Macromolecules

Mechanisms of Decreased Moisture Uptake in *Ortho*-Methylated Di(cyanate ester) Networks

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Ⓢ *Supporting Information*

ABSTRACT: Decreases of up to 50% in the moisture uptake of polycyanurate networks based on 2,2-bis(4-cyanatophenyl)-propane (BADCy) and 1,1-bis(4-cyanatophenyl)ethane (LECy) were observed when analogous networks containing a single methyl group *ortho-* to each aryl—cyanurate linkage were prepared by reduction and acid-catalyzed coupling of salicylic acid followed by treatment with cyanogen bromide and subsequent cyclotrimerization. The differences in water uptake were observed despite similar decreases in packing fraction as conversion proceeded in all networks studied. Conversely, the presence or absence of methyl groups at arylene bridges, remote from the cyanurate oxygen, had no influence on water uptake. Vitrification during cure had little effect on either free volume development or moisture uptake. These results confirm that steric hindrance from *ortho*-methyl groups inhibits absorption of water presumably by decreasing the thermodynamic favorability of sterically permitted interaction with the cyanurate oxygen. A further examination of the effect of two different catalysts, 2 parts per hundred of a 30:1 by weight mixture of nonylphenol and copper(II) acetylacetonate and 500 ppm of dibutyltin dilaurate (DBTDL), compared to analogous uncatalyzed networks, showed that hydrolytic stability was dramatically affected by catalyst choice, while thermochemical stability was also impacted. These results provide important insights into the mechanisms that determine structure—property relationships in polycyanurate networks.
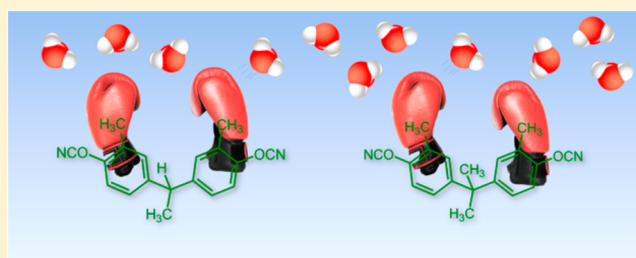
■ INTRODUCTION

Polycyanurate networks derived from the thermal cyclo-trimerization of cyanate ester monomers are becoming increasingly important high-performance materials[1−4] in technology areas including printed circuit boards,[5] rocket and missile structures,[6] spacecraft structures,[7] and thermonuclear fusion reactors[8,9] due to their advantageous stability characteristics in demanding environments involving elevated temperatures,[10] cryogenic temperatures,[11] exposure to vacuum,[12] and high-energy radiation.[13] In wet environments, these networks demonstrate a mixture of highly desirable traits, such as a very low coefficient of hygrothermal expansion during short-term exposure[14] and low moisture permeability,[15] along with undesirable characteristics such as blistering and loss of mechanical properties during long-term exposure to moisture at elevated temperatures.[16−18] Interestingly, many of the desirable traits stem from physical characteristics of the network, such as a high density of cross-links (typically 3 mmol/cm³ or greater) and the presence of microscale free volume with characteristic hole sizes large enough to accommodate water without swelling,[14] while many of the undesirable traits can be traced to unwanted chemical reactions with either unreacted cyanate ester groups and/or with cured cyanurate groups.[16−18] This distinction implies that tailoring of

the chemical structure of polycyanurate networks may enable mitigation of the undesirable traits while retaining the desirable ones.

In the 1980s, Shimp et al. discovered that a straightforward modification of the chemical structure of bis(aryl) cyanate ester monomers, namely the inclusion of methyl groups positioned *ortho* to the phenyl cyanate oxygen, resulted in decreased water uptake and improved hydrolytic stability of the network.[19,20] In this instance, as is common for thermosetting networks, hydrolytic stability was assessed by monitoring the decrease in glass transition temperature on exposure to water at elevated temperatures. From these results, it was speculated that the placement of methyl groups in a position *ortho* to the cyanurate oxygen resulted in steric hindrance of the oxygen, thereby slowing down hydrolytic reactions while inhibiting access to favored sites for water to occupy. A graphical illustration of this concept, along with the structures of the monomers investigated by Shimp, is provided in Figure 1.

Although the hypothesis put forward by Shimp is intuitively appealing, it is important to examine this hypothesis critically in
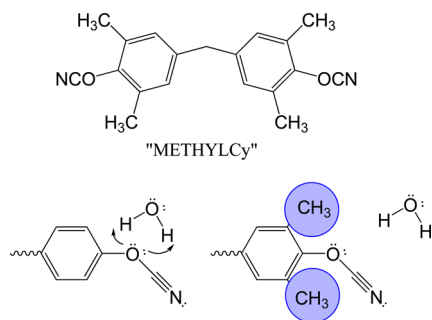
Figure 1. Methylated monomer investigated by Shimp (upper part) and proposed mechanism of improvement in hydrolytic stability (lower part). In the absence of methylation (lower left), water is free to approach the cyanurate oxygen, facilitating interaction, whereas in the presence of methylation (lower right), water is effectively blocked from accessing the oxygen.

order to advance our understanding of the mechanisms of water uptake in polycyanurate networks. In particular, *ortho*-methylation alters many characteristics of polycyanurate networks, such as monomer melting point, glass transition temperature at complete conversion to cyanurate, and bulk density of the cured resin. Because the short-term uptake of water in polycyanurates takes place without expansion,[14] it involves the filling of void space within the cured resin. Denser packing of the repeat units in the network would decrease the available space for water uptake and could explain some of the observed behavior without the need for steric hindrance of any particular moiety. Furthermore, as illustrated in Figure 2, a
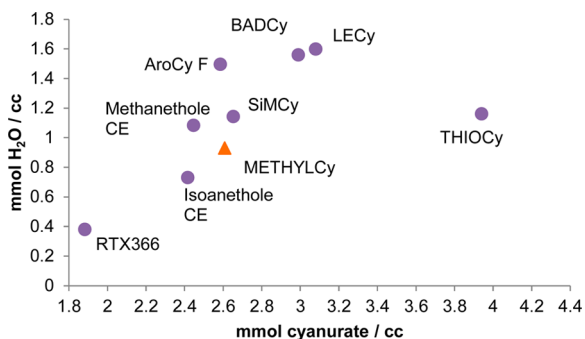
Figure 2. Moisture uptake as a function of cyanurate density for networks derived from di(cyanate ester) monomers. Data for BADCy, LECy, and SiMCy are from ref 21. Data for Isoanethole CE and Methanethole CE are from ref 22. Remaining data are from ref 23.

strong correlation (with some exceptions) exists between the number density of cyanurate groups in polycyanurate networks (defined as the gravimetric density divided by the molecular weight per cyanurate equivalent in the cured resin) and moisture uptake, as pointed out recently for copolymerized polycyanurate networks.[21] *Ortho*-methylation reduces the number density of cyanurate groups and would therefore be expected to lower the water uptake. Particularly in Figure 2, the water uptake of the networks examined by Shimp (labeled as "METHYLCy") is reasonably close to the general trend, suggesting that *ortho*-methylation is effective in reducing water uptake mainly because it reduces the number density of cyanurate groups.

Correlations such as the one in Figure 2 do not explicitly take into account the effects of conversion. They generally assume

complete conversion to cyanurate due to a lack of available data, even when the reported glass transition temperature (T_G) of the networks suggests that such an assumption is invalid. Because conversion strongly affects both water uptake and cyanurate density, a proper examination of the hypothesis put forward by Shimp requires explicit consideration of conversions. During cure, vitrification of the resin may affect the formation of free volume, and subsequently, it may affect moisture uptake, which needs to be considered. In addition, the effect of *ortho*-methylation should be tested in more than one type of monomer, and the effect of *ortho*-methylation should be compared to the effect of adding methyl groups at other locations within the repeat unit. Such a comparison will help distinguish between effects due simply to altering the geometry of the monomer and those effects due specifically to methylation that provides a sterically demanding environment around the cyanurate oxygen. As a final consideration, it should be noted that the presence of, and choice of, catalysts for cyanate ester cure are known to strongly influence the hydrolytic stability of the networks.[1,16,18,24] The variable of catalyst choice should also be examined.

In what follows, we report the results of a systematic study on the effect of methylation *ortho*- to the cyanurate oxygen on the properties of polycyanurate networks, taking into account important variables such as conversion and catalyst type. We do this by synthesizing *ortho*-methylated analogues of the well-known cyanate ester monomers Primaset BADCy and Primaset LECy, which are the cyanated forms of Bisphenol A and Bisphenol E, respectively. The *ortho*-methylated analogue of the di(cyanate ester) of Bisphenol E has not been synthesized previously to our knowledge. Using these four monomers allows for a comparative investigation of the effect of introducing methyl groups *ortho*- to the cyanurate oxygen (causing steric hindrance of this oxygen) and the effect of introducing methyl groups at the bridge between aryl groups, a location distant from the cyanurate oxygen.

We found that *ortho*-methylation strongly reduces the water uptake in the networks, in particular at high conversions, whereas methylation of the bridge made no difference. We further found that in systems catalyzed by copper(II) acetylacetonate/nonylphenol the hydrolytic stability of the networks was improved by *ortho*-methylation but not bridge methylation. However, in networks catalyzed by dibutyltin dilaurate the hydrolytic stability of the *ortho*-methylated systems was very poor. These results, along with the associated trends in variables such as network packing fraction and the presence or absence of vitrification during cure, tend to confirm the hypothesis that the local vicinity of the cyanurate oxygen (on the molecular scale) represents a preferred site for water uptake in systems with conversions greater than about 80% and that steric hindrance of the site can mitigate some forms of hydrolytic instability. These concepts are of great importance for the rational design of polycyanurate networks that exhibits superior performance in environments where exposure to moisture is a concern.

■ **EXPERIMENTAL SECTION**

**Monomer Synthesis.** *4,4′-(Ethane-1,1-diyl)bis(2-methylphenol) (5).* A cooled (<5 °C) flask containing *o*-cresol (300 mL, 2.86 mol, 3.8 mol equiv) was equipped with mechanical stirring and then had acetaldehyde (42 mL, 0.75 mol) added. Next, ether (30 mL) was added to dissolve the solids, and then to the entire mixture was added 3 mL of concentrated HCl. The temperature rose to 20 °C before

falling back to 5 °C. The clear pinkish solution was stirred for an additional 18 h at room temperature with stirring and then transferred to a 1 L single-necked round-bottom flask. Excess o-cresol was removed under reduced pressure at 100 °C to afford 237.25 g of a clear thick oil. This was distilled in a Kugelrohr to yield 178.91 g of a clear glassy material (97%). This is a mixture of 18 mol % of the 2,4′-isomer along with about 10 mol % of the trimer. ^{1}H NMR (CDCl₃): δ (ppm) 6.98 (s, 2H), 6.96 (d, 2H), 6.70 (d, 2H), 4.66 (br s, 2H), 3.98 (q, 1H), 2.23 (s, 6H), 1.57 (d, 3H).
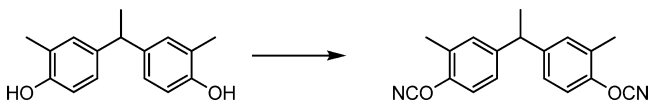

4,4′-(Ethane-1,1-diyl)bis((1-cyanato-2-methylbenzene) (3). A solution of 78.48 g of 4,4′-(ethane-1,1-diyl)bis(2-methylphenol) (0.324 mol) and 80 g of cyanogen bromide (0.755 mol, 2.3 mol equiv) in 1 L of ether was cooled to −5 °C (ice salt bath) while a solution of 108 mL of triethylamine (0.776 mol, 2.4 mol equiv) in 100 mL of ether was added dropwise over 30 min. The mixture was allowed to warm to room temperature and stirred for 3 h and then washed with water, dried (MgSO₄), and concentrated in a vacuum to give 102.07 g of an off-white solid. This was chromatographed on silica gel using methylene chloride as eluent to afford 45.27 g of a white solid (48%); mp 72.1 °C. ^{1}H NMR (CDCl₃): δ (ppm) 7.34 (d, 2H), 7.09 (d, 2H), 7.04 (s, 2H), 4.10 (q, 1H), 2.28 (s, 6H), 1.60 (d, 3H). ^{13}C NMR (acetone-d_6): 150.17, 144.98, 131.34, 126.81, 126.36, 114.45, 108.94, 43.18, 21.03, 14.39. GC/MS: major peak integrates to 94% 292 (M⁺), 277 (M⁺ − Me), minor peak integrates to 2% 292 (M⁺), minor peak integrates to 4% 267 (M⁺).
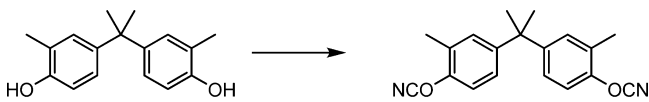
4,4′-(Propane-2,2-diyl)bis(1-cyanato-2-methylbenzene) (4). A solution of 75 g of 4,4′-(propane-2,2-diyl)bis(2-methylphenol) (0.293 mol) and 65 g of cyanogen bromide (0.614 mol, 2.1 mol equiv) in 1 L of ether was cooled to −5 °C in an ice−salt bath. A solution of 88 mL of triethylamine (0.633, 2.15 mol equiv) in 100 mL of ether was added dropwise over 30 min, keeping the temperature below 0 °C. The solution was allowed to warm to 10 °C and then washed with water, dried over MgSO₄, filtered, and the solution concentrated under reduced pressure to afford 88.75 g of a white solid (99%); mp 62−68 °C. A recrystallization of material from 400 mL of ether gave 70.66 g of a white solid (79%); mp 76−77 °C. ^{1}H NMR (CDCl₃): δ (ppm) 7.32 (d, 2H), 7.12 (d, 2H), 7.04 (s, 2H), 2.72 (s, 6H), 1.65 (s, 6H).

The nomenclature for all monomers is shown in Figure 3. Note that compounds **1−4** represent the monomers compared in this study. Networks **1−4** correspond to the thermally cyclotrimerized versions of monomers **1−4**. Note that **1** and **2** are commercially available as Primaset BADCy and Primaset LECy. The preparation of compound **4** has been reported previously.[25]
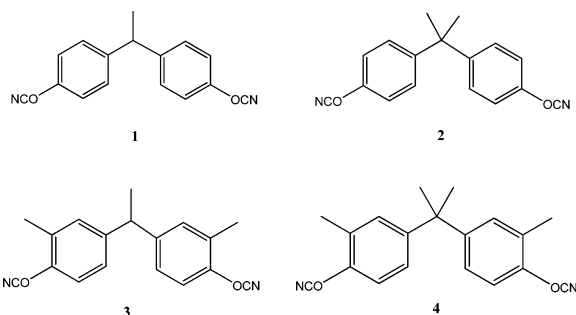
Figure 3. Chemical structures of compounds **1−4**.

Preparation of Networks. As-received monomers were further purified by dissolution in dichloromethane, followed by passage through a W-Prep2XY Yamazen flash chromatography column and rotary evaporation of the purified eluent to remove the solvent. The commercial monomers Primaset BADCy and Primaset LECy were obtained from Novoset, Inc. (Peapack, NJ) and used as-received. Catalyst systems utilized included a 30:1 weight mixture of copper(II) acetylacetonate (Roc-Ric, used as-received) dissolved in 4-nonylphenol (97%, mixture of isomers, Aldrich, used as-received), added to monomers at 2 parts per hundred weight, or dibutyltin dilaurate (DBTDL, Aldrich, 95%), added directly to monomers at 500 ppm by weight, in line with the procedure described by Marella et al.[18] All monomers except LECy, which is a supercooled liquid at room temperature, were first melted at 90 °C. Catalyst was then added to about 1 g of the liquid monomer in the desired type and amount, and the resultant liquid was stirred by hand for a few seconds to achieve homogeneity. (In some cases, no catalyst was added, and the preceding step was therefore omitted.) The formulated monomer was then placed directly into a hermetically sealed differential scanning calorimetry (DSC) pan and/or poured into one or more silicone rubber molds having a disk-shaped cavity and cured using a predetermined time−temperature schedule under flowing nitrogen and then cooled and demolded. The resultant disks measured approximately 12 mm in diameter by 4 mm thick.

Characterization Techniques for Networks. *Differential Scanning Calorimetry (DSC).* 5−10 mg pieces of cured networks were removed from a molded disk and hermetically sealed in an aluminum DSC pan. Samples were then ramped under 50 mL/min of flowing nitrogen at 10 °C/min, first heating to 350 °C, cooling to 100 °C, and then reheating to 350 °C, using a TA Instruments Q200 differential scanning calorimeter. For selected samples, the maximum temperature was reduced to 300 °C to assess the possibility of chemical degradation during analysis (see Supporting Information).

Thermogravimetric analysis (TGA). Pieces of cured disks weighing approximately 5 mg were removed and placed in a TA Instruments Q5000 thermogravimetric analyzer. These samples were then heated to 600 °C, under nitrogen, and, in separate experiments, in air, at 10 °C/min.

Oscillatory Thermomechanical Analysis (OTMA). Cured disks were also tested via oscillatory thermomechanical analysis (OTMA) with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. The disks were initially held in place with a compressive force of 0.2 N using 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 −50 and 200 °C (to aid in determination of thermal lag) followed by heating to 350 °C, cooling to 100 °C, and reheating to 350 °C, all at 50 °C/min. For samples previously exposed to hot water, the heating rate was decreased to 20 °C/min, and the order of segments was heating to 350 °C, cooling to 100 °C, two cycles between 100 and 200 °C for thermal lag determination, and finally heating to 350 °C. The details of the thermal lag determination procedure are reported in the Supporting Information.

Other Physical Characterization. Sample densities were determined using a Mettler Toledo analytical balance with an attachment for specific gravity determination. Deionized water was used as the immersion medium. A minimum of four weight measurements were collected and recorded per sample, making use of the cured disks prior to removal of portions for any other testing. For water immersion testing, cured disks were dried to a ±0.0001 g constant weight in a vacuum desiccator and then weighed and immersed in approximately 250 mL of deionized water maintained at 85 °C for 96 h. After removing from the water, samples were patted dry and weighed to determine the moisture uptake (on a dry weight basis).

■ **RESULTS AND DISCUSSION**

Monomer Characteristics. The overall experimental strategy involved the synthesis of *ortho*-methylated analogues

of the well-studied monomers Primaset LECy and Primaset BADCy and then performing structure–property relationship assessments in which important variables such as conversion and the state of the network during cure (i.e., rubbery or glassy) could be controlled sufficiently to disentangle their effects from those resulting from structural changes. From a structural perspective, LECy, BADCy, and their analogues constitute a set of monomers having 1 (LECy), 2 (BADCy), 3 (monomer **3**), and 4 (monomer **4**) methyl groups per monomer (hence, the numbering system also serves as the methyl group count). Networks made from **1** and **3** have a single methyl group per repeated network segment at the bridge between the two central phenyl rings. Monomers **2** and **4** have two such groups; thus, comparisons between **1** and **2**, and between **3** and **4**, show the effects of methyl group addition at the bridging unit. Monomers **3** and **4** differ from **1** and **2** by the addition of two methyl groups located *ortho*- to a cyanurate oxygen; thus, comparisons between **1** and **3** and between **2** and **4** show the effect of methyl group addition near the cyanurate oxygen. The ability to independently test the effect of methyl group addition at these two different locations within each repeat unit allows for a convenient way of separating effects that result from steric hindrance of the oxygen from effects that result simply from methylation.

The successful synthesis of monomers that function as analogues of LECy and BADCy can be confirmed by examination of DSC spectra, as shown in Figure 4a,b for monomers with no added catalyst and in Figure 5a,b for monomers with 2 phr of nonylphenol/copper(II) acetylaceto-
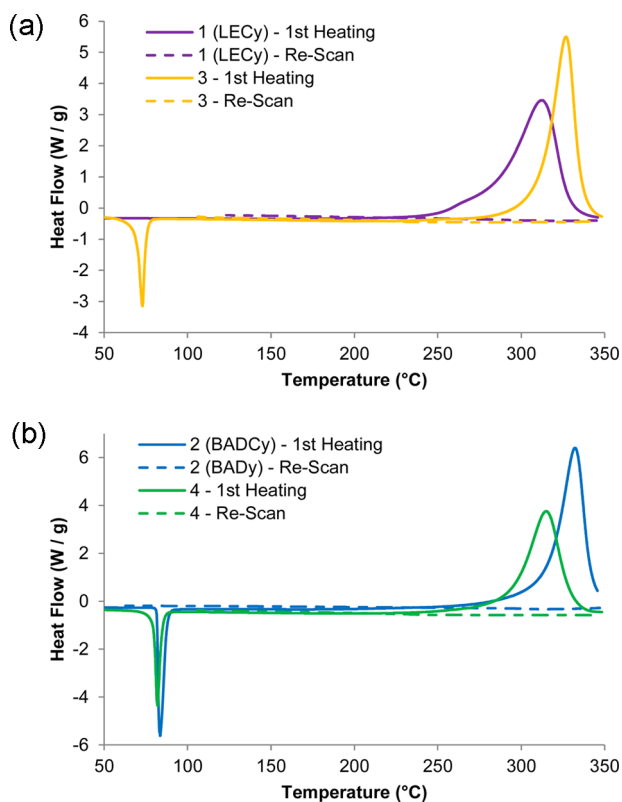
Figure 4. (a) Comparison of DSC scans for uncured ethylidene-bridged monomers **1** (LECy) and **3** (its *ortho*-methylated analogue) with no added catalyst. (b) Comparison of DSC scans for uncured isopropylidene-bridged monomers **2** (BADCy) and **4** (its *ortho*-methylated analogue) with no added catalyst.
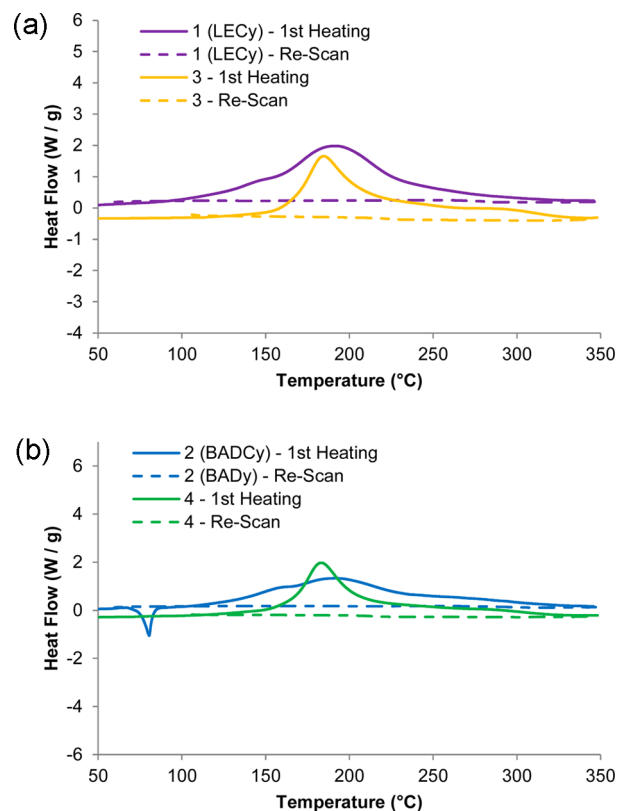
Figure 5. (a) Comparison of DSC scans for uncured ethylidene-bridged monomers **1** (LECy) and **3** (its *ortho*-methylated analogue) catalyzed with 2 phr nonylphenol/160 ppm of Cu. (b) Comparison of DSC scans for uncured ethylidene-bridged monomers **2** (BADCy) and **4** (its *ortho*-methylated analogue) catalyzed with 2 phr nonylphenol/ 160 ppm of Cu.

nate catalyst added (containing 160 ppm of Cu on an unmodified monomer weight basis). Despite some minor differences, such as a more rapid onset of cure in the *ortho*-methylated monomers, the shapes of the exotherm and their peak temperatures are similar in both cases.

Interestingly, the melting points of BADCy (**2**) and analogue **4** are nearly identical at 82−83 °C, as are the enthalpies of melting. Von't Hoff purity analyses showed these two compounds to be >99% pure. Unlike LECy (**1**), however, which melts at 29 °C,[26] the analogue **3** melts at 73 °C, and the Von't Hoff purity is only 96.5% for **3**. The very low melting point of LECy appears to result from the presence of two cocrystallizing forms;[27] thus, multiple crystalline forms of **3** may be present and result in an underestimate of purity by the Von't Hoff method. The presence of multiple crystal forms or disordered crystals may also complicate purification of **3**, resulting in a lower overall monomer purity. Overall, the DSC data indicate that the purity is high enough and the similarity in processing characteristics great enough that meaningful comparisons in properties with respect to methylation may be undertaken.

Water Uptake in Relation to Free Volume and Vitrification. As stated in the Introduction, the primary purpose of the investigation was to elucidate the mechanism of reduced moisture uptake in polycyanurates cured from *ortho*-methylated di(cyanate ester) monomers. In order to fulfill this purpose, four samples of each of the compounds **1−4** were cured using different cure conditions. These cure conditions

were designed to produce two different conversions at a given cure temperature by using a short and a long cure time at each of two temperatures. The temperatures and times were chosen in order to accomplish about 90% conversion via two separate routes: (1) curing for a long time at a lower temperature, with the network in the vitrified state for most of this time, and (2) curing for a shorter time at a higher temperature, with no vitrification. Under ideal conditions, this experimental design allows the effects of conversion, cure temperature, and vitrification to be checked independently.

Table 1 provides a list of the times and temperatures used for each of the monomers in the study, along with the resultant

Table 1. Experimental Design and Resultant Sample Parameters

monomer	cure temp (°C)	cure time (min)	conversion[a]	"as-cured" T_G[b] (°C)	vitrified during cure?[c]
1 (LECy)	210	30	0.901 ± 0.009	218	yes
1 (LECy)	210	1440	0.945 ± 0.007	249	yes
1 (LECy)	250	5	0.916 ± 0.013	229	no
1 (LECy)	250	210	0.971 ± 0.005	253	yes
2 (BADCy)	210	30	0.846 ± 0.014	204	no
2 (BADCy)	210	1440	0.912 ± 0.008	248	yes
2 (BADCy)	250	5	0.892 ± 0.013	226	no
2 (BADCy)	250	210	0.955 ± 0.007	258	yes
3	170	210	0.913 ± 0.006	175	yes
3	170	1440	0.862 ± 0.012	170	yes
3	210	30	0.922 ± 0.009	187	no
3	210	1440	0.992 ± 0.003	229	yes
4	170	210	0.783 ± 0.014	142	no
4	170	1440	0.869 ± 0.010	174	yes
4	210	30	0.855 ± 0.012	170	no
4	210	1440	0.984 ± 0.005	235	yes

[a]As measured by DSC with the method specified in Supporting Information Section S2. [b]Measured on first DSC scan of cured samples by midpoint of step change in heat capacity or turning point at onset of exotherm if no step change in heat capacity was visible. [c]"Yes" indicates "as-cured" T_G of sample was as high as, or higher than, cure temperature.

conversions and glass transition temperature (T_G) values at the end of cure, both of which were obtained by DSC. For compounds **2** and **4**, the experimental design achieved the goals well, producing samples cured both with and without vitrification at conversions differing by 3% or less at 90% and 85%, respectively, and allowing samples to be compared at points before and after vitrification during isothermal cure at two separate temperatures. For compounds **1** and **3**, the design was less successful but still useful, enabling a comparison of the effect of vitrification in samples with conversions differing by 2% or less at 91% and 92%, respectively. However, in these cases comparisons before and after vitrification could only be studies at one cure temperature. **3** had an unexpectedly low conversion when cured for 24 h at 170 °C and showed an unusual residual cure exotherm containing two peaks, indicating the presence of a side reaction. As a result, inferences based on the behavior of this sample were not attempted. In general, however, the experimental design was sufficient to achieve the goal of providing a means of comparing the different types of methylation while controlling for variables such as conversion and the physical state of the network during cure.

Figure 6 shows the water uptake as a function of conversion in cured networks of **1−4** after immersion at 85 °C for 96 h. In
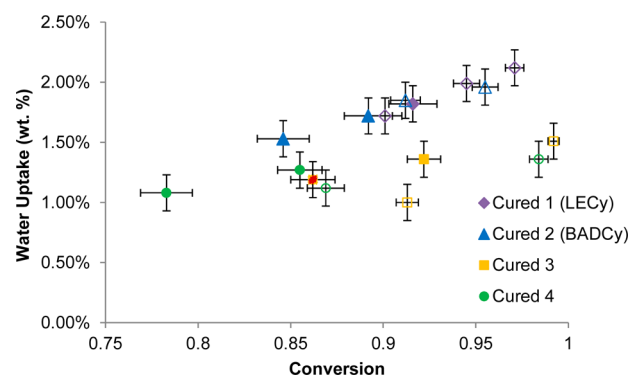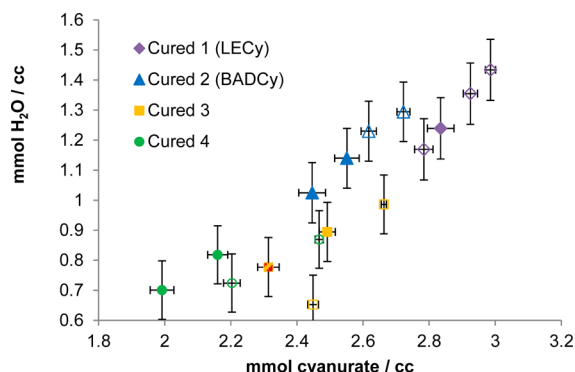

Figure 6. Water uptake as a function of conversion for cured **1−4**. Unfilled symbols represent samples that vitrified during cure; filled symbols represent samples that did not vitrify during cure. Symbols with red striping indicate samples where side reactions were evident. The same labeling scheme is used in subsequent figures.

this and subsequent figures, open symbols represent samples that vitrified during cure, while filled symbols represent samples that did not vitrify. The sample that showed side reactions is also identified. As described by Georjon and Galy for BADCy,[14] and as determined for di(cyanate ester) conetworks in our recent work,[21] there is a clear trend toward increasing water uptake with increasing conversion for all networks. At all conversions, the uptakes for **1** and **2** are identical, as are those for **3** and **4**. In contrast, the water uptake of **3** and **4** is always lower than that of **1** or **2** at the same conversion in all comparable cases shown. Methylation near the cyanurate oxygen therefore has a significant effect, whereas methylation at the bridge does not. These results provide strong evidence that the cyanurate oxygen is a preferred site for water uptake in polycyanurates and that creating steric interactions, that is imposing steric hindrance at the site of hydrogen bonding, is an effective means for reducing water uptake, particularly at conversions that approach 100%.

Figure 6 also shows that the presence or absence of vitrification appears to make no difference in water uptake at a given conversion. This result would not be expected if vitrification led to a more "open" network structure that could accommodate more water, as previously suggested by us[21,28] and others.[14] However, it would be consistent with the idea that a more "open" network is formed at higher conversions due to the necessary intramolecular cyclization[2] and the possible formation of short macrocyclic loops like those described by Fang and Shimp[2] or Simon et al.[29] Although an annealing experiment would be one way to further differentiate between these two explanations, such an experiment would need to be conducted on fully cured samples in order to avoid altering the conversion during the experiment. Even for the *ortho*-methylated networks, temperatures in excess of 230 °C would be required to conduct such an experiment on catalyzed samples, and such temperatures are just high enough to potentially cause some degradation of the networks.[30] Networks without added catalyst could be more chemically stable but would require even higher temperatures to reach full conversion. One possibility would be to perform an annealing experiment on a network cured from a monomer such as RTX-366, which has a fully cured T_G near 200 °C.[31]

As mentioned previously, there appears to be a correlation between cyanurate density and water uptake in polycyanurate networks (see Figure 2). This is due to methylation decreasing the number density of cyanurate rings (as confirmed by density data presented below). Therefore, it could be argued that a lower cyanurate density produced the lower water uptake in **3** and **4**. To further elaborate on this possibility, Figure 7 reprises


Figure 7. Water uptake as a function of cyanurate density for cured **1**–**4**. See Figure 6 for a guide to symbols.

Figure 6 in a different form; it shows the number density of water molecules absorbed as a function of the number density of cyanurate rings in the network. In a simple model in which each cyanurate ring (or, alternatively, each cyanurate oxygen) acts as a strongly preferred site for water uptake, the curves for all four networks should collapse into a single line. Instead, each network seems to follow a distinct trend. It should be noted that earlier work by us[32] and others[33] has shown that, at lower conversions, from around 70% to around 90%, water uptake decreases as conversion increases. As a result, the trends seen in Figure 7 cannot be reliably extrapolated to lower conversions (in other words, we know that at lower conversions each set of points must pass through a minimum). Furthermore, comparing the trends for **1** and **2**, methylation at the bridge also lowers cyanurate density but has a very different effect on water uptake than methylation *ortho*- to the cyanurate oxygens. There is thus no "universal" relationship between cyanurate density and moisture uptake that could be used to support the speculation that lower cyanurate density is responsible for the lower water uptake of *ortho*-methylated networks

To summarize, the water uptake results indicate that *ortho*-methylation is an effective method for reducing water uptake in polycyanurates networks, likely because of steric hindrance provided to the cyanurate oxygen, which appears to be a preferred site for water uptake. The differences are modest at conversions below 85% but become significant as conversions approach 100%. One potential explanation for such an effect is that conversions above 85% require the formation of more "open" (less tightly packed) network structures. In such "open" structures, thermodynamically favorable interactions between water and the cyanurate oxygens are facilitated, unless these oxygens are sterically hindered by *ortho*-methylation.

If the foregoing statements are true, then a decrease in density and packing fraction with conversion should be observed with increasing conversion in cyanate esters, regardless of cure conditions. Figures 8 and 9 respectively show the density and packing fraction at room temperature as a function of conversion for networks cured from monomers **1**–**4**. For networks **2** and **4**, there is a clear trend toward lower
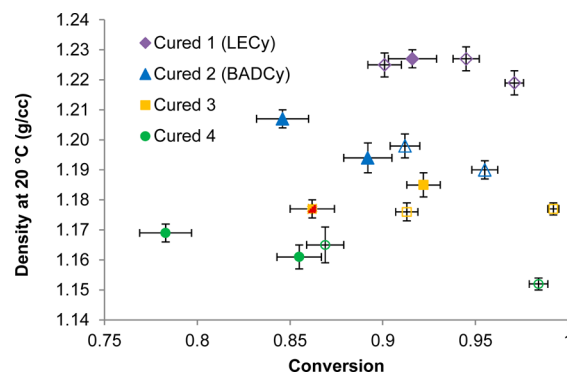
Figure 8. Density as a function of conversion for cured **1**–**4**. See Figure 6 for a guide to symbols.
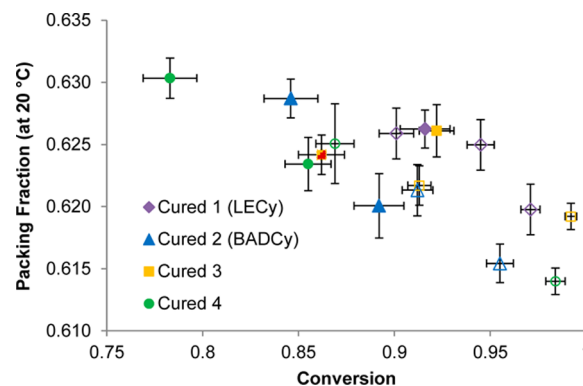
Figure 9. Packing fraction as a function of conversion for cured **1**–**4**. See Figure 6 for a guide to symbols.

density and packing fraction with increasing conversion that is not significantly affected by vitrification or cure temperature. For networks **1** and **3**, there appears to be a downward trend, but the smaller range of conversions studied limits the signal-to-noise ratio. Note that in previous work[32] the density of identically catalyzed **1** has been shown to decrease with increasing conversion. The packing fractions for networks **2** and **4** appear identical, while those of **1** and **3** may be slightly higher. Note that the correlation of Bicerano,[34] which has an average deviation of about 1% in this case when compared with other methods, was used to calculate the van der Waals volume (see Supporting Information). In terms of packing fraction then, systematic differences of less than about 0.006 could easily disappear if a different method of calculation of van der Waals volume were chosen. Thus, no significant differences in packing fraction among the four monomers could be detected.

An important question related to packing fraction and density is whether a significant difference exists between vitrified and nonvitrified samples. Of the four networks studied, only network **3** shows a lower density for vitrified samples. Given that network **3** showed anomalous behavior due to side reactions, and given that the difference is not reproduced in the other, very similar networks, the difference is likely due to an uncontrolled variation rather than to a systematic effect of vitrification that is unique to **3**. Thus, vitrification during cure, if it affects packing densities at all, is likely to affect packing much less than systematic effects due to an increase in conversion. Furthermore, if van der Waals volume was simply being converted to free volume during cure without an overall change in sample volume, then the actual density (deriving from an unchanging mass divided by an unchanging volume) should not

change with conversion, whereas there is ample evidence that it systematically declines. The decrease in the coefficient of thermal expansion with increasing conversion noted for polycyanurate networks would produce some overall decrease in density as conversion increased; however, the magnitude of the decrease in density with increasing conversion is much too large to be explained by this effect.

For the present study, it can be concluded that *ortho*-methylation of cyanurate groups does not lead to lower uptake because a lower T_G at full cure allows free volume to relax more readily in the sample under similar conditions. The best explanation appears to be that *ortho*-methylation lowers moisture uptake by steric hindrance of the cyanurate oxygen, a preferred site for water uptake. Note that because *ortho*-methylation does not appear to increase the packing fraction of the network, this effect is not simply due to methyl groups "filling holes" that water prefers to occupy, rather the local arrangements of atoms in the network are altered such that there are fewer favorable locations (and/or reduced thermodynamic favorability) for water to occupy near the polar cyanurate oxygen (and potential hydrogen-bonding site).

Thus, the density and packing data demonstrate that at higher conversions there is more free volume available within the networks, and as seen in Figure 6, water uptake becomes more sensitive to the local molecular structure of repeat unit segments near the cyanurate oxygen. At lower conversions, there is less free volume, and water is hindered from accessing favored sites regardless of the local repeat unit structure. Therefore, *ortho*-methylation makes less of a difference in water uptake at lower conversions. This particular aspect of water uptake in polycyanurate networks has not been widely recognized previously.

Hydrolytic Stability via Glass Transition Temperature Decreases. Although the reduced water uptake associated with *ortho*-methylated polycyanurate networks offers some direct technological advantages, such as lower outgassing for space structures, a modest reduction in takeoff weight for unprotected aerospace structures in humid environments, and reduced risk of blistering on rapid heating, much of the technological interest in attaining lower water uptake in polycyanurate networks stems from the presumed correlation between higher water uptake and greater "knockdown" in thermomechanical performance when the networks are utilized in wet environments. The most common measure of the "knockdown" is the decrease in the glass transition temperature of the networks produced by exposure to hot/wet conditions. The resultant measure of performance is the associated "wet" T_G of the network, which is typically utilized to establish a maximum service temperature in combination with an engineering safety factor.

Having established that *ortho*-methylation in polycyanurate networks leads to lower water uptake, an important follow-on consideration is the effect of *ortho*-methylation on the "wet" T_G of the networks. Figure 10 presents the dry T_G of networks **1**–**4** as a function of conversion. The dry T_G values follow the diBenedetto equation[35] as expected, with methylation at the bridge resulting in a roughly 15 °C increase in T_G at a given conversion. The addition of two *ortho*-methyl groups per monomer, however, decreases the dry T_G by 50–60 °C at a given conversion. To reconcile these very different effects of adding methyl groups, it is helpful to separate out the different structural effects with the aid of Figure 11, in which the dry T_G is plotted as a function of cross-link density. At identical
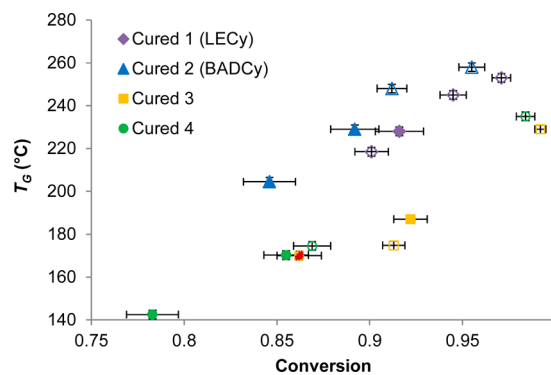
Figure 10. Dry T_G as a function of conversion for cured **1**–**4**. See Figure 6 for a guide to symbols.
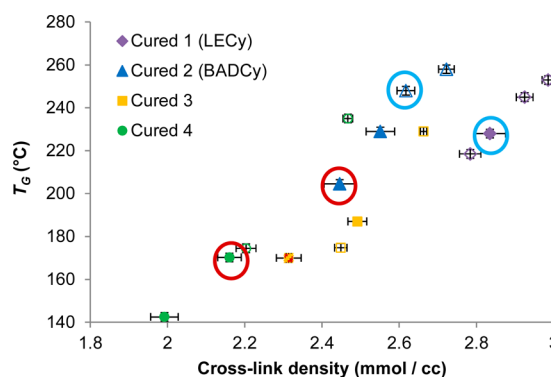

Figure 11. Dry T_G as a function of cross-link (i.e., cyanurate) density for cured **1**–**4**. See Figure 6 for a guide to symbols. The pairs of matched colored circles indicate samples with identical conversions (blue, ~90%, showing effect of bridge group methylation; red, ~85%, showing effect of *ortho*-methylation).

conversions (indicated by the circled points), bridge group methylation decreases cross-link density by 10%, while the addition of two *ortho*-methyl groups decreases cross-link density by 13%. At the same cross-link density, however, the addition of a bridge methyl group increases T_G by about 50 °C, while the addition of two *ortho*-methyl groups raises T_G by at most about 20 °C (to visualize this effect, compare the trends among identically colored points in Figure 11 and estimate the vertical offset). Methyl groups may therefore be thought of as "segment stiffeners" in networks with identical cross-link densities. The bridge methyl group, however, is more effective, as it constrains the degree of bending in the more flexible aliphatic backbone portion of the segment, whereas the aromatic methyl groups simply add side group bulk to the already rigid phenyl groups. The stiffening effect of methylation of the bridge is great enough to compensate for the decreased cross-link density, whereas the less potent stiffening effects of *ortho*-methyl groups only partly compensate for decreased cross-link density.

Figure 12 shows the "wet" T_G as a function of conversion for networks **1**–**4**. Although the effect of conversion is much smaller, and even near zero in network **3**, the general trends are qualitatively similar to those seen in Figure 10. Methylation at the bridge increases the "wet" T_G by about 0–10 °C while *ortho*-methylation results in a 30–40 °C decrease in "wet" T_G at the same conversion. In terms of "knockdown", there is thus an approximately 20 °C lower "knockdown" in the *ortho*-methylated networks; however, this improvement is insufficient
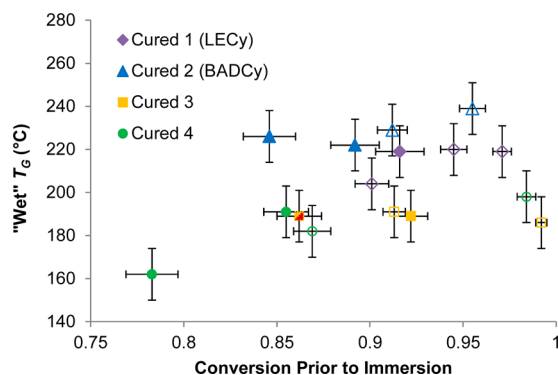
Figure 12. T_G as a function of conversion for cured **1**−**4** after immersion in 85 °C water for 96 h. See Figure 6 for a guide to symbols.

to compensate for the lower dry T_G of the *ortho*-methylated networks. The measured "knockdown" depends on plasticization of the networks by any moisture remaining after heating to the T_G (previous experiments[21,36] have shown that some, but not all, moisture remains under these conditions), along with permanent degradation of the network due to hydrolysis. Because these effects represent a mixture of intrinsic material properties and extrinsic sample properties, the interpretation should be limited to qualitative analysis of trends and differences. Thus, in terms of hot/wet performance, for the specific networks studied, there is actually a penalty for *ortho*-methylation in terms of the maximum use temperature. Whether or not *ortho*-methylation represents a useful strategy for applications therefore depends on the relative importance of reduced water uptake compared to maximum use temperatures.

The aforementioned results for copper-catalyzed polycyanurates are in contrast to the earlier work in zinc-catalyzed *ortho*-methylated polycyanurate networks reported by Shimp et al.[20] in which both reduced water uptake and improvements in "wet" T_G were observed. To gain some additional insight into what role, if any, the choice of catalyst played in the above results, some comparative studies using different catalyst types were undertaken. Specifically, polycyanurate networks with no added catalyst, the 2 parts per hundred nonylphenol/160 ppm of Cu-catalyzed networks for which detailed results are reported above (referred to herein as "Cu-Acac catalyzed"), and networks catalyzed by addition of 500 ppm of dibutyltin dilaurate (DBTDL) were compared. The DBTDL-catalyzed networks were of interest because recent work by Marella et al.[18] showed improved hot/wet performance in DBTDL-catalyzed networks of the cyanated phenol−formaldehyde resin PT-30 compared to systems catalyzed with other metals.

DBTDL has also been studied previously as a catalyst for **1** (LECy)[37] and **2** (BADCy).[38−43]

Table 2 compares the key characteristics of networks of **3** and **4** cured at 210 °C for 24 h using the three catalyst types mentioned previously. The addition of catalyst results in a higher degree of conversion but generally decreases the dry T_G at full conversion due to plasticization of the network by incorporated nonylphenol. The effects of adding the Cu-Acac catalyst package are small, but effects arising from addition of the DBTDL catalyst are more significant. In terms of the difference between dry (as-cured) T_G and "wet" T_G, the networks with no added catalyst fare best, with the T_G decreasing by only about 5 °C. This very small change is in line with previously studied polycyanurate networks.[26] The incorporation of the Cu-Acac catalyst causes a more significant reduction in T_G on exposure to hot water of 20−30 °C, in line with the observations of Marella et al.[18] as well as the slightly higher water uptake. The introduction of DBTDL, however, results in severe damage to the samples on exposure to hot water, with networks **3** and **4** undergoing disintegration during the 96 h test. In the case of **4**, the sample became so damaged that not even the remaining fragments could be tested after recovery. It is unclear why the effect of DBTDL addition on hydrolytic stability of networks **3** and **4** was markedly different from the reports of Marella et al., in which addition of DBTDL improved the hydrolytic stability of the cyanated phenolic resin PT-30.[18]

In addition to greatly decreasing hydrolytic stability, the incorporation of DBTDL as a catalyst also results in some loss of thermochemical stability, as seen by the decomposition temperature data in Table 2, whereas the incorporation of Cu-Acac results in no significant loss of thermochemical stability. The density of the DBTDL-catalyzed networks is also consistently higher than the others, and while the "as cured" T_G values are reasonable for the conversions measured, the fully cured T_G values are quite a bit lower than expected given the conversions and "as cured" T_G values. These features all suggest that side reactions, especially at elevated temperatures, are much more pronounced when DBTDL is used as a catalyst for networks **3** and **4**. The presence of side reactions will lead to errors in the measurement of conversion by DSC as well as to a potential decrease in T_G of the "fully cured" network on exposure to heating to 350 °C. Indeed, the T_G of the "fully cured" network is often a few °C lower than the "as cured" T_G, potentially due to side reactions in monomers **3** and **4** at elevated temperatures. In fact, some level of side reactions may be present in all versions of networks **1**−**4**; however, when all of the data are considered, the side reactions have more pronounced effects for the DBTDL-catalyzed networks. More

Table 2. Effect of Cure Catalyst on Key Properties of Networks 3 and 4

monomer	catalyst	conversion	"as cured" T_G^a (°C)	"fully cured" T_G^b (°C)	"wet" TG^c (°C)	TGA 5% weight loss in N_2/air (°C)	water uptake (%)	density (g/cm³)
3	not added	0.994 ± 0.002	246	244	240	401/403	1.21	1.142
3	Cu-Acac	0.995 ± 0.006	226	216	195	402/404	1.46	1.165
3	DBTDL	0.996 ± 0.012	196	199	<100*	395/396	13.82	1.180
4	not added	0.957 ± 0.017	226	233	222	401/401	1.05	1.159
4	Cu-Acac	0.990 ± 0.007	236	228	214	399/400	1.18	1.154
4	DBTDL	0.959 ± 0.047	185	192	68*	378/389	−3.68*	1.162

[a]Measured on first DSC scan of cured samples by midpoint of step change in heat capacity or turning point at onset of exotherm if no step change in heat capacity was visible. [b]Measured on second DSC scan of cured sample (after heating to 350 °C at 10 °C/min) by midpoint of step change in heat capacity. [c]Measured by OTMA by temperature at peak loss component of stiffness.

significant side reactions would be one possible reason for the greatly decreased hydrolytic stability of the DBTDL-catalyzed networks. The occurrence of these side reactions may be a direct consequence of the added steric hindrance around the reacting cyanurate during cyclotrimerization of the *ortho*-methylated monomers. A complete set of comparative data for the variously catalyzed networks may be found in the Supporting Information.

■ CONCLUSIONS

A comparison of the physical properties of polycyanurate networks based on 2,2-bis(4-cyanatophenyl)propane (BADCy) and 1,1-bis(4-cyanatophenyl)ethane (LECy) with and without a single methyl group *ortho-* to each aryl−cyanurate linkage showed that *ortho*-methylation was effective at reducing moisture uptake, particularly at conversions above 80%, whereas the effect of methylation at the bridges between phenyl rings in the network segments was negligible. These differences were observed even though *ortho*-methylation appeared to have no significant impact on either the packing fraction or its dependence on conversion in these networks. Vitrification during cure had little effect on either free volume development or moisture uptake. These results tend to confirm that steric hindrance from an *ortho*-methyl group inhibits absorption of water. Such an effect is likely best explained by decreasing the thermodynamic favorability of hydrogen bonding and/or dipole−dipole interaction with the cyanurate oxygen by creating an unfavorable steric environment. The hydrolytic stability of the *ortho*-methylated networks, as inferred from the relative decrease in glass transition temperature on immersion in water for 96 h at 85 °C, was moderately improved. However, because the dry glass transition temperature of the *ortho*-methylated networks was significantly lower, the "wet" glass transition temperature of the *ortho*-methylated networks was still 30−40 °C lower than the analogous commercial networks. An examination of the effect of two different catalysts, 2 parts per hundred of a 30:1 by weight mixture of nonylphenol and copper(II) acetylacetonate and 500 ppm of dibutyltin dilaurate (DBTDL), compared to analogous uncatalyzed networks, showed very significant differences in stability, with networks catalyzed by dibutyltin dilaurate showing significant side reactions at elevated temperature and severe hydrolytic degradation. These results show that *ortho*-methylation mitigates some, but not all, forms of hydrolytic instability in polycyanurate networks.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Section S1: tabulated list of all monomers, catalyst systems, and experiment types; Section S2: details of DSC conversion measurements; Section S3: raw DSC data; Section S4: details of OTMA thermal lag determination; Section S5: raw OTMA data; Section S6: raw TGA data; Section S7: determination of van der Waals volume. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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