

Synthesis of Biphenylated Cyanate Esters: Thermomechanical Resin Comparisons Within Two Isomeric Series

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ABSTRACT: Three isomeric tetraaryl cyanate esters containing biphenyl moieties {bis-[4-(4'-cyanatophenyl)phenyl]propane, 2,2-bis-[4-(3'-cyanatophenyl)phenyl]propane, and 2,2-bis-[4-(2'-cyanatophenyl)phenyl]propane} and three isomeric triaryl cyanate esters {2-(4'-hydroxyphenyl)-2-[4'-(4-hydroxyphenyl)phenyl]propane, 2-(4'-hydroxyphenyl)-2-[4'-(3-hydroxyphenyl)phenyl]propane, and 2-(4'-hydroxyphenyl)-2-[4'-(2-hydroxyphenyl)phenyl]propane} were synthesized from their corresponding bisphenols. The structures of the monomers were confirmed with IR and ¹H-NMR spectroscopy. The curing behavior was investigated with differential scanning calorimetry. Cyanate esters were cured thermally in the absence of a catalyst and were characterized by dynamic mechanical analysis. The results were compared to the properties of commercial bisphenol

A polycyanurate. Of the three tetraaryl isomers, 2,2-bis-[4-(2'-cyanatophenyl)phenyl]propane had the highest melting point, and its corresponding resin had the lowest glass-transition temperature (T_g). The para isomer displayed the highest T_g value of the three novel tetraaryl resins. The triaryl dicyanate isomers were low-melting solids, with the ortho and meta isomers existing as liquids at room temperature. The T_g value of the *para*-triaryl isomer was the highest of the three triaryl isomers and was about the same as that of bisphenol A polycyanurate. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 756–763, 2011

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INTRODUCTION

Few studies, if any, have examined the effects of ortho and meta substitution on bisphenols used as precursors for cyanate resins. This is not surprising because the synthesis of bisphenol A (BPA), which uses phenol and acetone as starting materials, overwhelmingly results in *p,p*-dihydroxylated BPA. For electronic reasons, the condensation of phenol with acetone yields primarily 2,2-bis(4-hydroxyphenyl)propane, which is accompanied by low and impracticable yields of materials contaminated with *o,p*-BPA and *o,o*-BPA.¹

Although *p,p*-dihydroxylated bisphenols may produce cyanate resins that are good enough for commercial purposes, there have been no literature reports of other isomers. It may, therefore, be possible to improve material properties through changes in the geometry of the bisphenol; that is, the relative hydroxyl-to-hydroxyl distance within the bisphenol could be changed, or the *para*-hydroxyl could be changed to ortho or meta positioning.

Over the past 50 years, intensive investigations of monomer alternatives to BPA for the synthesis of new BPA polycarbonates, for example, have demonstrated that the substitution of the central bridging isopropylidene group with groups larger than isopropylidene leads to polycarbonates that invariably have higher glass transitions than BPA polycarbonate but fail to retain the ductile properties of this unusual glassy polymer: the structural variation of the central bridging isopropylidene group between phenyl rings affords brittle materials and not ductile ones.^{2,3} When, however, additional phenyl rings, which effectively increase the hydroxyl-to-hydroxyl distance but leave the isopropylidene unit intact, are added, biphenylated materials demonstrably retain the characteristic ductility and toughness of BPA polycarbonate.⁴ Additionally, the new polycarbonates are less hydrolytically sensitive because they are more hydrophobic.

It is, therefore, interesting to examine similar structural variations in other classes of materials. This article focuses on dicyanates made from new bisphenols. These dicyanates had a greater cyanate-to-cyanate distance than BPA dicyanate. This was accomplished by the addition of phenyl rings in tandem with the isomeric variation of the location of the cyanate group on distal phenyl rings. The Suzuki

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asymmetric aryl coupling reaction was used to synthesize precursor bisphenols to afford biphenyl units as previously reported.^{5,6} Because of the commercial availability of para-, meta-, and ortho-substituted boronic acids for the Suzuki reaction, pure target bisphenol precursors free of contaminating isomers were readily obtainable. These bisphenols were subsequently converted into their corresponding cyanate esters by the usual method using nucleophilic substitution by the respective phenoxide ion on cyanogen bromide.

To the best of our knowledge, an examination of an isomeric series of polycyanurate esters has not previously been reported, and the literature is silent concerning how systematic, isomeric variation of the monomer structure or monomer geometry affects the thermomechanical properties of cured cyanate resin systems.⁷

We anticipated that polycyanurates made from the aforementioned isomeric dicyanate variants might result in variations in the molecular structure of the resulting cured resin networks. For example, the high symmetry of cured cyanate resins from para-, para-substituted dicyanates might be expected to form a more open, ideal lattice network. The introduction of asymmetry into meta and ortho materials by displacement of the cyanate group from the symmetrical 4,4' (para, para) position, which is in line with the biphenyl unit, to the lateral 3,3' (meta, meta) or 2,2' (ortho, ortho) position would be expected to cause deviations from a highly open lattice arrangement. However, the more open network structure would be expected to show a lower crosslink density and a concomitantly lower modulus and lower glass-transition temperature (T_g) in comparison with the opposite extreme of a closed network structure. With this in mind, we address the effect of the dicyanate monomer geometry on the properties of the resulting polycyanurate resins.

EXPERIMENTAL

Materials

The dicyanate ester of BPA, 2,2-bis(4-cyanatophenyl)propane, was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan). Cyanogen bromide (97%) and triethylamine (99%) were purchased from Aldrich Chemical Co. Triethylamine was distilled over solid KOH before use.

Synthesis of the cyanate ester monomers

Synthesis of bis-[4-(4'-cyanatophenyl)phenyl]propane (*para*-tetraaryl BPA dicyanate)

In a 250-mL, round-bottom flask, 20.00 g (0.0527 mol) of 2,2-bis-[4-(4'-hydroxyphenyl)phenyl]propane (tet-

raaryl BPA) and 11.16 g (0.1054 mol) of cyanogen bromide were dissolved in 150 mL of dry acetone. The flask was placed in an ice bath, and 14.76 mL (0.1054 mol) of dry triethylamine was added dropwise over 30 min with constant stirring. The reaction solution was allowed to spontaneously warm to room temperature; afterward, it was stirred for 24 h. The reaction mixture was poured into water and extracted with dichloromethane, washed with water three times, and then washed with brine. After it was dried over sodium sulfate, the solvent was removed by rotary evaporation, and light yellow crystals were produced. The material was purified by flash chromatography through silica gel with a dichloromethane mobile phase to yield white crystals.

Yield: 13 g (57%). mp: 137°C. IR (KBr, cm^{-1}): 3032, 2970, 2281, 2237, 1679, 1600, 1494, 1396, 1195, 1168, 1085, 1004, 823. $^1\text{H-NMR}$ [hexadeuterated dimethyl sulfoxide ($\text{DMSO-}d_6$), δ]: 7.78 (d, 4H, $J = 9$ Hz), 7.57 (d, 4H, $J = 9$ Hz), 7.48 (d, 4H, $J = 9$ Hz), 7.32 (d, 4H, $J = 9$ Hz), 1.66 (s, 6H). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.62–7.65 (d, 4H), 7.47–7.49 (d, 4H), 7.34–7.37 (d, 8H), 1.76 (s, 6H).

2,2-Bis-[4-(3'-cyanatophenyl)phenyl]propane (*meta*-tetraaryl BPA dicyanate)

This material was synthesized and purified in the method used for the para isomer to yield white crystals.

Yield: 17.41 g (77%). mp: 129°C. IR (KBr, cm^{-1}): 3062, 2968, 2274, 2233, 1614, 1579, 1481, 1178, 1163. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 7.56–7.69 (m, 8H), 7.48 (s, 2H), 7.39 (d, 2H, $J = 9$ Hz), 7.33 (d, 4H, $J = 9$ Hz), 1.66 (s, 6H). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.49–7.51 (m, 10H), 7.36 (d, 4H, $J = 9$ Hz), 7.24 (s, 2H), 1.76 (s, 6H).

2,2-Bis-[4-(2'-cyanatophenyl)phenyl]propane (*ortho*-tetraaryl BPA dicyanate)

This material was synthesized and purified in an analogous fashion to yield white crystals.

Yield: 16.20 g (70%). mp: 160°C. IR (KBr, cm^{-1}): 3059, 2976, 2270, 2239, 1575, 1558, 1483, 1178, 1128. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 7.63–7.66 (d, 2H), 7.53–7.57 (m, 4H), 7.43–7.48 (m, 8H), 7.36–7.39 (d, 2H), 1.69 (s, 6H). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.57–7.60 (d, 2H), 7.45–7.47 (d, 4H), 7.37 (s br, 10H), 1.78 (s, 6H).

2-(4'-Hydroxyphenyl)-2-[4'-(4-hydroxyphenyl)phenyl]propane (*para*-triaryl BPA dicyanate)

This material was synthesized and purified in an analogous fashion to yield white crystals.

Yield: 12.07 g (78%). mp: 79°C. IR (KBr, cm^{-1}): 3032, 2969, 2266, 2235, 1652, 1600, 1491, 1186, 1165. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 7.74–7.77 (d, 2H), 7.53–7.56 (d, 2H), 7.45–7.48 (d, 2H), 7.29–7.35 (m, 6H), 1.62 (s,

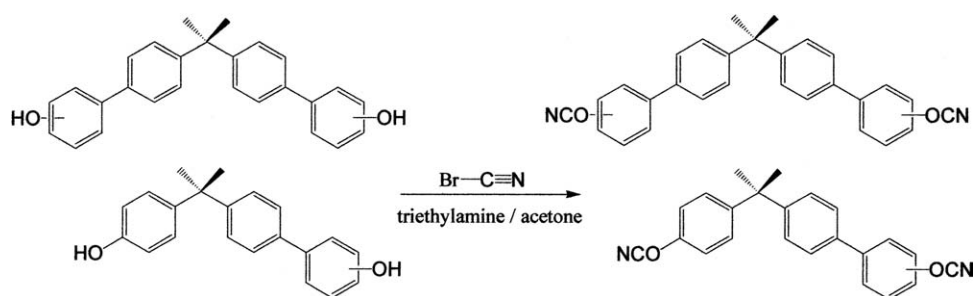


Figure 1 Synthesis of the cyanate ester monomers.

6H). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.62–7.65 (d, 2H), 7.46–7.48 (d, 2H), 7.20–7.37 (m, 8H), 1.72 (s, 6H).

2-(4'-Hydroxyphenyl)-2-[4'-(3-hydroxyphenyl)phenyl]propane (*meta*-triaryl BPA dicyanate)

This material was synthesized and purified in an analogous fashion to yield white crystals.

Yield: 5.94 g (78%). IR (KBr, cm^{-1}): 3059, 2964, 2272, 2236, 1616, 1582, 1500, 1289, 1197, 1171, 1077, 1014, 833. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 7.58–7.62 (m, 5H), 7.28–7.40 (m, 7H), 1.62 (s, 6H). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.48–7.52 (m, 5H), 7.23–7.32 (m, 7H), 1.72 (s, 6H).

2-(4'-Hydroxyphenyl)-2-[4'-(2-hydroxyphenyl)phenyl]propane (*ortho*-triaryl BPA dicyanate)

This material was synthesized and purified in an analogous fashion to yield white crystals.

Yield: 4.05 g (20%). IR (KBr, cm^{-1}): 3061, 2971, 2268, 2238, 1599, 1575, 1500, 1196, 1172. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, δ): 7.61–7.64 (d, 1H), 7.50–7.53 (d, 2H), 7.30–7.46 (m, 9H), 1.65 (s, 6H). $^1\text{H-NMR}$ (CDCl_3 , δ): 7.56–7.59 (d, 1H), 7.43–7.45 (d, 2H), 7.21–7.39 (m, 9H), 1.73 (s, 6H).

Polymerization of the cyanate ester monomers

Samples for thermomechanical analysis and dynamic mechanical analysis (DMA) were prepared by uncatalyzed thermal polymerization in a silicone rubber mold ($30 \times 12 \times 2 \text{ mm}^3$). Crystalline monomers were heated 20°C above their respective melting points for 2 h and then at 220°C for 18 h. The cured resin samples were rigid and clear yellow (which is typical of cyanate ester resins), except for *ortho*-tetraaryl BPA polycyanurate, which was red.

Instrumentation

$^1\text{H-NMR}$ spectra were recorded with a GE-QE300 at 300 MHz. ^1H chemical shifts were reported as δ values (ppm) with respect to $\text{DMSO-}d_6$ (2.49) or CDCl_3 (7.26). IR spectra were recorded with a Bio-Rad FTS-135 IR spectrometer.

Differential scanning calorimetry (DSC) was performed with a DSC Q100 in aluminum pans at heating and cooling rates of $10^\circ\text{C}/\text{min}$. The linear thermal expansion behavior was determined with a Q400 thermomechanical analyzer from TA Instruments. Cylindrical samples with typical dimensions of $4 \times 10 \text{ mm}^2$ were heated from 25 to 350°C at a rate of $5^\circ\text{C}/\text{min}$. This heating cycle was repeated until no evidence of postcure was observed. Thermal expansion coefficients are reported as the slopes of dimensional change/temperature plots in the range of $50\text{--}100^\circ\text{C}$.

DMA measurements were taken with a Q400 dynamic mechanical analyzer from TA instruments. The rectangular specimens ($30 \times 12 \times 2 \text{ mm}^3$) were secured in a single cantilever clamp and heated at a rate of $5^\circ\text{C}/\text{min}$ from the ambient temperature to 250°C while being oscillated at a frequency of 1 Hz and a drive amplitude of $10 \mu\text{m}$. The samples were then cooled to room temperature and heated again at $5^\circ\text{C}/\text{min}$ to 350°C . This heating cycle was repeated until no evidence of postcure was evident in the DMA curves; that is, no advancing T_g was observed.

RESULTS AND DISCUSSION

The bisphenol precursors to the isomers of tetraaryl BPA and triaryl BPA were synthesized in our laboratory according to previously reported procedures.^{5,6} The dicyanate monomers were brought to chromatographic purity by flash chromatography through silica gel. The structures of the dicyanates were confirmed with NMR and IR spectroscopy. No impurities were detected in the NMR spectra of the compounds.

Difunctional cyanate esters were prepared in a one-step reaction by the method patented by Grigat and Putter⁸ with a modified workup procedure. The dicyanate esters of *ortho*-tetraaryl BPA, *meta*-tetraaryl BPA, *para*-tetraaryl BPA, *ortho*-triaryl BPA, *meta*-triaryl BPA, and *para*-triaryl BPA were obtained through the reaction of cyanogen bromide with the corresponding bisphenol in acetone in the presence of the base scavenger triethylamine (Fig. 1). Materials

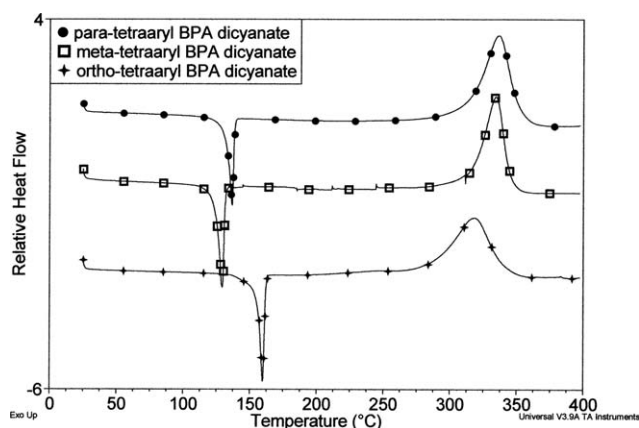


Figure 2 DSC thermograms of the tetraaryl BPA dicyanate esters.

were brought to chromatographic purity by flash chromatography.

Isomeric tetraaryl series

Tetraaryl cyanate esters, which were synthesized according to the aforementioned reaction scheme, were heated in a DSC instrument. The DSC thermograms of the materials are shown in Figure 2. All thermograms had a broad exotherm between 280 and 350°C that was characteristic of cyanate ester cyclotrimerization. The DSC thermograms of the monomers indicated relatively sharp melting transitions characteristic of the pure material. The order of melting points from highest to lowest was as follows: ortho > para > meta. All tetraaryl dicyanates had a wide processing window between the melting transitions and the polymerization exotherms, and this made the materials suitable for commercial processing.

The glass transitions of the polymerized tetraaryl dicyanates were determined by DMA (Fig. 3). The T_g values obtained from the loss modulus, storage modulus, and $\tan \delta$ curves are tabulated in Table I. The *para*-tetraaryl isomer had the highest T_g value of 315°C from the $\tan \delta$ curve, and the meta and ortho isomers had T_g values of 237 and 209°C, respectively. The storage modulus of *para*-tetraaryl BPA polycyanurate was the lowest of the three tetraaryl isomers across the measured temperature range and was lower than the storage modulus of BPA polycyanurate from approximately 150°C to the glass transition (Fig. 3). The tetraaryl isomer with the highest storage modulus was *ortho*-tetraaryl BPA polycyanurate. The width of the loss modulus and $\tan \delta$ curves of *para*-tetraaryl BPA polycyanurate at the glass transition was significantly wider than the widths for the other tetraaryl isomers and BPA polycyanurate. The height of the loss modulus and $\tan \delta$ peaks of *para*-tetraaryl BPA polycyanurate was the lowest of the three isomers and BPA polycyanurate.

Isomeric triaryl series

Triaryl cyanate esters synthesized by the reaction scheme in Figure 1 were heated in a DSC instrument. The DSC thermograms of the materials are shown in Figure 4. All materials demonstrated a broad exotherm between 200 and 350°C that was characteristic of cyanate ester cyclotrimerization. The DSC thermogram of *para*-triaryl BPA displayed a sharp melting transition characteristic of the pure material. The *meta*-triaryl BPA and *ortho*-triaryl BPA isomers were liquids at room temperature and therefore did not show a melting transition in the DSC thermograms.

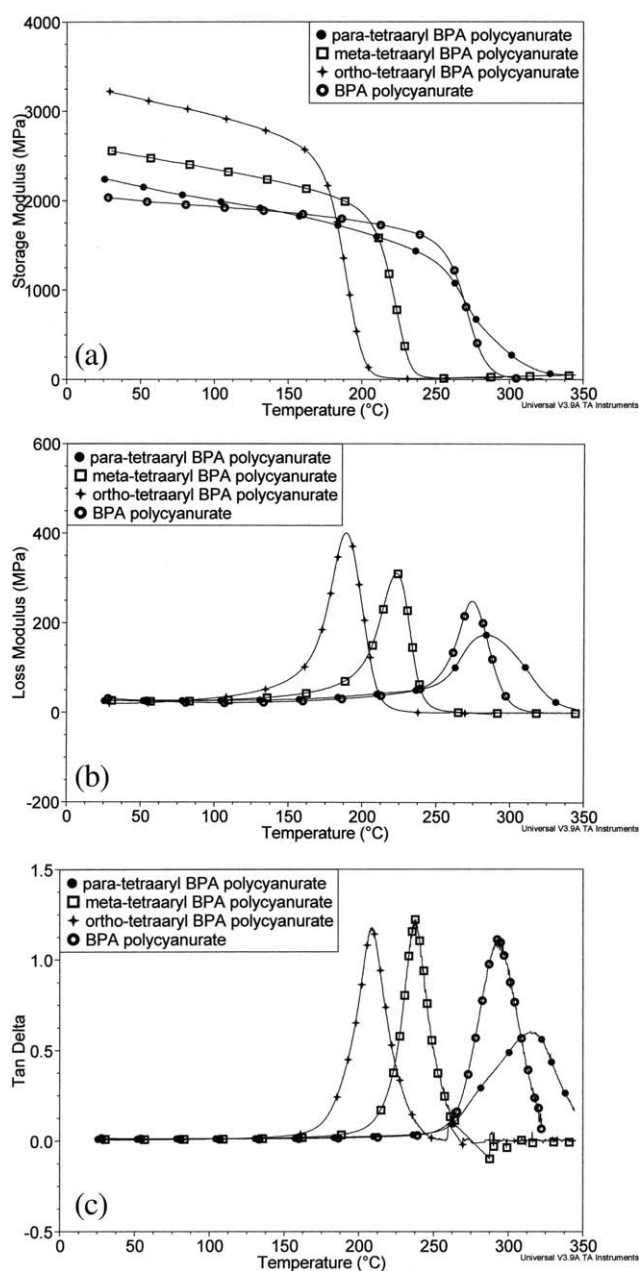


Figure 3 DMA curves of the tetraaryl BPA polycyanurate isomers.

TABLE I
 T_g Values ($^{\circ}\text{C}$) Obtained from DMA Curves

Polycyanurate	Storage modulus	Loss modulus	Tan δ
<i>para</i> -Tetraaryl BPA polycyanurate	253	285	315
<i>meta</i> -Tetraaryl BPA polycyanurate	207	233	237
<i>ortho</i> -Tetraaryl BPA polycyanurate	175	189	209
BPA polycyanurate	257	274	294

The glass transitions of the polymerized triaryl dicyanates were determined by DMA (Fig. 5). The T_g values obtained from the loss modulus, storage modulus, and tan δ curves are tabulated in Table II. The *para*-triaryl isomer had the highest T_g value of 298°C from the tan δ curve, and the meta and ortho isomers had T_g values of 234 and 210°C , respectively. The storage modulus of *para*-triaryl BPA polycyanurate was the lowest of the three triaryl isomers and BPA polycyanurate across the measured temperature range. The triaryl isomer with the highest storage modulus was *ortho*-triaryl BPA polycyanurate. The width of the loss modulus and tan δ curves of *para*-triaryl BPA polycyanurate at the glass transition was significantly larger than the widths for the other triaryl isomers and slightly wider than that for BPA polycyanurate. The height of the loss modulus and tan δ peaks of *para*-triaryl BPA polycyanurate was the lowest of the three isomers and BPA polycyanurate.

Property comparison within each series

As mentioned previously, polycyanurates made from *para*-substituted tetraaryl and triaryl cyanate esters might be expected to have lower T_g values and lower storage moduli than those made from meta- and ortho-substituted dicyanates. Surprisingly, the polycyanurate cured from the *para*-tetraaryl isomer had a T_g value higher than those of the *meta*-

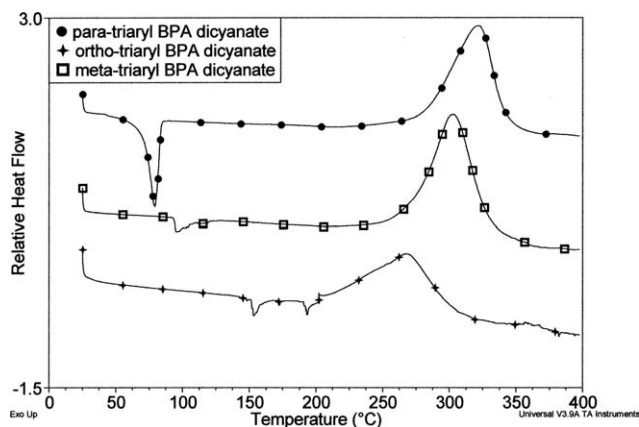


Figure 4 DSC thermograms of the triaryl BPA dicyanate esters.

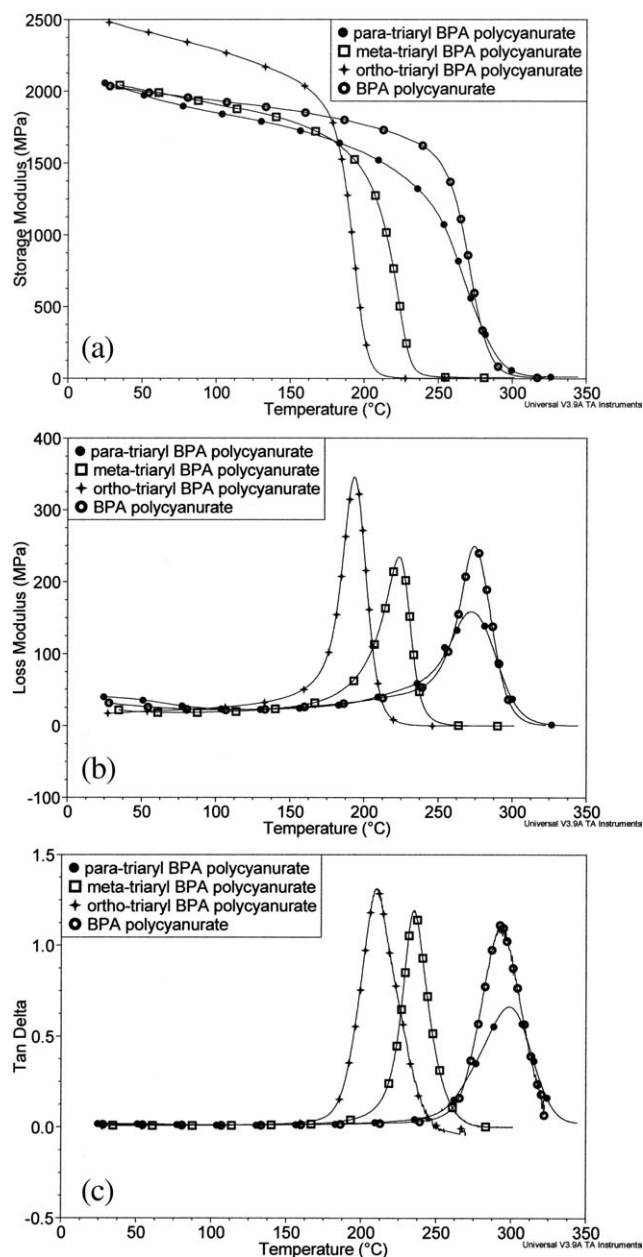


Figure 5 DMA curves of the triaryl BPA polycyanurate isomers.

tetraaryl BPA polycyanurate and *ortho*-tetraaryl BPA polycyanurate and slightly higher than that of BPA polycyanurate. Similarly, the polycyanurate cured from *para*-triaryl BPA had a T_g value higher than those of *meta*-triaryl BPA polycyanurate and *ortho*-triaryl BPA polycyanurate and approximately the same as that of BPA polycyanurate. This behavior of *para*-tetraaryl BPA polycyanurate and *para*-triaryl BPA polycyanurate with respect to T_g was different from what was expected. The polycyanurates made from *para*-tetraaryl dicyanate and *para*-triaryl dicyanate were expected to form a more open network structure and therefore display lower T_g values than the meta and ortho isomers.

TABLE II
 T_g Values (°C) Obtained from DMA Curves

Polycyanurate	Storage modulus	Loss modulus	Tan δ
<i>para</i> -Triaryl BPA polycyanurate	245	273	298
<i>meta</i> -Triaryl BPA polycyanurate	202	223	234
<i>ortho</i> -Triaryl BPA polycyanurate	180	193	210
BPA polycyanurate	257	274	294

The magnitude of the storage moduli of the polycyanurates made from tetraaryl and triaryl polycyanurates was in line with what was expected and showed a clear trend with the isomer used. Polycyanurates made from the *ortho*-dicyanate isomers had the highest storage moduli, and they were followed by those from the *meta*-dicyanate and *para*-dicyanate isomers. These results support the hypothesis that the *ortho*-dicyanate isomers would form a more closed network structure than the para and meta isomers and would, therefore, display higher storage moduli.

There was an apparent disparity between the T_g values and storage moduli of the isomeric tetraaryl and triaryl polycyanurate materials. The low storage moduli of para-substituted polycyanurates suggested that they existed as relatively open network structures, but the relatively high T_g values of the para-substituted polycyanurates suggested the opposite. To gain insight into the network structures of the three isomeric tetraaryl thermosets and three isomeric triaryl thermosets, we calculated the crosslink densities from the storage moduli in the rubbery state above the glass transition of the polymers with the following equation:

$$\text{Storage modulus} = 3NRT \quad (1)$$

where N is the crosslink density (mol/m³), T is the temperature (K), and R is the universal gas constant (8.314 J/mol K).⁹ Storage modulus values were chosen at least 20°C past the α transition of the samples. The crosslink densities of the materials showed a clear trend: the para isomer showed the highest crosslink density and was followed by the meta and ortho materials (Table III).

Interestingly, within the tetraaryl series, although *para*-tetraaryl BPA had the highest crosslink density, the storage modulus curves indicated that it was the least brittle of the three tetraaryl isomers below the glass transition and was less brittle than BPA polycyanurate near T_g . It might be expected that a polycyanurate with a higher crosslink density would have a higher modulus, but the opposite was observed.

The triaryl BPA polycyanurate series showed a parallel trend with the tetraaryl series. The *para*-triaryl BPA polycyanurate isomer had the highest

calculated crosslink density but had the lowest storage modulus of the three isomers.

This phenomenon of a decreasing modulus with an increasing crosslink density was observed in BPA polycyanurate systems with various crosslink densities, which were controlled by the variation of the extent of cure.¹⁰ Increasing the crosslink density of BPA polycyanurate led to a decrease in Young's modulus at room temperature. This trend was attributed to two effects: first, the cohesive energy density was calculated to be lower in the more crosslinked networks, and second, the magnitude of the sub- T_g relaxations, which were linked to localized molecular motions, were higher in the network with a high crosslink density. The same phenomenon was observed in bisphenol M polycyanurates with different degrees of resin conversion.¹¹

Because the polymerization exotherms in the DSC scans of the tetraaryl and triaryl materials occurred at approximately the same temperature, the difference in the crosslink density may not have been due to reactivity differences of the isomers. This conclusion, however, should be approached carefully because it is appreciated that the polymerization exotherm of aryl cyanate esters can differ greatly with even small amounts of impurities.⁷

The width of the loss modulus and tan δ peaks for *para*-tetraaryl polycyanurate and *para*-triaryl polycyanurate was the highest of the three isomers. This suggests that the *para*-polycyanurate isomers had a more open network structure that could represent a population of interpenetrating segments broader than that tolerable by the ortho structure (if any). Although this is difficult to rationalize without further study, this corresponds to the crosslink density calculations.

If polycyanurates made from para-substituted materials form more open network structures, it is surprising that these materials also have the highest crosslink density. This phenomenon can be rationalized if we acknowledge that different types of crosslinks may exist in these materials. Certainly, the predominant type of crosslink for these resins is covalent crosslinking through the formation of triazine rings. However, the crosslink density is

TABLE III
 Crosslink Densities of the Tetraaryl and Triaryl Cyanate Resins

Polycyanurate	Crosslink density (mol/m ³)
<i>para</i> -Tetraaryl BPA polycyanurate	9170
<i>meta</i> -Tetraaryl BPA polycyanurate	1918
<i>ortho</i> -Tetraaryl BPA polycyanurate	1265
<i>para</i> -Triaryl BPA polycyanurate	2277
<i>meta</i> -Triaryl BPA polycyanurate	1650
<i>ortho</i> -Triaryl BPA polycyanurate	607
BPA polycyanurate	3070

calculated to be greater than what an open lattice containing only covalent crosslinks would allow; therefore, to rationalize this, we suggest that an open network may contain mostly covalent crosslinks but also noncovalent crosslinks, which may be the result of interpenetrating segments through the network. This would correspond to the higher value of the calculated crosslink density and the broader loss modulus and $\tan \delta$ peaks.

It has been suggested that intramolecular cyclization occurs during the polymerization of cyanate esters.^{12–17} The formation of intramolecular cycles has been thought to explain the anomalous gel point at approximately 60% conversion, which is higher than the predicted conversion of 50%. The presence of intramolecular cycles has also been proposed as an explanation of the amazingly high conversion attainable for cyanate resins despite the polymerization being diffusion-limited past the gel point.¹⁸ Evidence of possible cages formed through cyclization has been found spectroscopically.^{12,18–20} Evidence of a dimer species covalently linked with a four-membered ring has been observed, and this has also been proposed to affect the delayed gelation of BPA dicyanate.²¹

From a purely heuristic standpoint, one might expect the ortho and meta isomers of tetraaryl BPA and triaryl BPA to be geometrically favorable for intramolecular cyclization and therefore a more closed network. If intramolecular cycles were present in the ortho and meta isomers, a lower T_g value and a lower modulus (in comparison with the para isomer) in the glassy state would be expected despite the system reaching the highest possible cure. These trends were observed in this work, and this suggests that intramolecular cycles may have formed to a greater extent in the *ortho*-tetraaryl and *meta*-tetraaryl materials. Further work, such as the determination of the structures formed in the sol content of partially polymerized materials via high-performance liquid chromatography and mass spectrometry, needs to be done to substantiate this hypothesis. Such a study by other researchers found evidence of the cycles by this characterization.¹² A greater concentration of cyclic compounds might be expected for the ortho and meta isomers in the sol content of the partially cured resins. The degree of cure at the gel point also needs to be determined to examine this hypothesis. If the *ortho*-tetraaryl BPA and *meta*-tetraaryl BPA isomers favor cyclic compounds during curing, one would expect the degree of curing at the gel point to increase from lowest to highest in the following order: para < meta < ortho.

Property comparison between series

In general, the T_g values, storage moduli, and crosslink densities were higher for the tetraaryl series

than those for the corresponding isomers of the triaryl series. It may be significant that a more appropriate comparison exists between *para*-tetraaryl BPA dicyanate and *para*-triaryl BPA dicyanate because the cyanate groups were at the para positions at both ends of both molecules, whereas the *meta*-triaryl BPA dicyanate and *ortho*-triaryl BPA dicyanate had but one cyanate group in the para position. However, the synthesis of *o,o*-dicyanates, and *m,m*-dicyanates may not be feasible for the same reasons that prevent ortho and meta isomers of BPA from forming to an appreciable extent.

CONCLUSIONS

Six novel dicyanate esters with biphenyl moieties were synthesized through the reaction of the respective bisphenol with cyanogen bromide. The dicyanates were cured thermally without a catalyst and yielded resinous materials. The polycyanurate made from *para*-tetraaryl BPA dicyanate had the highest T_g value of the six resins, and this value was slightly higher than T_g of its BPA analogue. The calculation of the crosslink density from the rubbery portion of the storage moduli in the DMA scans of the materials suggested that *para*-tetraaryl BPA polycyanurate had the highest crosslink density. The thermo-mechanical properties of the resin supported this hypothesis. The *para*-tetraaryl resin had the lowest glassy-state storage modulus and the highest T_g value. The *para*-tetraaryl BPA polycyanurate T_g value was slightly higher than the T_g value of commercial BPA polycyanurate, and the *para*-triaryl BPA polycyanurate T_g value was approximately the same as that of BPA polycyanurate.

Polycyanurates made from *para*-substituted dicyanates were expected to display low storage moduli, low T_g values, and low crosslink densities because of a more open network structure. Although the *para*-substituted polycyanurates did have the lowest storage moduli of the three isomers, the T_g values and crosslink densities were surprisingly high. This anomaly was rationalized by the fact that an open network structure forms mostly covalent crosslinks but may be more favorable to the formation of noncovalent crosslinks as the result of interpenetrating segments through the network. Additional studies addressing the molecular structure and densities of the cured resin materials are in progress and will be reported in due course.

References

1. Fennhoff, G.; Buysch, H. J.; Fengler, G. U. S. Pat. 6,191,316 (1998).
2. Li, X.; Yee, A. F. *Macromolecules* 2003, 36, 9421.
3. Bendler, J. T. *Comput Theor Polym Sci* 1998, 8, 83.

4. Boyles, D. A.; Dehmer, P.; Bendler, J. T.; Filipova, T. SAMPE Tech Conf Proc 2006, 51, 4.
5. Boyles, D. A.; Filipova, T. S.; Bendler, J. T.; Longbrake, G.; Reams, J. Macromolecules 2005, 38, 3622.
6. Filipova, T.; Reams, J.; Boyles, D. A. Polym Prepr (Am Chem Soc Div Polym Chem) 2005, 46, 971.
7. Hamerton, I. Chemistry and Technology of Cyanate Ester Resins; Chapman & Hall: London, 1994.
8. Grigat, E.; Putter, R. Ger. Pat. 1,195,764 (1965).
9. Treloar, L. R. G. The Physics of Rubber Elasticity, 3rd ed.; Clarendon: Oxford, 1975.
10. Georjon, O.; Galy, J. J Appl Polym Sci 1997, 65, 2471.
11. Simon, S. L.; Gillham, J. K. J Appl Polym Sci 1994, 51, 1741.
12. Qingxiu, L.; Simon, S. L. Macromolecules 2007, 40, 2246.
13. Gupta, A. M. Macromolecules 1991, 24, 3459.
14. Gupta, A. M.; Hendrickson, R. C.; Macosko, C. W. J Chem Phys 1991, 95, 2097.
15. Bauer, J.; Bauer, M. Acta Polym 1987, 38, 16.
16. Bauer, J.; Bauer, M. J Macromol Sci Chem 1990, 27, 97.
17. Lin, R.-H.; Su, A.-C.; Hong, J.-L. J Appl Polym Sci 1999, 73, 1927.
18. Fang, T.; Houlihan, F. M. Polym Prepr (Am Chem Soc Div Polym Chem) 1994, 35, 535.
19. Wang, F. L.; Hong, J. L. Polymer 1998, 39, 4319.
20. Fang, T.; Shimp, D. A. Prog Polym Sci 1995, 20, 61.
21. Grenier-Loustalot, M. F.; Lartigau, C.; Metras, F.; Grenier, P. J Polym Sci Part A: Polym Chem 1996, 34, 2955.