray diffraction, in the aligned networks the extended short segments are aligned parallel to the direction of the applied field.

Conclusions

Dicyanate rigid-rod compounds of ring-substituted bis-(4-hydroxyphenyl) terephthalate (4a and 4b) have been

synthesized. Novel liquid crystalline triazine rigid-rod networks (**5a** and **5b**) were prepared by the thermal cyclotrimerization of these dicyanate monomers. As the cross-linking reaction occurred, birefringent droplets appeared which coalesced to form a continuous mesophase with a schlieren texture. The model triazine compound 2,4,6-tris[4-[(4-butoxybenzoyl)oxy]phenoxy]-1,3,5-triazine (**10**) was prepared to investigate the possibility that the phenoxy 2,4,6-substituted triazine ring structure might pass through a discotic mesophase on curing. However, the triazine model system proved not to be liquid crystalline.

As the cross-link density increased, the LC phase was frozen into the final network. The resulting triazine networks have glass transition temperatures of $\sim 190^\circ\text{C}$ and show little decomposition until $\sim 440^\circ\text{C}$. Magnetic field alignment of the LC phase formed during the curing reaction resulted in highly ordered cross-linked triazine networks, with a characteristic smecticlike molecular organization. While we cannot completely rule out the formation of a discotic mesophase, none of the present evidence supports it. The growing networks can only exhibit liquid crystalline behavior if rotation about the ether group linking the mesogenic group to the triazine ring allows parallel placement of the rigid mesogenic groups. Such a structure is reminiscent of hyperbranched molecules.

Remarkably well-oriented triazine networks were obtained ($f \sim 0.50$). The anisotropy of these aligned networks is readily apparent from the difference in the values of the coefficients of thermal expansion (CTE) measured parallel and perpendicular to the direction of alignment. As expected, low values of CTE were observed (17 ppm/ $^\circ\text{C}$) parallel to the direction of the applied field. The preparation of these highly anisotropic rigid-rod networks as well as being of scientific interest may prove to be valuable in the microelectronic and composite industries.

Acknowledgment. NSF Grant DMR-8717815 is acknowledged for partial support of G.G.B. We also acknowledge the use of facilities of the Materials Science Center at Cornell University. Financial support on the part of IBM Corporation, Systems Technology Division, Endicott, NY, is gratefully appreciated. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank MIT for the use of facilities of the Francis Bitter National Magnet Laboratory and the very useful help of Dr. L. Rubin. Finally, many thanks to Prof. G. Galli (Pisa) for our extremely helpful discussions.

References and Notes

- (1) Ballauff, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1130.
- (2) Vilgis, T. A.; Boué, F.; Edwards, S. F. *Springer Proc. Phys.* **1989**, *42*, 170.
- (3) Boué, F.; Edwards, S. F.; Vilgis, T. A. *J. Phys. Fr.* **1988**, *49*, 1635.
- (4) Hoyt, A. E.; Benicewicz, B. C. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 3405.
- (5) Eich, M.; Reck, B.; Yoon, D. Y.; Willson, C. G.; Bjorklund, G. C. *J. Appl. Phys.* **1989**, *66*, 3241.
- (6) Bouligand, Y.; Cladis, P. E.; Liebert, L.; Strzelecki, L. *Mol. Cryst. Liq. Cryst.* **1974**, *25*, 233.
- (7) Clough, S. B.; Blumstein, A.; Hsu, E. C. *Macromolecules* **1976**, *9* (1), 123.
- (8) Conciatori, A. B.; Choe, E. W.; Farrow, G. U.S. Patent 4,440,945, 1984.
- (9) Conciatori, A. B.; Choe, E. W.; Farrow, G. U.S. Patent 4,452,993, 1984.
- (10) Conciatori, A. B.; Choe, E. W.; Farrow, G. U.S. Patent 4,514,553, 1985.
- (11) Calundann, G. W.; Rasoul, H. A.; Hull, H. K. U.S. Patent 4,654,412, 1987.
- (12) Stackman, R. W. U.S. Patent 4,683,327, 1987.
- (13) Dhein, R.; Muller, H. P.; Meier, H.-M.; Gipp, R. U.S. Patent 4,762,901, 1988.
- (14) Muller, H. P.; Gipp, R.; Heine, H. U.S. Patent 4,764,581, 1988.
- (15) Hoyt, A. E.; Benicewicz, B. C. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 3417.
- (16) Barclay, G. G.; McNamee, S. G.; Ober, C. K.; Papathomas, K. I.; Wang, D. W. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
- (17) Korshak, V. V.; Pankratov, V. A.; Ladovskaya, A. A.; Vinogradova, S. V. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 1697.
- (18) Huang, S. J.; Feldman, J. A.; Cercena, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 348.
- (19) Barclay, G. G.; Ober, C. K.; Papathomas, K. I.; Wang, D. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (3), 337.
- (20) Haut, S. A.; Schroeder, D. C.; Schroeder, J. P. *J. Org. Chem.* **1972**, *37*, 1425.
- (21) Wang, D. W. In *Electronic Packaging Materials Science III*, Proceedings of the Materials Research Society; Jaccodine, R., Jackson, K. A., Sundahl, R. C., Eds.; *Materials Research Society*: Pittsburgh, PA, **1989**; Vol. 108, p 125.
- (22) Ober, C. K.; Jin, J. L.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 103.
- (23) Shimp, D. A.; Christenson, J. R.; Ieing, S. J. *SAMPE Symp.* **1989**, *34* (1), 222.
- (24) Shimp, D. A.; Craig, W. K. *SAMPE Symp.* **1989**, *34*, 1336.
- (25) Pankratov, V. A.; Vinogradova, S. V.; Korshak, V. V. *Russ. Chem. Rev. (Engl.)* **1977**, *46*, 278.
- (26) Reck, B.; Ringsdorf, H. *Makromol. Chem., Rapid Commun.* **1985**, *24*, 1299.
- (27) Balta-Calleja, F. J.; Vonk, C. In *Polymer Science Library 8*; Jenkins, A. D., Ed.; Elsevier Science Publishers B. V.: Amsterdam, The Netherlands, **1989**; p 205.
- (28) Blumstein, A.; Vilasager, S.; Ponrathnam, S.; Clough, S. B.; Blumstein, R. B. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 877.

Registry No. **1**, 100-20-9; **2a**, 95-71-6; **2b**, 615-67-8; **3a**, 115218-91-2; **3b**, 140413-48-5; **4a**, 137964-13-7; **4b**, 137964-15-9; **5a**, 137964-14-8; **5b**, 137964-16-0; **8**, 33905-62-3; **9**, 140413-46-3; **10**, 140413-47-4; cyanogen bromide, 506-68-3.