Macromolecules

Bisphenol-1,2,3-triazole (BPT) Epoxies and Cyanate Esters: Synthesis and Self-Catalyzed Curing

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ABSTRACT: Novel bisphenol-1,2,3-triazole (BPT) resins, including epoxy (DGE-BPT) and cyanate ester (BPTCE) systems, were prepared and used in curing chemistry with no added reagents or catalysts. The materials were characterized relative to conventional epoxies and cyanate esters, in terms of



curing and thermal properties, and the curing process and products were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), pyrolysis combustion flow calorimetry (PCFC), and small scale flame tests. These novel BPT-based resins cure in the absence of added catalysts and exhibit exceptionally low heat release and high char residue. Despite the absence of antiflammable additives (either halogenated or inorganic compounds), BPTCE itself was found to be nonignitable, with extremely high char residue value (67%) and extraordinarily low heat release capacity (HRC of \sim 10 J/(g K)).

INTRODUCTION

Polymer matrix composites such as blends and filled systems are exceptionally useful for a wide range of industrial applications that require high performance-to-weight ratio and corrosion resistance, such as in transportation, construction, and electronic materials. Because of their excellent adhesive properties, processability, and low cost, epoxy and cyanate ester resins are used prominently as the polymer matrix in such composites.¹⁻⁴ For example, bisphenol A (BPA) epoxy formulations dominate the epoxy resin market but generally contain fillers, curing agents, and flame retardants (FRs).⁵ The inherent flammability of such materials is particularly problematic in settings that require flame resistance, such as vehicles and electronic and construction materials. Brominated FR small molecules such as polybrominated diphenyl ethers, hexabromocyclododecane, and tetrabromobisphenol A (TBBPA) have been implemented widely to reduce flammability.^{6,7} However, many brominated FRs were recently classed together with halogenated FRs and face legislative restrictions in Europe and the United States due to health and environmental concerns, such as bioaccumulation and associated carcinogenicity.⁸⁻¹⁹ Potential negative effects of such molecules on the environment, and in animals and humans, remain controversial and under continued investigation.²⁰⁻²³

While most epoxy resins require added curing agents (e.g., multifunctional amines), cyanate ester (CE) resins cure thermally by cyclotrimerization to give polycyanurates (Figure 1). Polycyanurates exhibit high glass transition temperatures, toughness, and low dielectric properties, making them useful in high-performance structural and electronics applications.²⁴ Halogenfree CE resins (e.g., BPA, bisphenol-E, and bisphenol-M CE resin) exhibit undesirably high flammability, with a heat release capacity (HRC) of 240-320 J/(g K), total heat release (THR) of 15-23 kJ/g, and char yield of 26-42%.²⁵ Moreover, the long gelation time of CE resins is frequently adjusted by the addition

of curing catalysts, such as imidazoles or transition metal complexes. $^{\rm 24-27}$

We recently reported the preparation of novel polymers containing bisphenol-1,2,3-triazole (BPT) moieties, which undergo a thermally induced triazole-to-phenylindole rearrangement,^{28–31} releasing nitrogen gas and giving high levels of char with little burning.³² For example, BPT-containing aromatic polyesters were prepared and found to exhibit exceptionally low heat release properties. BPT-polyesters gave a heat release capacity (HRC) of <50 J/(g K), total heat release (THR) of ~7 kJ/g, and char yields of 47–56%. HRC, an inherent materials property, is defined as the maximum specific heat release divided by the heating rate during a controlled thermal decomposition and is now a wellestablished method for evaluating flammability characteristics of combustible materials.^{33–36} We measured HRC by a standard oxygen combustion calorimetry technique³⁷ and judged self-extinguishing properties in small scale flame tests.

Here we describe an effort designed to test whether BPT units could be integrated successfully into cross-linked epoxy and cyanate ester networks and, if so, whether the resulting materials would represent any potential advantage over existing materials. As described below, we found that these novel BPT-epoxies function effectively as one-component resins (i.e., requiring no curing catalyst) and that BPT-cyanate ester resins exhibit a markedly reduced gelation time (5 min at 170 °C) relative to more conventional versions.

RESULTS AND DISCUSSION

BPT-Diglycidyl Ether Synthesis. Bisphenol-1,2,3-triazoles 1 and 2, containing meta- and para-substitution patterns, respectively,

| Received: | April 1, 2011 | | |
|------------|---------------|--|--|
| Revised: | June 3, 2011 | | |
| Published: | June 21, 2011 | | |



Figure 1. Curing networks based on bisphenol A epoxy (top) and bisphenol A cyanate ester (bottom).



Figure 2. DSC thermograms of 3-DGE-BPT (--) and 4-DGE-BPT (--) resins.

were prepared by the click cycloaddition reactions that we reported previously.³² Then, the corresponding diglycidyl ether derivatives (DGE-BPTs) were prepared by reaction of the phenols with epichlorohydrin in a sodium hydroxide solution in water/isopropanol. 3-DGE-BPT, compound 3, was obtained as a yellow solid in 82% yield and 4-DGE-BPT, compound 4, as a pale brown solid in 62% yield. Nuclear magnetic resonance (NMR) spectroscopy confirmed the desired structure of 3 and 4, as seen for example in the ¹H NMR spectrum of 4 showing the characteristic glycidyl ether resonances centered at 4.35, 3.41, 2.97, and 2.82 ppm. Differential scanning calorimetry (DSC) analysis of 4-DGE-BPT showed a small endotherm from 190 to 195 °C, and a large exotherm at 195-250 °C (Figure 2), reflecting an initial melting that is followed immediately by self-curing. In contrast, 3-DGE-BPT 3 did not exhibit a clear melting point, showing only a glass transition at \sim 20 °C, likely an effect of the meta-substitution. However, 3-DGE-BPT also showed a large exotherm from 160 to 280 °C upon self-curing. High-resolution mass spectroscopy of 3 (366.1462 m/z of [M + $[H]^+$) and 4 (366.1426 m/z of $[M + H]^+$) (calculated 366.1454 m/z confirmed the expected molecular weight of each compound in fast atom bombardment (HRMS-FAB) mode. Interestingly, in electron impact mode (HRMS-EI), the expected signal at 365.14 m/z of $[M]^+$ was absent, but instead a signal at

337.13 m/z of $[M - N_2]^+$ was observed, due to the loss of N_2 from triazole under these ionization conditions.

As the postcured BPT-containing products are insoluble, and thus difficult to characterize by standard solution spectroscopy, we prepared the dimethyl ester version of BPT, shown as compound 5 in Scheme 2, for the purpose of examining its reaction with the aromatic monoglycidyl ether 6. A mixture of 5 and 6 was heated to 180 C for 1.5 h, and the resulting reaction mixture was readily soluble and could be characterized by ¹H NMR spectroscopy. The glycidyl ether methylene and methyne resonances were absent, indicating the anticipated epoxide ring-opening, and new resonances from 4.43 to 4.05 ppm reflect the formation of an oligomeric ethylene oxide structure. The broadening of the triazole proton peak (from 8.22 ppm of 5 to 8.23-8.14 ppm in the product) suggests its reaction with the glycidyl ethers that might lead to a zwitterionic structure, as shown in Scheme 2. As for curing with tertiary amines and imidazoles,³⁸⁻⁴⁰ the triazole moiety can react with the electronpoor methylene of the epoxide and then propagate further to an oligomeric product. While this experiment confirms participation of the triazole in the curing mechanism, we note that concurrent participation of adventitious nucleophilic initiators (water, base, etc.) cannot be ruled out, despite our efforts to purify BPT and the other reagents used.

We found that these novel DGE-BPT epoxy resins can be used alone in curing chemistry or as a component of blends with other epoxides. Blends of DGE-BPT with BPA-based epoxy (DGE-BPA) and deoxybenzoin-based epoxy (DGE-BHDB)⁴¹ were prepared to determine the properties of these mixtures. By DSC, each blend showed a large exotherm in the temperature range 160–320 °C (Figure 3) due to catalytic curing at over 160 °C (regardless of para- or meta-substitution) under homogeneous melt conditions.

The heat release and char properties of self-cured DGE-BPT resins and their blends with other diglycidyl ethers were characterized by pyrolysis combustion flow calorimetry (PCFC) and thermogravimetric analysis (TGA). Samples for PCFC and TGA were prepared by curing the homogeneous mixture (in the melted state) for 2 h at 160 °C and for 1 h at 180 °C, followed by a 1 h postcure at 200 °C in a Teflon mold. The data obtained from these formulations are listed in Table 1. DGE-BHDB resins

Scheme 1



Scheme 2



Figure 3. DSC thermograms of DGE-BPA/3-DGEBPT (1/1, w/w, ---) and DGE-BEDB/4-DGE-BPT (4/1, w/w, ---) blend.

cured with the aromatic diamines diaminodiphenyl sulfone (DDS) and diaminodiphenylmethane (DDM) (Table 1, entries 3 and 4) exhibited moderately lower heat release properties than those of the BPA version (entry 1) due to the known char-forming

properties of the deoxybenzoin moiety⁴¹⁻⁴³ (increasing from 12% to 30-35%). Impressively, despite the significant aliphatic character inherent to diglycidyl ethers, the HRC and THR values of the blended triazole containing resins (entries 2, 5, 6, and 7)

| entry formulation HRC (J/(g K)) THR (kJ/ | g) char $(\%)^b$ |
|---|------------------|
| 1 DGE-BPA/DDS ^{<i>a</i>} 513 ± 10 25.3 ± 0.0 | 2 12 |
| 2 DGE-BPA/3-DGE-BPT (1/1, w/w) 408±10 16.9±0. | 2 26 |
| 3 DGE-BHDB/DDS ^{<i>a</i>} 420 ± 14 17.2 $\pm 0.$ | 2 30 |
| 4 DGE-BHDB/DDM ^{<i>a</i>} 439 ± 7 17.6 ± 0. | 2 35 |
| 5 DGE-BHDB/4-DGE-BPT (4/1, w/w) 265±5 16.6±0. | 4 35 |
| 6 DGE-BHDB/3-DGE-BPT (1/1, w/w) 222±5 12.5±0. | 2 43 |
| 7 3-DGE-BPT (self-cured) 200 ± 7 10.9 ± 0.0 | 3 45 |

^{*a*} Equivalent amount of aromatic diamine (DDS: diaminodiphenyl sulfone; DDM: diaminodiphenylmethane) was used (data taken from the ref 41). ^{*b*} Data obtained from TGA at 850 °C in a nitrogen atmosphere (heating rate 10 °C/min).



Figure 4. Adhesion demonstration using the 3-DGE-BPT resin ((a) before loading additional weight and (b) after loading 700 g of metal weight).

decreased significantly with increasing DGE-BPT content. The self-cured 3-DGE-BPT resin was most impressive in this regard, with a HRC of only $200 \pm 7 \text{ J/(g K)}$, and an impressively high char value of 45%.

The adhesive properties of self-cured BPT-containing epoxies were confirmed by demonstrating adhesion of a metal alloy rod (30 g, 1 cm diameter) on a glass surface. The adhesion of the selfcured 3-DGE-BPT specimen was sufficiently robust to bear an additional 700 g loading (see Figure 4). Quantitative adhesive studies (i.e., lap shear tests) of BPT-epoxy will be possible following development of these experimental scale materials into a larger scale process.

Bisphenol-1,2,3-triazole Cyanate Ester (BPTCE). We anticipated that combining the benefits of BPT with aryl cyanurate structures into a resin formulation would improve these conventional systems by reducing curing time and their enhancing flame resistance, even in the absence of added catalyst. The cyanate ester of 3-BPT (3-BPTCE, 7) was prepared in the good yield by reaction of 3-BPT with cyanogen bromide in the presence of triethylamine (Scheme 3). 3-BPTCE was obtained as a pale brown solid and seen to have a significantly higher melting point (155–160 °C) than the BPA version (78–82 °C). The ¹³C NMR spectrum of cyanate ester 7 showed signals at 108.6 and 108.9 ppm, in the expected regions for cyanate esters, with the two separate peaks arising as a consequence of the unsymmetrical



Figure 5. Measured gelation time of BPACE, 3-BPTCE, and BPACE/ BPTCE blends.

nature of BPT (i.e., having a nonequivalent electronic environment around the two cyanate ester carbon atoms). Mass spectrometry analysis confirmed the desired structure, with BPTCE 7 giving a mass of 275.1 m/z by HRMS-EI ($[M - N_2]^+$) and 304.0822 m/z by HRMS-FAB ($[M + H]^+$, calculated 304.0834 m/z).

Unlike BPA cyanate ester (BPACE), which requires implementation of heating cycles to achieve curing in the absence of added catalysts (e.g., 18 h at 150 °C, 4 h 200 °C, and 4 h 240 °C),²⁰ BPTCE gelled rapidly after melting. This rapid gelation of BPTCE allowed the curing reaction to be completed within 30 min by heating the material from 160 to 280 °C at 5 °C/min. Anticipating that BPTCE might be most useful in blends with commercially available BPACE, the effect of blend ratios on curing was investigated, in BPACE-to-BPTCE weight ratios of 9:1, 8:2, 7:3, and 1:1. Gelation times were measured using a magnetic stir bar (1 cm) in 100 mg of sample at 170 °C, noting the time required for a mixture stirring initially at 200 rpm to stop completely (Figure 5). At 170 °C, BPACE alone showed



Figure 6. Left: diagram of a small scale flame test; middle: the specimens (a) before test and (b-d) after test; right: flame test results as a function of cyanate ester composition.

 Table 2. Heat Release and Char Properties of Cured BPACE,

 BPTCE, and Blend Resins

| entry | composition (w/w) | $HRC\left(J/(g\;K)\right)$ | THR (kJ/g) | char $(\%)^a$ | |
|---|-------------------|----------------------------|--------------|---------------|--|
| 8 | BPACE | 332 ± 10 | 14.5 ± 0.2 | 44 | |
| 9 | BPACE/BPTCE (9/1) | 285 ± 14 | 13.4 ± 0.3 | 44 | |
| 10 | BPACE/BPTCE (8/2) | 280 ± 15 | 12.5 ± 0.2 | 46 | |
| 11 | BPACE/BPTCE (7/3) | 261 ± 12 | 11.2 ± 0.4 | 48 | |
| 12 | BPACE/BPTCE (5/5) | 200 ± 15 | 9.2 ± 0.2 | 53 | |
| 13 | BPTCE | 10 ± 2 | 2.0 ± 0.2 | 67 | |
| a Data obtained from TGA at 850 $^\circ C$ in nitrogen (heating rate 10 $^\circ C/min).$ | | | | | |

no reduction in rpm for 6 h. However, for 9:1 and 7:3 BPACE: BPTCE blends, gelation time decreased dramatically from 230 to 55 min, likely due to catalysis of the cyclotrimerization by the triazole group.^{4,24} Such mixtures may prove convenient for processes that require rapid online wetting or continuous fiber reinforcement such as wet filament winding, resin transfer molding, and pultrusion.⁴⁴

As a precursor to small scale flame tests, PCFC, and TGA experiments, BPACE/BPTCE blends were prepared by curing a homogeneous mixture of the two cyanate esters for 4 h at 170 °C, then for 4 h at 240 °C, followed by postcuring at 280 °C for 1 h. BPACE samples were cured for 18 h at 150 °C, then for 4 h at 200 °C, 4 h at 240 °C, and finally postcured at 280 °C for 1 h. In the case of 3-BPTCE, samples were cured for 30 min at 170 °C and then heated to 280 at 5 °C/min. Small scale flame tests were conducted by placing a sample specimen ($\sim 1 \times 0.35 \times 0.1$ cm) in a propane torch flame at a 45° angle for 3 s, noting the time required for the sample to self-extinguish following removal from the flame (Figure 6).⁴⁵ Striking differences were observed among these samples as a function of BPTCE content. BPACE exhibited self-sustained burning in air following removal from the flame, with moderate visible smoke. In the blended materials, intumescence increased with the BPTCE content, possibly due to N₂ gas evolution upon burning. Such intumescence can provide an effective barrier to release of fuel from the material surface. The specimens containing 50 wt % BPTCE (entry 12) burned for only 1-2 s, while BPTCE samples (entry 13) were seen to extinguish immediately after removal from the flame, with little noticeable smoke evolution. We also note that BPTCE exhibited an impressive char volume, expanding outward from the specimen in the flame (Figure 6c,d). Such char formation is exceptionally useful as it contributes further to effective suppression of flame spread.

The PCFC and TGA results of BPACE/BPTCE materials are listed in Table 2. Heat release values (HRC and THR values) of the cured blends decreased with increasing BPTCE weight



Figure 7. TGA thermograms of cured BPACE (black), BPTCE (red), and BPACE/BPTCE (5/5, w/w, blue).

percent, approximately following the rule of mixtures. Notably, the cured BPTCE exhibited miniscule HRC (10 J/(g K)) and THR (2 kJ/g), extraordinary low values, even lower than halogen-containing CE resins such as hexafluorobisphenol A (62 J/(g K) HRC and 4.6 kJ/g THR) and bisphenol C containing CE resins (24 J/(g K) HRC and 4.2 kJ/g THR).²⁵ TGA of BPTCE showed a two-step weight loss curve (about 10% weight loss at 330–430 °C), which would be expected from the loss of N₂, and a 67% char yield at 850 °C (Figure 7). With increasing of BPT content in the blends, the slope of weight loss decreased and the residual mass (char) increased, indicating an enhanced flame-retardancy through char by aromatization during combustion.

In summary, we have described the synthesis of novel bisphenol-1,2,3-triazole epoxy and cyanate ester resins as selfcatalyzed, self-extinguishing systems. BPT epoxy resins and their blends with BHDB epoxy are self-curable in the absence of aromatic diamines and have significantly lower heat release properties than conventional non-halogenated versions. The presence of the BPT moiety in cyanate ester resins dramatically reduced the gelation time of blends relative to the conventional BPA version and suppressed heat release properties and flammability. Most importantly, BPTCE, though halogen-free, clearly possesses ultralow heat release properties even lower than halogenated resins and as such opens another opportunity for replacing halogenated molecules in many settings.

EXPERIMENTAL SECTION

Materials. Ethynyltrimethylsilane (ETMS), pyridine, 4-iodophenol, 4-aminophenol, 3-iodophenol, 3-aminophenol, 2,2'-bipyridyl, sodium azide, sodium nitrite, *N*,*N*-diisopropylethylamine (DIPEA), copper bromide (CuBr), copper iodide (CuI), bis(triphenylphosphine)palladium(II) dichloride (PdCl₂(PPh₃)₂), deoxyanisoin, pyridine hydrochloride, epichlorohydrin, and cyanogen bromide were purchased from Sigma-Aldrich and used without further purification. Bisphenol A cyanate ester (BPACE) was obtained from Lonza and used as received. Toluene, dichloromethane, and triethylamine were distilled prior to use. Silica gel (60 Å, 40–63 μ m) was purchased from Sorbent Technologies.

Characterization. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DPX300 NMR spectrometer. Fourier transform infrared spectroscopy (FT-IR) was conducted on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with ATR accessory. High-resolution mass spectroscopy data (HRMS) of the final products were obtained on a JEOL JMS 700 mass spectrometer. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere on a DuPont TGA 2950 at a heating rate of 10 °C/min. Char yields were determined by TGA from the mass residue at 850 °C. Specific heat release rate (HRR, W/g), heat release capacity (HRC, J/(gK)), and total heat release (THR, kJ/g) were measured by pyrolysis combustion flow calorimetry (PCFC) on 3-5 mg samples of cured resins. PCFC was conducted from 100 to 900 °C at a heating rate of 1 °C/s in an 80 cm³/min stream of nitrogen. The anaerobic thermal degradation products in the nitrogen gas stream were mixed with a $20 \text{ cm}^3/\text{min}$ stream of oxygen prior to entering the combustion furnace (900 °C). The heat is determined by standard oxygen consumption methods. During the test, HRR is obtained by dividing dQ/dt, at each time interval, by the initial sample mass, and HRC is obtained by dividing the maximum value of HRR by the heating rate. Three to five sample runs were conducted for each sample.

Synthesis of BPT-Based Resins and BHDB-Based Epoxy Resin (DGEBHDB). 1,4-Bis(3-hydroxyphenyl)-1,2,3-triazole (3-BPT), 1,4-bis(4-hydroxyphenyl)-1,2,3-triazole (4-BPT), and diglycidyl ether of 4,4'-bishydroxydeoxybenzoin (DGE-BHDB) were prepared by following the literature procedures.^{32,41-43}

3-Azidophenol. An aqueous solution (15 mL) of NaNO₂ (3.79 g, 54.9 mmol) was added dropwise to 3-aminophenol (5.0 g, 45 mmol) in 2 N HCl (100 mL) at 0-5 °C. The solution was stirred for 30 min, followed by addition of an aqueous solution of sodium azide (4.5 g, 69 mmol, in 35 mL of water). The mixture was stirred at room temperature for 24 h and extracted with 300 mL of ethyl acetate. The combined organic layer was washed with water and dried over MgSO₄. Solvents were removed by rotary evaporation, and the residue was purified by column chromatography (EtOAc/hexanes, 1/4) to give the desired product as a dark red oil (4.52 g, 73% yield). ¹H NMR (acetone-*d*₆, 300 MHz, ppm): 8.69 (s, 1H, Ar–OH), 7.24 (t, 1H, *J* = 8.1 Hz, Ar–H), 6.70–6.53 (m, 3H, Ar–H). ¹³C NMR (CDCl₃, 75 MHz, ppm): 157.2, 141.6, 130.9, 112.4, 111.5, 106.5. FT-IR (cm⁻¹): 3348, 2109.

4-Azidophenol. 4-Azidophenol was prepared similarly to 3-azidophenol, using 4-aminophenol (5.0 g) instead of 3-aminophenol. This gave 5.27 g (85% yield) of a dark red oil. ¹H NMR (acetone- d_{6r} 300 MHz, ppm): 8.48 (s, 1H, Ar–OH), 6.94 (m, 4H, Ar–H). ¹³C NMR (MeOD- d_4 , 75 MHz, ppm): 156.4, 132.4, 121.1, 117.7. FT-IR (cm⁻¹): 3372, 2113, 2072.

3-(2-Trimethylsilylethynyl)phenol (3-TMSE-phenol). To 3-iodophenol (5.0 g, 23 mmol) in 50 mL of toluene were added $PdCl_2(PPh_3)_2$ (479 mg, 689 μ mol), CuI (432 mg, 2.27 mmol), DIPEA (4.8 mL, 27 mmol), and ETMS (3.90 mL, 27.3 mmol). The mixture was stirred at 30 °C for 24 h and then cooled to room temperature. After filtering, solvents were removed by rotary evaporation. The residue was purified by column chromatography (EtOAc/hexane, 1/9) to give 4.1 g

(95% yield) of a brown oil. ¹H NMR (acetone-*d*₆, 300 MHz, ppm): 8.57 (s, 1H, Ar–OH), 7.02 (m, 1H, Ar–H), 6.96–6.86 (m, 3H, Ar–H), 0.23 (s, 9H, TMS). ¹³C NMR (CDCl₃, 75 MHz, ppm): 155.5, 129.8, 124.8, 124.4, 118.8, 116.3, 105.0, 94.5, 0.1.

4-(2-Trimethylsilylethynyl)phenol (4-TMSE-phenol). 4-TMSE-phenol was prepared in a similar manner as 3-TMSE-phenol, using 4-iodophenol (5.0 g) instead of 3-iodophenol. This gave 3.5 g (82% yield) of a brown oil. ¹H NMR (acetone- d_{63} 300 MHz, ppm): 8.80 (s, 1H, Ar–OH), 7.34 (d, 2H, J = 8.4 Hz, Ar–H), 6.85 (d, 2H, J = 8.4 Hz, Ar–H), 0.21 (s, 9H, TMS). ¹³C NMR (CDCl₃, 75 MHz, ppm): 156.1, 133.9, 115.6, 115.5, 105.3, 92.7, 0.2.

1,4-Bis(3-hydroxyphenyl)-1,2,3-triazole (3-BPT). To 3-TMSEphenol (4.0 g, 21.02 mmol) in 35 mL of DMF were added 3-azidophenol (3.41 g, 25.2 mmol), CuBr (153 mg, 1.05 mmol), and 2,2'-bipyridyl (328 mg, 2.10 mmol). The mixture was heated at 80 °C for 24 h, cooled to room temperature, and then diluted with 250 mL of EtOAc. The combined organic mixture washed with water and dried over MgSO₄. Solvents were removed by rotary evaporation, and the residue was recrystallized in acetic acid/water to give 3.70 g (70% yield) of a brown crystalline solid. ¹H NMR (MeOD-*d*₄, 300 MHz, ppm): 8.80 (s, 1H, triazol-*H*), 7.43–7.26 (m, 6H, Ar-*H*), 6.95–6.91 (m, 1H, Ar-*H*), 6.84–6.83 (m, 1H, Ar-*H*). ¹³C NMR (MeOD-*d*₄, 75 MHz, ppm): 158.6, 157.7, 148.1, 137.9, 131.1, 130.4, 129.7, 118.8, 116.7, 115.6, 115.1, 112.1, 110.7, 107.1.

1,4-Bis(4-hyroxyphenyl)-1,2,3-triazole (4-BPT). 4-BPT was prepared in a similar manner as 3-BPT, using 4-TMSE-phenol (3.50 g, 18.4 mmol) and 4-azidophenol (3.73 g, 27.9 mmol) instead of 3-TMSE-phenol and 3-azidophenol. This gave 2.79 g (60% yield) of a purple crystal. ¹H NMR (MeOD- d_4 , 300 MHz, ppm): 8.62 (s, 1H, triazol-H), 7.75–7.68 (m, 4H, Ar-H), 6.99 (d, 2H, J = 9.0 Hz, Ar-H), 6.90 (d, 2H, J = 8.7 Hz, Ar-H). ¹³C NMR (MeOD- d_4 , 75 MHz, ppm): 159.7, 159.3, 149.8, 131.0, 128.4, 123.4, 123.0, 119.4, 117.3, 116.9.

4,4'-Bishydroxydeoxybenzoin (BHDB). Desoxyanisoin (5.00 g, 19.5 mmol) and pyridine hydrochloride (9.02 g, 78.0 mmol) were added to a round-bottom flask equipped with a condenser. The mixture was refluxed for 5 h at 200 °C, cooled to room temperature, and poured into water. The precipitate was filtered and recrystallized from acetic acid to give 3.8 g (85% yield) of a pale yellow crystalline solid. ¹H NMR (DMSO-*d*₄, 300 MHz, ppm): 10.35 (s, 1H, HO–Ar–CO), 9.28 (s, 1H, HO–Ar–CH₂), 7.91 (d, 2H, *J* = 8.7 Hz, Ar–*H*), 7.04 (d, 2H, *J* = 8.5 Hz, Ar–*H*), 6.84 (d, 2H, *J* = 8.7 Hz, Ar–*H*), 6.68 (d, 2H, *J* = 8.5 Hz, Ar–*H*), 4.11 (s, 2H, Ar–CO–CH₂–Ar). ¹³C NMR (DMSO-*d*₆, 75 MHz, ppm): 196.5, 162.3, 156.2, 131.3, 130.7, 128.1, 125.9, 115.5, 115.4, 43.7.

Diglycidyl Ether of 4,4'-Bishydroxydeoxybenzoin (DGE-BHDB). Epichlorohydrin (5.0 g, 54 mmol), BHDB (1.24 g, 5.43 mmol), 2-propanol (2.7 g, 4.5 mmol), and water (0.43 mL) were added to a round-bottom flask and stirred at 65 °C. A 20% aqueous sodium hydroxide solution (1.95 g) was added dropwise over 45 min, and stirring was continued for 30 min. The mixture was cooled to room temperature, and chloroform (50 mL) was added. The organic layer was washed extensively with water, and the combined organic extract was dried over magnesium sulfate. Solvents were removed by rotary evaporation, and the residue was dissolved in chloroform then precipitated into hexanes to give 1.48 g (80% yield) of the product as a pale yellow solid. ¹H NMR (CDCl₃, 300 MHz, ppm): 7.99 (d, 2H, J = 8.8 Hz, Ar-H), 7.18 (d, 2H, J = 8.4 Hz Ar-H), 6.91 (d, 2H, J = 8.8 Hz, Ar-H), $6.88 (d, 2H, J = 8.4 Hz, Ar - H), 4.32 - 4.17 (m, 2H, 2(-O - CH_2 - oxirane)),$ 4.17 (s, 2H, Ar-CO-CH2-Ar), 4.01-3.92 (m, 2H, 2(-O-CH2oxirane)), 3.39-3.32 (m, 2H, 2(oxirane CH)), 2.94-2.88 (m, 2H, 2(oxirane CH₂)), 2.78-2.74 (m, 2H, 2(oxirane CH₂)). ¹³C NMR (CDCl₃, 75 MHz, ppm): 196.5, 162.3, 157.4, 130.9, 130.5, 130.0, 127.5, 114.8, 114.4, 68.9, 68.8, 50.2, 49.9, 44.7, 44.6, 44.4. HRMS-EI m/z [M]⁺ calcd: 340.1311; found: 340.1293.

Diglycidyl Ether of 1,4-Bis(3-hydroxyphenyl)-1,2,3-triazole (3-DGE-BPT). 3-DGE-BPT was prepared in a similar manner as DGE-BHDB, using 3-BPT (1.00 g, 39.5 mmol) instead of BHDB. This gave 1.18 g (82% yield) of a yellow amorphous solid. ¹H NMR (CDCl₃, 300 MHz, ppm): 8.19 (s, 1H, triazol-*H*), 7.55–7.36 (m, 6H, Ar-*H*), 7.05–6.94 (m, 2H, Ar-*H*), 4.41–4.33 (m, 2H, 2($-O-CH_2-$ oxirane)), 4.05–4.01 (m, 2H, 2($-O-CH_2-$ oxirane)), 3.42–3.41 (m, 2H, 2(oxirane CH)), 2.96–2.95 (m, 2H, 2(oxirane CH₂)), 2.82–2.81 (m, 2H, 2(oxirane CH₂)). ¹³C NMR (CDCl₃, 75 MHz, ppm): 161.1, 160.6, 149.7, 139.6, 133.1, 132.3, 131.7, 120.3, 119.4, 116.8, 114.5, 113.2, 108.6, 70.8, 70.4, 51.7, 51.6, 46.3, 46.2. HRMS-FAB m/z [M + H]⁺ calcd: 366.1454; found: 366.1462.

Diglycidyl Ether of 1,4-Bis(4-hydroxyphenyl)-1,2,3-triazole (4-DGE-BPT). 4-DGE-BPT was prepared in a similar manner as DGE-BHDB, using 4-BPT (1.00 g, 39.5 mmol) instead of BHDB. This gave 890 mg (62% yield) of a pale purple solid. ¹H NMR (CDCl₃, 300 MHz, ppm): 8.06 (s, 1H, triazol-*H*), 7.86 (d, 2H, J = 8.7 Hz, Ar-*H*), 7.72 (d, 2H, J = 9.0 Hz, Ar-*H*), 7.11 (d, 2H, J = 9.0 Hz, Ar-*H*), 7.05 (d, 2H, J = 8.7 Hz, Ar-*H*), 4.38–4.29 (m, 2H, 2($-O-CH_2$ oxirane)), 4.06–3.99 (m, 2H, 2($-O-CH_2-$ oxirane)), 3.42–3.41 (m, 2H, 2(oxirane CH)), 2.99–2.95 (m, 2H, 2(oxirane CH₂)), 2.84–2.81 (m, 2H, 2(oxirane CH₂)). ¹³C NMR (CDCl₃, 75 MHz, ppm): 158.7, 158.6, 147.9, 130.9, 127.3, 123.5, 122.3, 117.4, 115.7, 115.2, 69.2, 68.9, 50.3, 50.2, 44.8, 44.7. HRMS-FAB m/z [M + H]⁺ calcd: 366.1454; found: 366.1426.

Dicyanate Ester of 1,4-Bis(3-hydroxyphenyl)-1,2,3-triazole (3-BPTCE). 1.89 mL of an acetonitrile solution of cyanogen bromide (1.00 g, 94.8 mmol) was added to 3-BPT (1.00 g, 39.5 mmol) in 60 mL of acetone at 0-5 °C. After stirring for 20 min, triethylamine (1.16 mL, 82.9 mmol) was added dropwise at 0-5 °C. The mixture was stirred for 1 h and diluted with 200 mL of dichloromethane. The combined organic mixture was washed with 10% aqueous Na₂CO₃ solution and water. Solvents in the organic extract were removed by rotary evaporation, and the precipitate was washed with methanol to give 1.08 g (90% yield) of the desired product as a pale brown solid. ¹H NMR (DMSO-*d*₆, 300 MHz, ppm): 9.36 (s, 1H, triazol-*H*), 8.05 (m, 4H, Ar-H), 7.88 (m, 1H, Ar-H), 7.71 (m, 1H, Ar-H), 7.63-7.59 (m, 1H, Ar-H) 7.46-7.42(m, 1H, Ar-H). ¹³C NMR (DMSO-d₆, 75 MHz, ppm): 153.5, 153.4, 146.3, 138.2, 133.1, 133.0, 132.2, 124.3, 121.5, 118.7, 116.1, 115.7, 112.2, 108.9, 108.6, 108.1. HRMS-FAB m/z $[M + H]^+$ calcd: 304.0834; found: 304.0822.

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ACKNOWLEDGMENT

The authors acknowledge the financial support of the Federal Aviation Administration (FAA-09-G-013) and the member companies and organizations of the Center for UMass-Industry Research on Polymers (CUMIRP) that support antiflammable polymer research, including Boeing, SABIC, Sekisui, Solvay Advanced Polymers, and the U.S. Army. Facilities support from the Materials Research Science and Engineering Center (MRSEC) (DMR-0820506) is also acknowledged.

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