Di(cyanate Ester) Networks Based on Alternative Fluorinated Bisphenols with Extremely Low Water Uptake

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Ⓢ *Supporting Information*

ABSTRACT: A new polycyanurate network exhibiting extremely low moisture uptake has been produced via the treatment of perfluor-ocyclobutane-containing Bisphenol T with cyanogen bromide and subsequent thermal cyclotrimerization. The water uptake, at 0.56 ± 0.10% after immersion in water at 85 °C for 96 h, represents some of the most promising moisture resistance observed to date in polycyanurate networks. This excellent performance derives from a near optimal value of the glass transition at 190 °C at full cure. Superior dielectric loss characteristics compared to commercial polycyanurate networks based on Bisphenol E were also observed. Polycyanurate networks derived from this new monomer appear particularly well-suited for applications such as radomes and spacecrafts where polycyanurates are already widely recognized as providing outstanding properties.
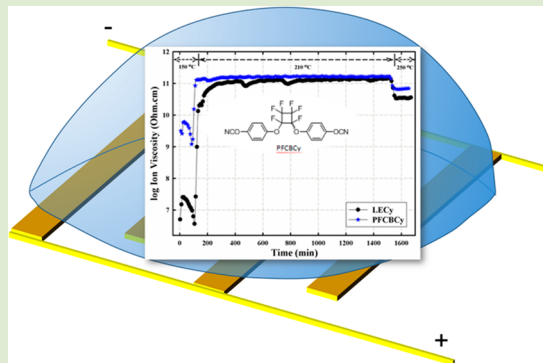
Among thermosetting polymers, polycyanurates (also known as "cyanate ester resins")[1−4] offer an outstanding combination of physical properties that have made them highly desirable for applications ranging from printed circuit boards[5] and radomes[6] to magnet casings for thermonuclear fusion reactors[7,8] and support structures for interplanetary space probes.[9] These properties include excellent flame, smoke, and toxicity characteristics,[10] glass transition temperatures of up to 400 °C in fully cured networks,[11] low moisture uptake, and a very low coefficient of hygroscopic expansion,[12] as well as an unusually low dielectric constant and dielectric loss factor compared to other thermosetting resins of similar expected polarity.[13] In addition, cyanate ester monomers typically afford low melting points and melt viscosities, making them suitable for use in a wide variety of processing operations from nanomolding[14] to filament winding.[15] Because the cyclo-trimerization chemistry that forms polycyanurates involves a single, well-defined end product with few side reactions[16] and because the conversion is relatively easy to quantify via methods such as FT-IR spectroscopy,[17] investigations of structure−property relationships in polycyanurate networks enable straightforward optimization of properties, while often yielding insights into thermosetting networks[18] that can be applied to more complex cure chemistries.[19]

Many of the desirable physical properties of cyanurate networks, such as low dielectric constant and chemical inertness, are shared with fluorinated polymers.[20] A logical way to further optimize the performance of polycyanurate networks has been to pursue incorporation of fluorinated chemical moieties. For instance, AroCy F, a cyanate ester synthesized from Bisphenol AF (the hexafluoroisopropylidene analogue of Bisphenol A), provides a reduction in moisture content of around 30% on a concentration per unit weight basis[21,22] (but only 15% on a concentration per unit volume basis) compared to AroCy B, which is synthesized from Bisphenol A. A variation on the AroCy F monomer in an oligomeric liquid form has also been studied by Yameen et al.[23]

Recently, the use of polymers containing Bisphenol A has emerged as a public health concern in many countries[24−26] due to the ability of some bisphenol compounds to function as endocrine disruptors under certain conditions. Additional investigations have shown that bisphenol compounds with a molecular shape similar to Bisphenol A, including Bisphenol AF,[27,28] can also interact with human hormone receptors in a

similar fashion.[29] Although densely cross-linked polymers, such as cyanate esters, severely limit the mobility of small molecules, trace quantities of precursor bisphenols may be found in cyanate ester resins, either as residuals from synthetic precursors (as in epoxies) or as products from hydrolytic or thermal degradation.[30] The availability of fluorinated cyanate esters based on alternative fluorinated bisphenol precursors, particularly those with a molecular geometry substantially different from Bisphenol A, could drastically reduce such concerns by eliminating the "lock and key" fit to hormone receptors that facilitates at least some modes of endocrine disruption.[29,31]

Loudas and Vogel,[32,33] and later Snow and co-workers,[34−36] synthesized a variety of fluoroaliphatic dicyanate ester monomers. These monomers were liquids at room temperature and cured into either elastomers or glassy polymer networks with moisture uptake as low as 0.68% after 96 h in boiling water (equal to about a 55% reduction in moisture uptake on a molar basis compared to AroCy B). Although such cyanate esters do not involve bisphenol precursors, they lack the high-temperature resistance and mechanical stiffness associated with aromatic content, which limits their potential for high-performance applications.

An interesting alternative to Bisphenol A is Bisphenol T, which contains a perfluorocyclobutane moiety and, being bridged by four atoms between phenyl groups, is significantly different in shape compared to Bisphenol A and Bisphenol AF (both of which feature bridges with a single atom). Perfluorocyclobutanes have already emerged as an established fluorinated moiety in polymer thermoplastic materials.[37,38] These cyclic fluoroaliphatic structures offer good thermochemical stability and have recently been shown to exhibit thermally induced self-healing[39] and mechanophore[40] characteristics. Although thermosetting resins containing perfluorocyclobutane groups have been formed from trifunctional perfluorovinyl ethers,[41−44] to date there have been no reports of cyanate esters that incorporate this relatively new and interesting class of fluorine-containing monomer.

Herein we present the synthesis and physical properties of a new dicyanate ester monomer ("PFCBCy") containing a perfluorocyclobutane group, as well as its cure characteristics and the physical properties of the resultant polycyanurate networks. We discovered that the combination of hydrophobic character and the optimal degree of flexibility in the network chain segments led to an extremely low moisture uptake of only $0.56 \pm 0.10\%$ in the polycyanurate network at full cure, a 70% decrease on a moles per unit volume basis compared to AroCy B, and among the lowest values measured for any polycyanurate network. Such low moisture uptake, along with a high level of fluorination, also led to significant improvements in dielectric performance compared to more conventional polycyanurate networks. The PFCBCy therefore offers both the high performance of an aromatic fluorinated cyanate ester and the potential for new and exciting properties such as the mitigation of some health and safety concerns and/or thermal mending characteristics.

Synthesis of the PFCBCy monomer was accomplished in a single, straightforward step via treatment of commercially available Bisphenol T with 3.5 equiv of cyanogen bromide at −78 °C, using 3.0 equiv of triethylamine added dropwise over 15 min followed by 2 h of additional stirring. These conditions are typical for the synthesis of cyanate esters using cyanogen bromide[45] (complete details with characterization are provided

in the Supporting Information). Following purification by washing in methanol, PFCBCy was obtained in 56% yield at the 1 g scale as a white powder with a melting point of 103 °C. The yield was reasonable considering the scale of the reaction and the fluorinated nature of the product, while the melting point is only modestly higher than that of AroCy F (87 °C).[22] The identity of the product was confirmed by high-resolution mass spectroscopy, along with ATR-FTIR spectroscopy, which showed the characteristic doublet at 2237 and 2270 cm^{-1} for cyanate ester groups, and ^{19}F NMR, which revealed the characteristic signature of perfluorocyclobutyl groups.

Scheme 1 shows the synthesis and cure of the PFCBCy to form a macromolecular network. A differential scanning
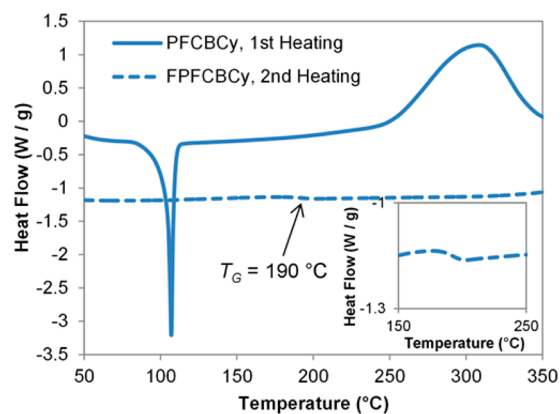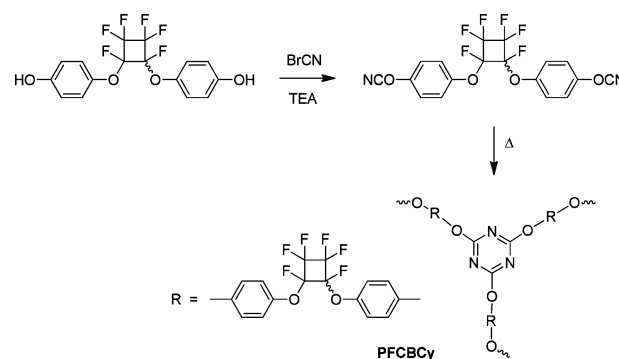
Scheme 1

Figure 1. DSC scan of a perfluorocyclobutane (PFCB) dicyanate ester monomer.

calorimetry (DSC) thermogram of the PFCBCy (Figure 1) exhibited the expected thermal properties of a high-purity, uncatalyzed cyanate ester monomer (cure exotherm of 97 kJ/ equiv with a peak above 300 °C). A second DSC scan revealed the postcure glass transition temperature (T_G) near 190 °C. The purity of the monomer as determined by automated analysis of the melting curve with the van't Hoff equation was only around 85 mol %, a likely reflection of the fact that the monomer exists as a pair of stereoisomers. The lower value of the postcured T_G compared to fully cured networks derived from more common dicyanates (such as the dicyanate esters of Bisphenol A and Bisphenol E, at around 300 °C) likely arises from flexible −O− linkages in the network segments along with a roughly 20% lower number density of cross-links (a rough estimate of cross-link density is derived in the Supporting

Information). In contrast, dicyanate networks containing cyclohexyl moieties but not ether linkages in the backbone, which also feature a lower cross-link density compared to the dicyanate esters of Bisphenol A and E, show T_G values as high as 300 °C.[46]

Additional studies using oscillatory thermomechanical analysis (TMA) (details provided in the Supporting Information) indicated an "as cured" T_G of 186 °C (following cure at 150 °C for 1 h followed by 210 °C for 24 h) and a "fully cured" T_G (after heating to 350 °C) of 197 °C, in good agreement with the DSC data. This small difference in "as cured" and "fully cured" T_G values indicates that 98 ± 1% conversion was achieved using a final temperature of 210 °C. The use of cure temperatures above about 210 °C often leads to degradation in the performance of polycyanurate networks,[47] but for many monomers, such as AroCy B and AroCy F, higher cure temperatures are necessary to achieve complete cure. The need for higher cure temperatures is a consequence of the higher T_G of the fully cured networks. The T_G of the fully cured PFCBCy is thus near the highest possible value that allows the network to be cured without risking degradation. Note also that the need to avoid vitrification through the use of high cure temperatures applies even when cure catalysts are used.[48]

Another key benefit of curing near the T_G in polycyanurate networks is the minimization of moisture uptake. Positron annihilation lifetime studies of AroCy B undertaken by Georjon and Galy[12] showed clearly that when polycyanurate networks cure below T_G the net effect of cyclotrimerization is the conversion of van der Waals volume to free volume. The free volume, which is frozen in place, then allows moisture to occupy locations near the (relatively) hydrophilic cyanurate rings, leading to an increase in moisture uptake. In PFCBCy, the combination of a lower density of cyanurate rings, a T_G at full cure that permits rapid cure without leading to network degradation, and the hydrophobicity of the perfluorocyclobutyl group enables an extremely low moisture uptake to be achieved.

The observed moisture uptake for the PFCBCy after cure at 210 °C, which results in 98 ± 1% conversion, was measured at 0.56 ± 0.10% (see Supporting Information for experimental details). On a weight basis, this value is significantly lower than AroCy B (2.4−2.5%) or AroCy F (1.6−1.8%) at full conversion[49] and is as low as the values reported by Snow and Buckley for highly fluorinated aliphatic polycyanurates (0.7%).[35] Interestingly, networks made from the cyanate ester RTX-366, which also features a 35% reduction in the density of cyanurate rings relative to AroCy B and a fully cured T_G near 200 °C,[50] show moisture uptake of 0.6−0.7% at full cure.[51] In comparison, the perfluorocyclobutane moiety appears to allow a modestly higher cyanurate density in combination with very low moisture uptake, an enabling factor for improved stiffness and environmental resistance.

An important consequence of the very low moisture uptake of the PFCBCy network along with the high −F content is significantly lower dielectric constant and dielectric loss relative to commercial polycyanurates. To examine these effects in detail, dielectric spectroscopy was performed using a drop of monomer cured between interdigitated electrodes, developed by Netzsch Instruments North America, LLC, as illustrated in Figure 2 (experimental details are provided in the Supporting Information) using a cure protocol of 150 °C for 1 h, followed by 24 h at 210 °C, with a postcure at 250 °C for 2 h. Both PFCBCy and Primaset LECy, a nonfluorinated dicyanate ester
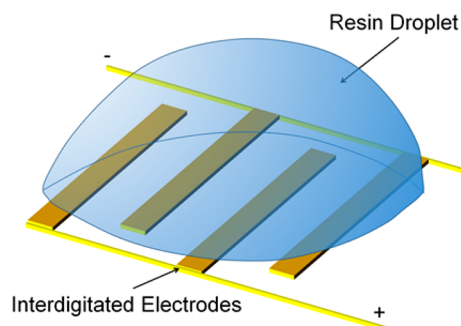
Figure 2. Interdigitated remote electrode sensor for the dielectric spectroscopy measurements.

for which dielectric data are readily available for benchmarking,[13] were tested for comparison.

During the cure cycle, ion viscosity was determined as a function of cure time to identify resin gel points and to analyze curing kinetics. Dielectric spectroscopy can monitor resin cure by measuring electrical properties closely tied to viscoelastic properties. Ion viscosity (IV) is a measure of ion mobility which is a function of polymer chain segmental mobility. It is derived from the dielectric loss permittivity, ε'', through the relation which holds at low frequency, f

$$\text{Ion viscosity} = \text{IV} = 1/\sigma; \quad \sigma = 2\pi f \varepsilon'' \varepsilon_o \tag{1}$$

in which σ is the electrical conductivity reflective of long-range charge migration and ε_o is the vacuum permittivity. As the fluid system of monomers becomes increasingly polymerized and cross-linked, there is an increase in viscosity, and gel point is defined as the point at which the curve reaches a plateau after the rapid increase.

The results, shown in Figure 3, reveal numerous interesting features of network development. The periods in which the ion
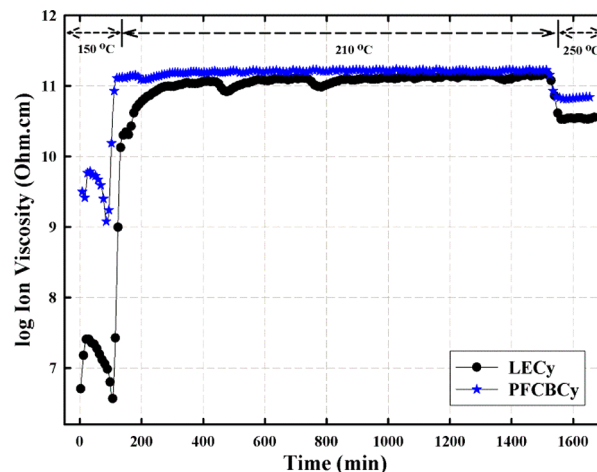
Figure 3. Log ion viscosity vs curing time at 100 Hz for PFCB cyanurate and Primaset LECy in "dielectric cure monitor" mode.

viscosity rapidly decreases over time correspond to the ramps with increasing temperature during the cure protocol, while the periods in which ion viscosity rapidly increase correspond to network formation. Network formation at 210 °C takes place much faster for PFCBCy than for LECy as indicated by Figure 4, which shows that ion viscosity reaches a plateau value after 115 min for PFCBCy and after 250 min for LECy. Although some evidence has been gathered suggesting that the electron-
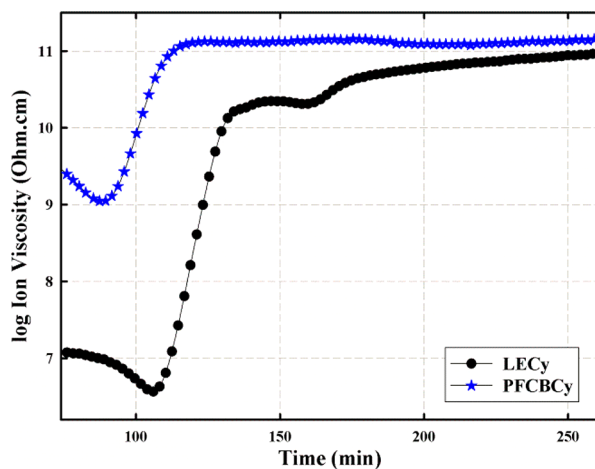
Figure 4. Expansion of initial data shown in Figure 3 to illustrate different rates of cure for the samples.

Figure 5. Thermogravimetric analysis (TGA) thermogram of uncured PFCBCy under N_2 at a heating rate of 10 °C/min.

withdrawing effects of the −6F group in AroCy F lead to faster cure,[52] more detailed experiments would be needed to confirm a similar effect for the PFCBCy since the relative levels of impurities tend to greatly affect the rates of cyclotrimerization in cyanate esters. Ion viscosity for the PFCBCy sample drops during the postcure step at 250 °C due to facilitated dipole mobility resulting from softening of the resin as the material moves deeper into the rubbery region. This explanation is supported by the drop in storage modulus as the temperature is increased to ≅ 220 °C (see Figure S3.1, Supporting Information). At both 210 and 250 °C, the ionic viscosity in PFCBCy is higher than in LECy, correlating to a lower dielectric loss. The lower dielectric loss is likely a direct consequence of lower water uptake and the presence of fluorine.

The interdigitated electrode experiment also provides a rough estimate of the dielectric constant, subject to significant uncertainty due to electrode blocking and other interfacial effects.[53] The estimate for the dielectric constant of PFCBCy using this approach was roughly 2, which is in general agreement with values for fluorinated macromolecular networks and thermoplastics. A check of repeatability using Primaset LECy showed a standard deviation of around 1.0 for the variation in the dielectric constant as determined by this technique, as expected based on the aforementioned limitations. Despite these limitations, the interdigitated electrode experiments may also provide a useful means for assessing cure kinetics and mechanisms, a subject beyond the scope of the present work.

Although the very low water uptake and excellent dielectric properties indicate suitability for numerous high-performance applications such as radomes or spacecraft structures, the stability of the network toward thermal degradation is also an important consideration. Though one might expect some improvement in these properties due to incorporation of fluorinated groups, the "weak link" in polycyanurate networks is well-known to be the cyanurate cross-linking group;[54] therefore, the use of more thermally stable moieties in the network chains does not delay the onset of decomposition, which takes place between 400 and 425 °C under both nitrogen and air, as seen in Figure 5. Char yields are also similar to cyanate esters such as LECy (see Supporting Information for additional data and comparisons).
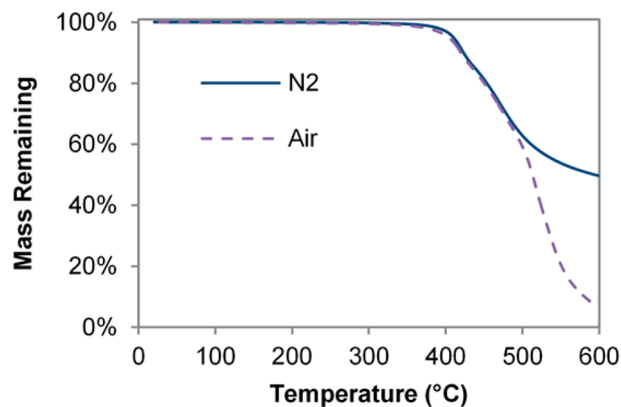
In summary, a new polycyanurate network exhibiting extremely low moisture uptake has been discovered based on the treatment of perfluorocyclobutane-containing Bisphenol T with cyanogen bromide and subsequent thermal cyclotrimerization. The water uptake, at 0.56 ± 0.10% after immersion in water at 85 °C for 96 h, represents some of the best performance observed to date in polycyanurate networks. This excellent performance derives from a near optimal value of the glass transition temperature at full cure, in contrast to earlier fluorinated polycyanurates in which the glass transition temperature was either too high (AroCy F) or too low (fluoroalkyl cyanates). These new networks are particularly well-suited for applications such as radomes and spacecrafts where polycyanurates are already widely recognized as providing outstanding properties. In addition, the use of an alternative bisphenol precursor with a shape significantly different from that of Bisphenol A has the potential to address some public health concerns,[29,31] and the use of mechanophoric perfluorocyclobutyl groups[40] has the potential to introduce interesting self-healing characteristics.[39] Thus, the new perfluorocyclobutane derivative represents a potentially very important advance in the field of thermosetting networks.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Experimental details (synthesis and characterization); cross-link density estimation; TMA data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Harvey of the Naval Air Warfare Center, Weapons Division, for helpful discussions.

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