A New Room-Temperature Liquid, High-Performance Tricyanate Ester

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ABSTRACT: A new tricyanate ester monomer of a tris(4-hydroxyphenyl)benzene derivative was synthesized in 6-steps with a 63% overall yield. The geminal substitution of phenyl rings on ethane, in addition to the creation of a racemic/diastereomeric mixture, resulted in a liquid monomer whereas compounds with similar structure and symmetry have melting points typically over 100 °C. Key properties of the polycyanurate, such as the glass transition temperature and moisture resistance, were positively influenced by the higher crosslink density provided by the monomer. © 2010 Wiley Periodicals, Inc.† J Polym Sci Part A: Polym Chem 48: 4547–4554, 2010

KEYWORDS: cyclopolymerization; differential scanning calorimetry; high performance polymers; thermosets

INTRODUCTION Polycyanurates (also known as "cyanate ester resins") have emerged as an important class of thermosetting polymers in both current and developmental aerospace, automotive, and electronics applications.[1–3] Polycyanurates are valued for their inherent fire resistance, low moisture uptake, stability in cold water, and maximum use temperatures that significantly exceed those of epoxy resins with corresponding temperature-dependent monomer viscosity characteristics.[4(a)] In addition, cyanate ester monomers exhibit low toxicity, very little shrinkage or outgassing upon cyclotrimerization, and particularly for systems that are liquids at room temperature, favorable solubility and viscosity characteristics for the addition of comonomers[4(b)] or toughening agents.[4(c)]

Cyanate ester monomer systems that are liquids at room temperature may suffer from limitations due to lowered maximum use temperature (typically determined by the glass transition temperature), comparatively higher moisture uptake, brittleness, or unfavorable solubility and viscosity characteristics for blending and/or toughening. Decreased thermomechanical performance is often the result of incorporating asymmetric or highly flexible chemical functionalities into the monomer backbone, while the other limitations are typically associated with highly aromatic cyanate esters that are rendered oligomeric to prevent crystallization. Recent efforts to overcome these limitations include the creation of polydisperse room temperature liquids from mixtures of oligomers with (monodisperse) melting points well over 100 °C by Laskoski et al.,[5,6] and the synthesis of room temperature liquids from mixed oligomers with balanced flexible, aromatic, and hydrophobic chemical groups by Yameen et al.[7]

One of the few commercially available dicyanate ester monomers that can be handled as a low-viscosity (supercooled) liquid at room temperature is Primaset® LECy.[8] The monomer's low melting point (29 °C)[9] may be the result of the unique thermochemical properties[10] of the parent hydrocarbon, 1,1-diphenylethane. As can be seen from Table 1, the geminal substitution of two phenyl rings on ethane is associated with a large depression in melting temperature compared to various aromatic hydrocarbon analogs. This relative trend in melting point is somewhat mirrored in the corresponding cyanate esters.

We therefore sought to use 1,1-diphenylethane as a template on which to build a tricyanate ester monomer, which would be liquid at or near room temperature. An additional feature of the approach is the creation of a racemic/diastereomeric mixture of compounds containing multiple chiral centers. This approach enables further depression of the melting point[12] by mixing monomers of the same molecular weight and identical nonenantiomeric chemical functionality. It thus maintains virtually equal reactivity of the constituent cyanate ester groups and the solubility and viscosity characteristics necessary for successful toughening, while reducing the need to incorporate flexible chemical linkages and/or asymmetry in the chemical structure of the monomer. We report on both the results of the successful monomer synthesis and the properties of its cured polycyanurate.

Additional Supporting Information may be found in the online version of this article. Correspondence to: M. C. Davis (E-mail: matthew.davis@navy.mil)

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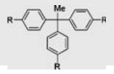
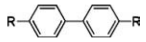
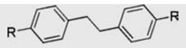
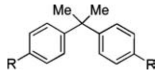
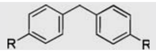
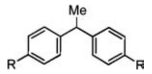
TABLE 1 Melting Points of Parent Aromatic Hydrocarbons and Corresponding Di and Stricyanate Esters

R=OCN			R=H	
Mp (°C)[a]	Name	Compound Structure	Name	Mp (°C)
104	1,1,1-Tris(4-cyanatophenyl)ethane ESR-255		1,1,1-Triphenylethane	95–96[b]
131	4,4′-Dicyanatodiphenyl		Diphenyl	69–72[c]
112–114[d]	1,2-Bis(4-cyanatophenyl)ethane		1,2-Diphenylethane	50–53[c]
79	2,2′-Bis(cyanatophenyl)isopropylidene Primaset® BADCy		2,2-Diphenylpropane	29[c]
108	4,4′ Dicyanatodiphenylmethane		Diphenylmethane	22–24[c]
29	1,1-Bis(4-dicyanatophenyl)ethane Primaset® LECy		1,1-Diphenylethane	−18[e]

[a] Ref. 9.
[b] Ref. 11.
[c] Sigma-Aldrich Chemical catalog 2003–2004.
[d] Synthesis and characterization of this compound will be published elsewhere.
[e] Material Safety Data Sheet OHS33053.

EXPERIMENTAL

Materials

The 4-methoxyacetophenone, *N*,*N*-dimethylformamide dimethyl acetal, pyridine, methyltriphenylphosphonium bromide, potassium *tert*-butoxide, 5% Pd/C, pyridine hydrochloride, cyanogen bromide, triethylamine and solvents were purchased from Sigma-Aldrich (Milwaukee) and used as received.

Measurement and Characterization

General Methods

Melting points were collected on a Mel-Temp II from Laboratory Devices (Holliston, MA) and are not corrected. Infrared analysis of monomer **7** and all cured and uncured samples were analyzed by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy using a single bounce diamond ATR crystal. The instrument used was a Nexus 870 FTIR spectrometer with a liquid N_2 cooled mercury cadmium telluride (MCTA) detector. Each spectrum is an average of 28 scans at 4 cm^{-1} resolution. All NMR data were collected on a Bruker Avance II 300 MHz spectrometer. Nuclear magnetic resonance data (free-induction decay's) were processed using NUTS software from Acorn NMR (Livermore, CA). All spectra are referenced to solvent or tetramethylsilane. Elemental analyses were performed by Atlantic Microlab, (Norcross, GA).

Thermal Analysis

Prior to cyclotrimerization, monomer **7** was partially degassed along with a silicone mold at 95 °C for 30 minutes under reduced pressure (300 mm Hg). The monomer was then poured into the mold and cured under flowing nitrogen for 1 h at 150 °C followed by 24 h at 210 °C to produce void-free discs measuring ~13.7 mm in diameter and 1.6 mm thick and weighing 200–300 mg. The temperature ramp rate during cure was 5 °C/min.

The density of the cured resin was determined by placing some discs in solutions of $CaCl_2$ (as the dihydrate) and deionized water and varying the $CaCl_2$ concentration until neutral buoyancy was observed on bubble-free samples over a period of several minutes. The density of the neutrally buoyant solution was determined by placing 10.00 mL in a volumetric flask (calibrated with deionized water at 20 °C) and weighing, and checked against the predicted density of the solution at ambient temperature based on the known concentration of $CaCl_2$. Prior to thermomechanical analysis, some discs were also placed in ~300 mL of deionized water at 85 °C for 96 h with sample dimensions and weight measured before and after exposure.

Differential scanning calorimetry (DSC) was performed on ~10 mg of monomer reserved after degassing using a TA Instruments Q2000 calorimeter under 50 mL/min of flowing nitrogen. Samples were heated to 350 °C, then cooled to 100 °C and reheated to 350 °C, all at 10 °C/min. Thermogravimetric analysis (under both nitrogen and air) was performed on ~10 mg samples of the cured discs that were removed immediately after cure, using a TA Instruments Q5000 analyzer, at a gas flow rate of 10 mL/min (balance) and 25 mL/min (purge), heating the samples at 5 °C/min to 600 °C followed by a 2-h isothermal hold. The discs were then tested via dynamic thermomechanical analysis (dynamic TMA) with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. The discs were initially held in place via a 0.2 *N* compressive force with the standard ~5 mm diameter flat cylindrical probe. The force was then modulated at 0.05 Hz over an amplitude of 0.1 *N* (with a mean force of 0.1 *N*) and the temperature was ramped twice (heating and cooling) between 100 and 200 °C (to determine thermal lag) with a final heating to 350 °C, all at 10 °C/min. For samples previously exposed to hot water, the heating

TABLE 2 Crystal Structure Data and Refinement Details for Compound **4**

Compound	4
Empirical formula	$C_{33}H_{30}O_3$
Formula weight	474.57
Temperature (K)	296(2)
Crystallization Solvent	2-propanol
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions (Å, °)	
a	10.0023(2)
b	9.2100(2)
c	14.5901(5)
α	90°
β	100.7870(10)°
γ	90°
Volume (Å^3)	1320.31(7)
Z	2
Density (Mg/cm^3)	1.194
Crystal size (mm)	0.17 × 0.20 × 0.47
Reflections collected	25409
Independent reflections	4675
Completeness (%)	100.0
Data/restraints/parameters	4675/1/329
Goodness-of-fit on F^2	1.024
Final R [I > 2sigma(I)]	$R_1 = 0.0373$, $wR_2 = 0.1012$

rate was increased to 20 °C/min and the segments were run in reverse order to minimize drying before determination of the glass transition temperature. All reported dynamic TMA temperatures are corrected for thermal lag (typically 3–10 °C) determined separately for each sample.

X-Ray Structure Determination of 4

Some selected data and refinement details are collected in Table 2. CCDC 776623 (**4**) contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting CCDC 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Synthesis of the Monomer

3-(Dimethylamino)-4′-methoxyacrylophenone (2)

A 2-L round-bottomed flask equipped with magnetic stirbar and reflux condenser was charged with 4-methoxyacetophenone (300.4 g, 2 mol) and *N,N*-dimethylformamide dimethyl acetal (358 g, 3 mol, 1.5 equiv) and the mixture was refluxed. The reaction progress was followed by ^{1}H NMR analysis and was complete after 48 h reflux. Shortly after cooling to RT the reaction mixture solidified. Filtration on a medium porosity glass frit gave a first crop of product (160.22 g) as yellow microcrystals after washing with Et_2O. The filtrate was rotary evaporated leaving a second crop of product (181.3 g). The title compound was obtained as light yellow plates from toluene. Yield: 341.5 g (83%). Mp: 82–85 °C (lit.[13] 90 °C). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.91 (d, $J = 8.8$ Hz, 2H), 7.76 (d, $J = 12.5$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.69 (d, $J = 12.4$ Hz, 1H), 3.81 (s, 3H), 2.96 (bs, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 187.15, 161.86, 153.66, 133.07, 129.31, 113.21, 91.59, 55.21. Anal. calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.38; H, 7.33; N, 6.79.

1,3,5-Tris(4-methoxybenzoyl)benzene (3)

A 2-L round-bottomed flask equipped with magnetic stirbar and reflux condenser was charged with glacial HOAc (683 mL, 11.4 mol) followed by pyridine (171 mL, 2.16 mol) and then 3-(dimethylamino)-4′-methoxyacrylophenone (**2**) (341.5 g, 1.66 mol) was added. The mixture was refluxed for 12 h. The mixture was allowed to cool to RT whereby copious solids precipitated. An addition funnel was equipped and H_2O (300 mL) was added dropwise with vigorous stirring. The mixture was filtered on a medium porosity glass frit to obtain a light tan, granular solid that was recrystallized from toluene. Yield: 223.3 g (84%). Mp: 179–183 °C (lit.[14] 175–176 °C). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.14 (s, 3H), 7.83 (d, $J = 8.8$ Hz, 6H), 7.08 (d, $J = 8.8$ Hz, 6H), 3.84 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 192.97, 163.43, 138.03, 132.89, 132.44, 128.73, 114.10, 55.63. Anal. calcd for $C_{30}H_{24}O_6$: C, 74.99; H, 5.03. Found: C, 75.03; H, 4.80.

1,3,5-Tris(1-(4-methoxyphenyl)vinyl)benzene (4)

A 250 mL round-bottomed flask equipped with magnetic stirring bar and reflux condenser was charged with methyltriphenylphosphonium bromide (43.48 g, 122 mmol, 3.5 equiv), KO*t*Bu (13.7 g, 122 mmol, 3.5 equiv) and THF (300 mL). After 1 h, 1,3,5-tris(4-methoxybenzoyl)benzene (**3**) (16.73 g, 34.8 mmol) was added portionwise over 30 min. After the addition, the mixture was refluxed for 1 h. Upon cooling to RT, H_2O (50 mL) was added and the mixture was neutralized by adding HOAc (1 g, 17 mmol, 0.5 equiv). The organic layer was separated and washed with brine (50 mL). The organic layer was dried over anhydrous $MgSO_4$ and rotary evaporated to a thick oil, which slowly crystallized. The crude was dissolved in hot *i*PrOH (200 mL) and allowed to cool, whereby the title compound crystallized. Filtration on a medium porosity glass frit gave the title compound as white needles. Yield: 13.29 g (97%). Mp: 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.30 (d, $J = 8.8$ Hz, 6H), 7.28 (s, 3H), 6.85 (d, $J = 9$ Hz, 6H), 5.36 (d, $J = 1.0$ Hz, 3H), 5.33 (d, $J = 1.0$ Hz, 3H), 3.82 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 159.56, 149.43, 141.77, 133.88, 129.48, 128.08, 113.78, 113.33, 55.49. Anal. Calcd for $C_{33}H_{30}O_3$: C, 83.51; H, 6.37. Found: C, 83.31; H, 6.35.

Racemic 1,3,5-Tris(1-(4-methoxyphenyl)ethyl)benzene (5)

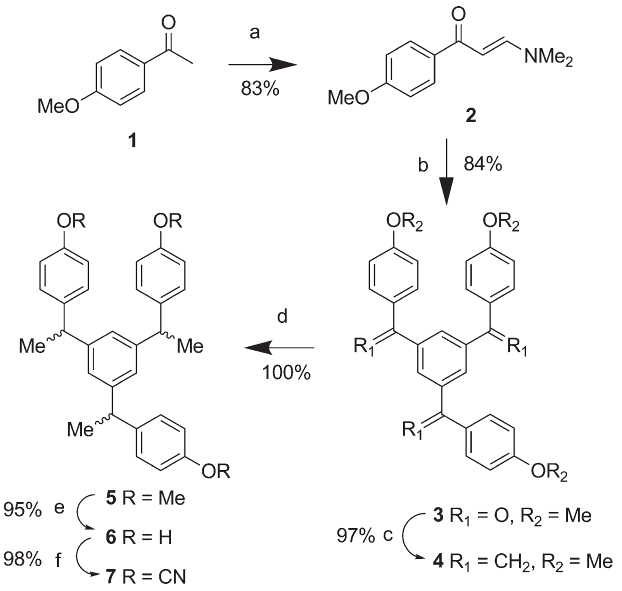
A mixture of 1,3,5-tris(1-(4-methoxyphenyl)vinyl)benzene (**4**) (19.61 g, 41 mmol), 5% Pd/C (500 mg), THF (50 mL), and EtOH (50 mL) was hydrogenated (50 torr) on a Parr® apparatus for 5 h. After this time the uptake of hydrogen ceased. The mixture was filtered through diatomaceous earth to remove the catalyst and rotary evaporated leaving the title compound as a colorless, viscous oil. Yield: 19.6 g (100%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.06 (d, $J = 8.7$ Hz, 6H), 6.88–6.84 (m, 3H), 6.79 (d, $J = 8.9$ Hz, 6H), 4.0 (q, $J = 7.5$ Hz, 3H), 3.78 (s, 9H), 1.52 (d, $J = 7.3$ Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 157.16, 145.83, 145.78, 145.74, 138.03, 137.99, 137.97, 127.55, 123.54, 123.46, 123.41, 113.36, 54.61, 42.94, 42.92, 21.29. Anal. calcd for $C_{33}H_{36}O_3$: C, 82.46; H, 7.55. Found: C, 82.23; H, 7.40.

Racemic 1,3,5-Tris(1-(4-hydroxyphenyl)ethyl)benzene (6)

A 250 mL round-bottomed flask equipped with magnetic stirring bar was charged with racemic 1,3,5-tris(1-(4-methoxyphenyl)ethyl)benzene (**5**) (19.6 g, 41 mmol) and pyridine hydrochloride (56.8 g, 0.49 mol, 12 equiv). The mixture was protected with an N_2 bubbler and heated in a 180 °C oil bath for 5 h. The mixture was allowed to cool briefly to $\sim$120 °C and then 55 °C H_2O (100 mL) was added slowly to the mixture with vigorous stirring. The mixture was extracted three times with EtOAc (100 mL portions). The collected organic phase was washed with brine (200 mL) and dried over anhydrous $MgSO_4$. Rotary evaporation gave a thick, colorless oil that foamed under vacuum. Yield: 17.17 g (95%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 9.12 (s, 3 OH), 6.98 (d, $J = 8.6$ Hz, 6H), 6.90 (s, 3H), 6.63 (d, $J = 8.6$ Hz, 6H), 3.92 (q, $J = 7.2$ Hz, 3H), 1.44 (d, $J = 7.5$ Hz, 9H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 155.35, 146.59, 146.53, 146.48, 136.69, 136.67, 136.65, 128.04, 123.88, 123.65, 114.96, 43.49, 43.46, 22.09, 22.04. Anal Calcd for $C_{30}H_{30}O_3 \cdot 0.65\ H_2O$: C, 80.02; H, 7.01. Found: C, 80.38; H, 7.41.

Racemic 1,3,5-Tris(1-(4-cyanatophenyl)ethyl)benzene (7)

A 250 mL round-bottomed flask equipped with magnetic stirring bar was charged with racemic 1,3,5-tris(1-(4-hydroxyphenyl)ethyl)benzene (**6**) (4.36 g, 99 mmol), cyanogen bromide (3.68, 34.7 mmol, 3.5 equiv) and anhydrous acetone (50 mL). The mixture was cooled in a −20 °C bath before dropwise addition of TEA (2.99 g, 297 mmol, 3 equiv). Near the end of the addition, copious solids (TEA·HBr) precipitated. After 1 h, ice cold H_2O (100 mL) and CH_2Cl_2 (100 mL) were added and the phases were separated. The organic layer was washed with cold saturated $NaHCO_3$ (50 mL) and then brine (50 mL). After drying over anhydrous $MgSO_4$, the solvent was evaporated leaving a viscous, pale yellow oil. The crude product was dissolved in CH_2Cl_2 and filtered through a pad of silica gel and rotary evaporated to give the title compound in analytically pure form as a thick, colorless oil. Yield: 5.0 g (98%). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.21 (s, 12 H), 6.84–6.81 (m, 3H), 4.09 (q, $J = 7.2$ Hz, 3H), 1.57 (d, $J = 7.2$ Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 151.44, 146.23, 146.19, 146.15, 145.45, 145.42, 145.39, 129.66, 125.13, 125.08, 115.47, 109.14, 44.29, 22.16. FTIR (KBr, cm^{-1}): 2263 (OCN), 2233 (OCN). Anal Calcd for $C_{33}H_{27}N_3O_3$: C, 77.17; H, 5.30; N, 8.18. Found: C, 77.17; H, 5.32; N, 8.33.



Reagents & conditions: a) $Me_2NCH(OMe)_2$, reflux; b) HOAc, pyridine, 120 °C; c) $MeP(Ph)_3Br$, KO*t*Bu, THF; d) H_2, 5% Pd/C, EtOH, THF; e) pyridine·HCl, 180 °C; f) BrCN, TEA, $CHCl_3$.

SCHEME 1 Synthetic route to monomer **7**.

RESULTS AND DISCUSSION

Synthesis

The synthesis of tricyanate ester **7** is shown in Scheme 1. Condensation of 4-methoxyacetophenone (**1**) with *N*,*N*-dimethylformamide dimethyl acetal by the reported method[15] gave the enaminoketone **2**[16] in good yield. Cyclotrimerization of **2** using conditions of Elghamry[17] gave the 1,3,5-tribenzoylbenzene **3**[18–20] in good yield. Triple Wittig reaction[21,22] of **3** with methyltriphenylphosponium bromide using potassium *tert*-butoxide as base gave the new triene **4** but only after partially selective recrystallization from heptane followed by silica gel chromatography to remove the byproduct triphenylphospine oxide (TPPO). It was discovered that the three equivalents of TPPO could be completely removed from **4** simply by recrystallizing the crude product from *iso*-propanol as demonstrated by Carey and coworkers.[23] A crystal structure for triene **4** was obtained, Figure 1, along with some selected crystallographic data in Table 2. In the following step, catalytic hydrogenation of **4** reduced the methylene bridges and gave liquid product **5** presumably as a statistical mixture (1:3) of a pair of racemic diastereomers (*R*,*R*,*R*/*S*,*S*,*S*:*S*,*S*,*R*/*R*,*R*,*S*).[24] Demethylation of **5** to give the glass-like[25] tris(4-hydroxyphenyl) derivative **6**[26] by molten pyridine hydrochloride[27] was a clean and convenient procedure when compared to the typical boron tribromide method.[19] Finally, cyanation of **6** with cyanogen bromide in the presence of triethylamine gave the tricyanate ester **7** in excellent yield. Traces of the impurity diethylcyanamide, from von Braun degradation, could be eliminated by maintaining the reaction temperature below −10 °C. The ^{1}H and ^{13}C NMR of **7** is shown in Figure 2. Although, ^{1}H NMR did not indicate a mixture, ^{13}C NMR clearly shows three multiplets in the aromatic region

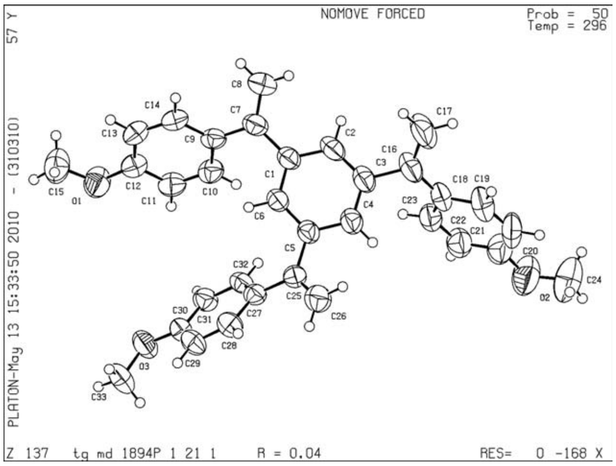


FIGURE 1 Crystal structure of **4**.

attibuted to the diasteromeric nature of monomer **7**. No attempts were made to separate and characterize the diastereomers. The product was found to be a viscous oil at room temperature or even several months at −20 °C.

Characterization

Based on a comparison of qualitative flow characteristics with other epoxy and cyanate ester resins of known viscosity, the room temperature viscosity of monomer **7** was estimated to be on the order of 10,000 cP. While about two orders of magnitude thicker than the analogous dicyanate ester Primaset® LECy, the viscosity is similar to low molecular weight "novolac" type tricyanate esters (such as Primaset® PT-15).[28] Although storage for several days at −20 °C induced a hazy appearance, no other signs of phase separation or crystallinity could be detected. Based on these physical characteristics and the structural similarity to the readily toughened Primaset® LECy, monomer **7** should be relatively easy to toughen via the addition of thermoplastic modifiers. Taken together, these results indicate that monomer **7** exhibits very favorable processing characteristics for a tricyanate ester.

The cure characteristics of monomer **7** also compared favorably to that of typical cyanate esters. Figure 3 presents DSC data for the uncatalyzed cyclotrimerization of monomer **7** caused by heating the sample at 10 °C/min. The peak exotherm temperature of 323 °C provided corroboration that a

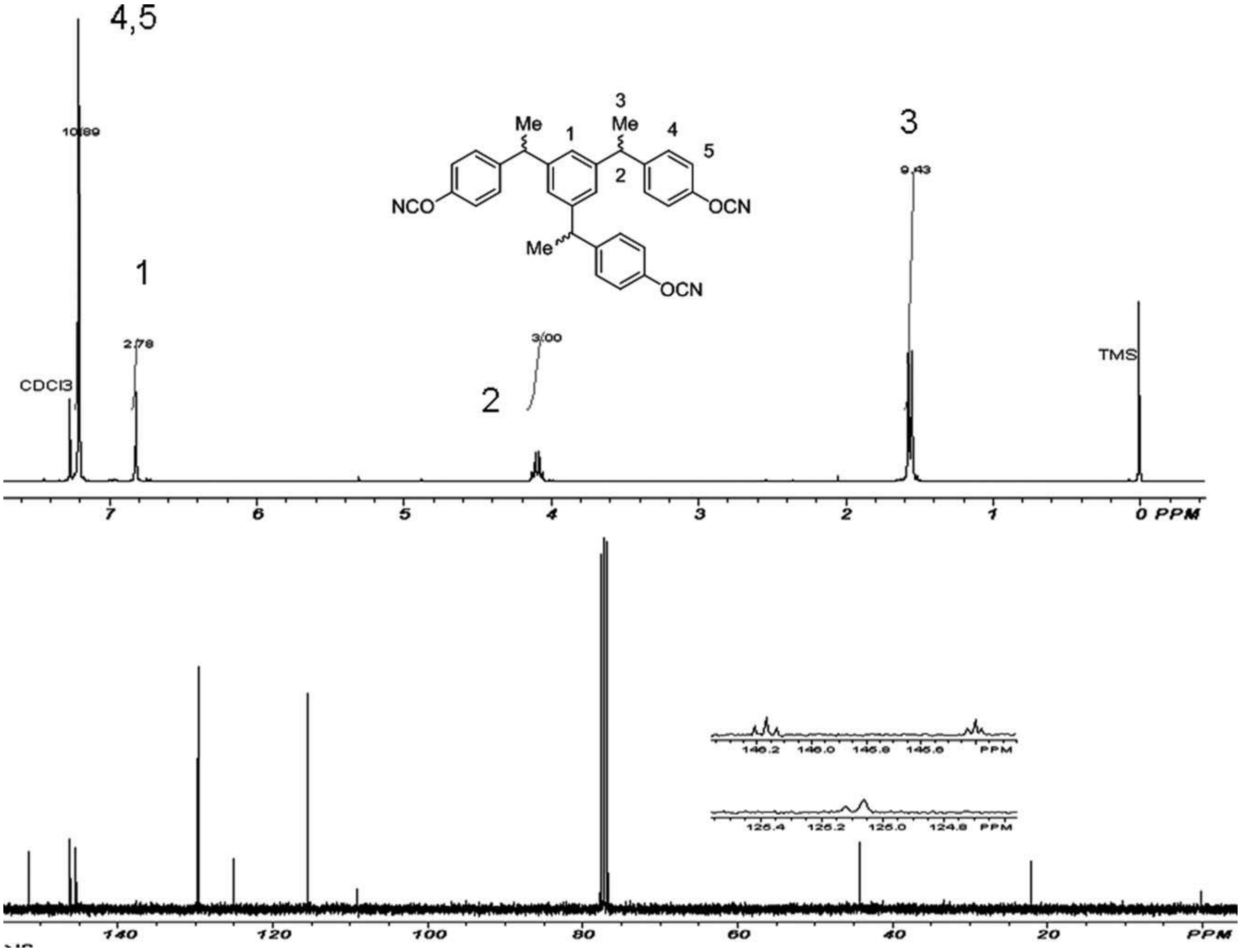


FIGURE 2 ^{1}H and ^{13}C NMR for monomer **7** with expanded regions for clarity.

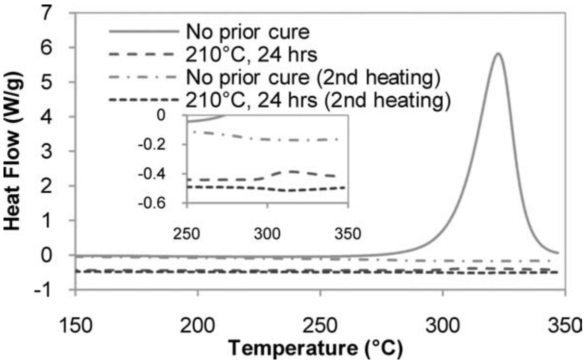


FIGURE 3 DSC traces of monomer **7** illustrating that nearly complete cure was achieved without the addition of catalyst at 210 °C. The curves have been offset on the vertical axis for convenience.

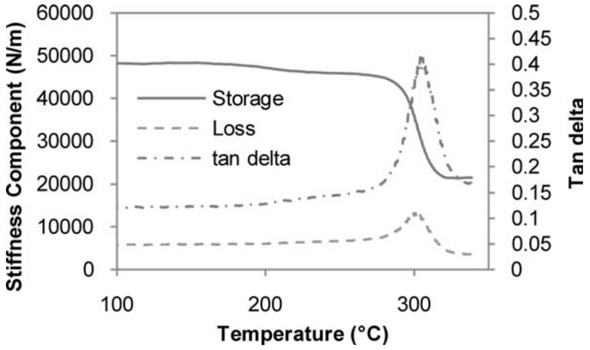


FIGURE 5 Dynamic TMA of monomer **7** after cure at 210 °C and storage under vacuum.

near quantitative conversion of the hydroxyl groups to cyanate ester during the preparation of compound **7** was achieved. The enthalpy of polymerization (given by the area under the large peak) was approximately −660 J/g, or −110 kJ/cyanate equiv, which equaled the high end of the range of values typically reported for Primaset® BADCy[8] (90–110 kJ/cyanate equiv), and was somewhat higher on a molar equivalent basis than the value measured for Primaset® LECy using the same method (−730 J/g or −93 kJ/cyanate equiv).[9] The discrepancy may have been due to a small amount of exothermic degradation in monomer **7** as it cured at temperatures approaching 350 °C.

To avoid any chance of thermal degradation, the uncatalyzed sample was successfully cured at 150 °C for 1 h followed by 210 °C for 24 h. The lower DSC traces of Figure 3 show that the T_g of the system cured at 210 °C (and then heated to 350 °C in the DSC) was ∼305 °C. The residual cure exotherm (∼−20 J/g) amounted to less than 3% of the total monomer cure exotherm, while the ATR-FTIR spectrum of the cured sample, shown in Figure 4 revealed essentially no residual cyanate ester groups (which appeared clearly in the uncured monomer as the characteristic doublet near 2250 cm^{-1}) but showed strong bands for the cyanurate ring (near 1360 and 1560 cm^{-1}). These combined results prove that nearly complete cure was obtained while avoiding exposure to temperatures above 210 °C. In contrast, a similarly complete cure of Primaset® LECy could not be achieved under identical conditions (see Supplemental Information), and resins of the "novolac" type (Primaset® PT-30) often require significantly higher post-cure temperatures to achieve full cure.[29]

Thermomechanical analysis (results shown in Figs. 5 and 6) revealed that cured **7** exhibited good resistance (for a polycyanurate) to degradation by hot water. Figure 5 compares the storage and loss components of the stiffness (i.e., of the oscillatory force amplitude divided by oscillatory displacement amplitude) obtained for cured **7** (uncatalyzed, with a final cure temperature of 210 °C as described in the Experimental section) after storage under vacuum. Based on the tan delta peak shown in the figure, the "dry" T_g of cured **7** was near 305 °C, in agreement with the value from determined by DSC, and also similar to the value reported for the polycyanurate from the experimental compound 1,1,1-tris(4-cyanatophenyl)ethane (also known as ESR-255, a tricyanate ester developed by Shimp).[30] Note that because the contact area between the probe and the sample cannot be determined precisely in this type of TMA measurement, quantitative modulus values were not calculated, and only qualitative interpretation of the stiffness data is warranted.

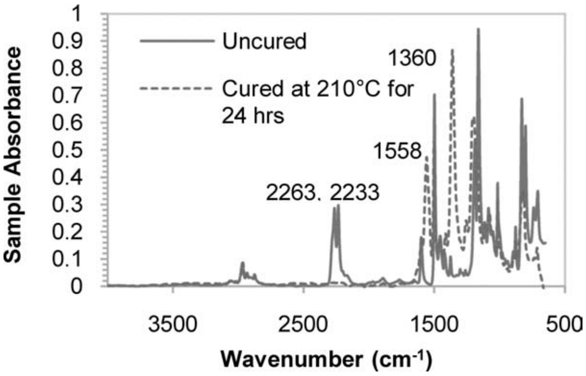


FIGURE 4 ATR-IR spectra of monomer **7** before and after cure at 210 °C, normalized to the aliphatic C—H stretch region.

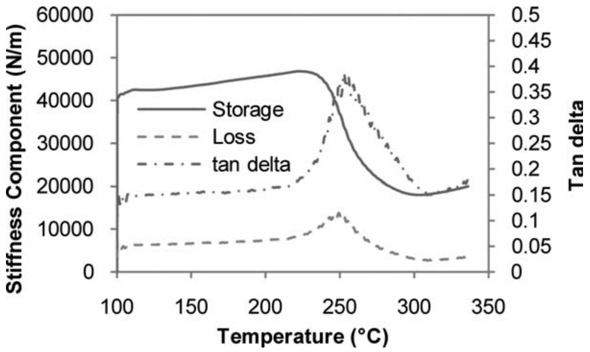


FIGURE 6 Dynamic TMA of monomer **7** after cure at 210 °C and immersion in water for 96 h at 85 °C.

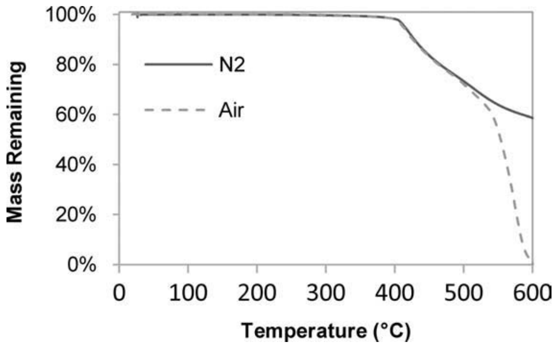


FIGURE 7 TGA of monomer **7** after cure at 210 °C.

Figure 6 compares the storage and loss components of the stiffness for a separate sample of cured **7** immersed in water at 85 °C for 96 h. For the "wet" sample, the T_g was around 255 °C similar to the "wet" HDT reported for ESR-255.[30] It should be noted that after heating to temperatures significantly higher than its boiling point, most of the water evaporated from the samples prior to measurement of T_g, as confirmed by weighing experiments done during interrupted TMA tests performed on separate samples. For cyanate esters, however, the reversible decrease in T_g that accompanies plasticization by water is known to be smaller and less important than the irreversible decrease associated with polycyanurate-network degradation. The increase in the storage component of the stiffness during heating seen for the "wet" sample was likely related to the gradual loss of water from the sample. However, since such losses create dimensional instabilities in the sample, only a rough correspondence between the observed stiffness and the sample storage modulus as a function of temperature is likely under these conditions.

For comparison purposes, both "dry" and "wet" TMA tests were run on Primaset® LECy, cured with and without added catalyst, (data shown in the Supplemental Information), and resulted in apparent T_g values of 280–285 °C (dry) and approximately 190–230 °C (wet). The "wet" T_g values were approximate due to outgassing that took place during rapid heating of the wet Primaset® LECy samples. Nonetheless, the data indicated that cured **7** exhibited improved overall thermomechanical performance when compared to its dicyanate ester analog. In terms of water uptake, the weight of cured **7** increased 2.3%, while the weight increases for cured Primaset® LECy were 2.1% (uncatalyzed) and 2.3% (catalyzed) after immersion in water at 85 °C for 96 h.

To provide further characterization of cured **7**, both TGA data (shown in Fig. 7) and density measurements were obtained. The TGA traces under nitrogen and air both resemble those of other cyanate esters closely, with 5% weight loss temperatures of 410–415 °C. The density measurements show a value of 1.177 +/−0.001 g/cc for cured **7**. The resultant theoretical cyanurate crosslink density for the fully cured **7** is 1.38 × 10^{21}/cc, however, considering that the central 1,3,5-substituted phenyl ring also acts as a physical crosslink, the total rigid crosslink density for cured **7** would be 2.76 × 10^{21}/cc, considerably higher than the ~1.8 × 10^{21}/cc for fully cured Primaset® LECy based on its cured density. A higher density of physical crosslinks can lead to brittleness in polycyanurates, but our admittedly qualitative experience during cutting and handling of cured samples of both Primaset® LECy and monomer **7** did not reveal any noticeable differences in brittleness. Though a complete investigation of the subject is beyond the scope of this work, the probable ease of creating toughened polycyanurates from monomer **7** could likely be used to compensate for any increased brittleness.

CONCLUSIONS

A successful six step synthesis was carried out to produce the racemic tricyanate ester monomer 1,3,5-tris(1-(4-cyanatophenyl)ethyl)benzene (**7**) in 63% overall yield. The monomer exhibited favorable processing characteristics, including moderate viscosity as a stable liquid at room temperature, and the ability to be cured to at least 97% conversion using a final cure temperature of 210 °C, without added catalyst. Both the dry and "wet" glass transition temperature of the resultant polycyanurate (305 and 254 °C, respectively) were comparable with those of polycyanurates made from previous tricyanate esters, such as 1,1,1-tris(4-cyanatophenyl)-ethane (ESR-255), which melts at 104 °C. Thus, both the favorable processing characteristics of cyanate esters based on 1,1-diphenylethane (Bisphenol E) repeat units and the enhanced thermomechanical performance in wet environments associated with tricyanate esters were realized in a single monomer.

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