

Development of an Oligomeric Cyanate Ester Resin With Enhanced Processability

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General Information

All starting materials were of reagent grade and used without further purification. Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min⁻¹ and a nitrogen purge of 50 cm³ min⁻¹. The glass transition temperature (T_g) was reported as the temperature centered at the midpoint between the linear baselines of a DSC scan. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min⁻¹ under a nitrogen or air purge of 50 cm³ min⁻¹. Infrared (IR) spectra were recorded as films on NaCl plates using a Nicolet Magna FTIR 750 spectrometer. ¹H-NMR was performed on a Bruker ADVANCE 300 spectrometer.

A TA Instruments AR-2000 Rheometer, in conjunction with an environmental testing chamber for temperature control and torsion fixtures, was used to monitor the response of samples (50 mm x 13 mm x 2 mm) to oscillatory testing. The measurements were made in nitrogen over the temperature range of ~ 40 to 250 °C. A temperature ramp of 3 °C min⁻¹ was used to determine the storage modulus and tan δ of the material at a frequency of 1 Hz and a strain of 2.5×10^{-2} %. Normal force control was utilized throughout the tests to keep the samples taut.

Synthesis of the Hydroxyl-Terminated Oligomeric Aromatic Ether (3)

To a 250 mL three neck flask fitted with a thermometer, a Dean-Stark trap with condenser, and a argon inlet were added bisphenol A6F (**1**) (15.0 g, 44.6 mmol), 1,3-dibromobenzene (**2**) (5.29 g, 22.4 mmol), 1,10-phenanthroline (0.350 g, 1.94 mmol), toluene (10 mL) and N,N-dimethylformamide (DMF) (80 mL). The resulting mixture was degassed thoroughly with argon for 10 min followed by the addition of copper (I) iodide (0.330 g, 1.74 mmol). After filling the Dean-Stark trap with toluene, the mixture was heated to reflux at 135-145 °C for 30-60 min in order to completely dissolve all the starting materials and remove any residual water contained in the solvent. At this time, the mixture was cooled to 100 °C and K₂CO₃ (5.00 g, 36.2 mmol) was added in one portion. The mixture was then refluxed at 135-145 °C for 2 to 4 hours. The water formed in the reaction was removed by azeotropic distillation. An additional portion of K₂CO₃ (5.00 g, 36.2 mmol) was added. The mixture was refluxed for 9-12 h until no more water was observed being collected in the Dean-Stark trap. Next, the toluene was removed by distillation and the reaction mixture was cooled to ambient temperature. Water was then added (300 mL) to the reaction mixture. At this point, the mixture was

slightly basic and 2 M HCl (300 mL) was added. The mixture was then extracted with ether (2 x 100 mL) and the combined ether layers were washed with 2 M HCl (1 x 100 mL) and water (1 x 100 mL) until neutral. Carbon black (2 g) was added and the ether extract was filtered through a short plug of silica gel to remove any insoluble components. The solvent was removed *in vacuo* and the amber solid was vacuum dried to yield the pure 2:1 hydroxyl terminated oligomer (**3**) (16.1 g, 97 %). IR [cm^{-1}]: ν 3418 (O-H), 3033 (C=CH), 1594 (aromatic), 1509 (aromatic), 1479 (aromatic), 1242 (-CF₃), 1220 (C-O), 1172, 1133 (C-O), 968 (C-OH), 831 (aromatic). ¹H-NMR (300 MHz, CDCl₃): δ 7.66-7.56 (m, aromatic-H), 7.56-7.46 (m, aromatic-H), 7.28-7.18 (m, aromatic-H), 7.13-7.02 (m, aromatic-H), 5.55 (bs, OH).

Synthesis of the Oligomeric Aromatic Ether Cyanate Ester (**4**)

The hydroxyl-terminated oligomer **3** (11.1 g, 14.9 mmol) was transferred to an oven-dried 250 mL three-neck flask fitted with a thermometer. Cyanogen bromide (3.77 g, 35.6 mmol) and dry acetone (100 mL) were added under argon. The resulting mixture was cooled to between -30 to -20°C and triethylamine (4.50 mL, 3.29 g, 32.5 mmol) dissolved in 1 mL acetone was added drop-wise so as to keep the temperature of the reaction mixture below -20 °C. After the addition, the reaction was stirred at around -20 °C for an additional 1 h resulting in the formation of a voluminous white precipitate of Et₃N⁺Br⁻. The solvent was removed *in vacuo* and the resulting residue was mixed with 100 mL of a hexane/methylene chloride mixture (1:1). The mixture was then filtered through a short silica plug to remove the Et₃N⁺Br⁻ salt and the solvent was removed *in vacuo* to yield the cyanate ester terminated oligomer **4** (11.2 g, 95 %) as a pale yellow oil. IR [cm^{-1}]: ν 3073 (C=CH), 2276 (CN), 2244 (CN), 1593 (aromatic), 1507 (aromatic), 1479 (aromatic), 1242 (-CF₃), 1212 (C-O), 1176 (C-O), 1017, 969 (C-OCN), 830 (aromatic). ¹H-NMR (300 MHz, CDCl₃): δ 7.55-7.42 (m, aromatic-H), 7.38-7.22 (m, aromatic-H), 7.02-6.93 (m, aromatic-H), 6.88-6.77 (m, aromatic-H).

Polymerization of Cyanate Ester Monomers with Chromium (III) Acetylacetonate /Nonylphenol Catalyst System

To the melt of cyanate ester oligomer **4** was added 4 phr of a chromium (III) acetylacetonate dissolved in nonylphenol (0.17 g of chromium (III) acetylacetonate dissolved in 4.80 g nonylphenol) with stirring. Once the catalyst had been evenly dispersed, the sample was cooled and used in the DSC (uncured) or TGA studies. For the TGA studies, the sample was cured by heating at 150 °C for 1h, 200 °C for 12h, 250 °C for 2h and 300 °C for 4h. The cured CE polymer formed as a film on the bottom of the TGA pan. TGA analyses of the polymer were then determined on the films from 25-1000 °C under nitrogen or air.

Rheometric Measurement Sample Preparation

Samples for rheometric measurements were prepared by degassing **4** under vacuum at 150 °C for 2 h in a mold with cavity dimensions of 50 mm x 13 mm x 4 mm. The

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temperature of the mold was reduced to 100 °C and 4 phr of chromium (III) acetylacetonate dissolved in nonylphenol was added with stirring. The resulting mixtures were degassed for an additional 30 min. The samples were placed in an oven under an argon atmosphere and heated at 150 °C for 1h, 200 °C for 12h, 250 °C for 2h and 300 °C for 4h. The cured sample **5** was removed from the mold and sanded to a thickness of approximately 2 mm.