# A Hyperbranched Aromatic Fluoropolyester for Photonic Applications

Seok Ho Kang,<sup>†</sup> Jingdong Luo,<sup>†</sup> Hong Ma,<sup>†</sup> Richard R. Barto,<sup>‡</sup> Curtis W. Frank,<sup>‡</sup> Larry R. Dalton,<sup>†</sup> and Alex K.-Y. Jen<sup>\*,†</sup>

Department of Materials Science and Engineering, Box 352120, University of Washington, Seattle, Washington 98195-2120, and Department of Chemical Engineering, Stanford University, Stanford, California 94305

Received December 2, 2002; Revised Manuscript Received April 16, 2003

ABSTRACT: A highly fluorinated hyperbranched aromatic polymer was prepared by a mild one-step polyesterification of an AB<sub>2</sub> type monomer at room temperature using dicyclohexylcarbodiimide and 4-(dimethylamino)pyridium 4-toluenesulfonate as the condensation agents. It was then postfunctionalized with thermally cross-linkable aromatic trifluorovinyl ethers to enhance its thermal and mechanical properties for optical waveguide applications. The cross-linked polymer exhibited low optical loss (0.58 dB/cm at 1310 nm) and high thermal stability with less than 5 wt % loss at 470 °C. The degree of branching, as determined by quantitative <sup>13</sup>C NMR spectroscopy, was found to be 0.50.

## Introduction

Over the past decade, hyperbranched polymers have received considerable attention as a class of very promising material due to their simplicity in synthesis and resemblance of many of the dendrimer's architectural features and properties.<sup>1</sup> By incorporating fluorine atoms into dendrimers and hyperbranched polymers, it imparts an increased thermal stability, hydrophobicity, chemical resistance, and decreased intermolecular attractive forces compared to their hydrocarbon analogues.<sup>2,3</sup> The absorption optical loss due to the vibration overtone of the polymer at the key telecommunication wavelength of 1.3  $\mu$ m can also be minimized by substituting hydrogen with fluorine.<sup>4</sup> In addition, these desirable properties can be further improved by modifying the peripheral functional groups on hyperbranched polymers. These versatilities make them an ideal candidate for applications in high-performance optical waveguides.

Usually, a hyperbranched polymer such as the aromatic polyesters can be prepared from the melt polymerization of an AB<sub>2</sub> type monomer containing activated hydroxyl groups or activated carboxylic acid groups at an elevated temperature between 160 and 250 °C with a proper catalyst.<sup>5</sup> These reaction conditions often lead to undesirable side products like the cyclic oligomers during the polycondensation process.<sup>6</sup> Despite these problems, there is no report in the literature attempting to improve the synthesis of the hyperbranched aromatic polyesters.

In this paper, we report the synthesis and characterization of a highly fluorinated hyperbranched aromatic polyester prepared via a mild  $AB_2$  polyesterification at room temperature using dicyclohexylcarbodiimide (DCC) as the activating agent and 4-(dimethylamino)pyridium 4-toluenesulfonate (DPTS) as the catalyst. The resulting polymer possessed a quite low hydrogen content and was further functionalized at the last stage with a crosslinkable aryl trifluorovinyl ether (TFVE) group at its peripheral functional groups.<sup>7</sup> This polymer can be thermally cross-linked to produce a perfluorocyclobutane-containing (PFCB) thermoset with high thermal stability and good mechanical properties for applications in low optical loss waveguides. Optical loss at 1310 nm was measured by photothermal deflection spectroscopy (PDS).

#### **Experimental Section**

**Materials.** The solvents were dried and distilled over sodium (THF) or over calcium hydride (dichloromethane and DMF). 4-(Dimethylamino)pyridium-4-toluenesulfonate (DPTS) was synthesized according to a literature procedure.<sup>8</sup> All other reagents purchased from Aldrich were used without further purification unless otherwise indicated.

**Characterizations.** <sup>1</sup>H NMR spectra were recorded on a Bruker AF 300 (300 MHz) or DMS 750 (750 MHz) spectrometer with the solvent proton signal as standard. <sup>13</sup>C NMR spectra were recorded at 188 MHz on the same instrument using the solvent carbon signal as a reference. <sup>19</sup>F NMR spectra were recorded at 282 MHz on a Bruker AF 300 spectrometer using external C<sub>6</sub>F<sub>6</sub> as standard. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters Styragel (HR 4E, 7.8 × 300 mm) column with polystyrene as the standard and THF as the solvent. Thermal properties of the polymers were analyzed with a TA Instruments thermal analysis and rheology system (TGA 2950, DSC 2010) under nitrogen at a heating rate of 10 °C/min.

**4-Hydroxy-2,3,5,6-tetrafluorobenzoic Acid (2).** To a solution of 2,3,5,6-tetrafluorophenol (5.71 g, 34.38 mmol) in THF (15 mL) was added dropwise *n*-butyllithium (29 mL of a hexane solution, 2.5 M) in THF (80 mL) at -65 °C over 15 min. After 45 min, carbon dioxide was bubbled into the reaction mixture. One hour later, the cooling bath was removed, and the reaction mixture was warmed to room temperature with continued carbonation for 2 h. The mixture was then hydrolyzed with 6 N HCl (60 mL) and phase separated, and the organic layer was dried and evaporated to dryness. The crude product was crystallized from xylene and then sublimed at 125 °C/0.05 Torr to yield 4-hydroxy-2,3,5,6-tetrafluorobenzoic acid monohydrate. Yield: 5.81 g (81%); mp 154–156 °C (lit.<sup>9</sup> 157 °C).

**2,2,2-Trichloroethyl 4-Hydroxy-2,3,5,6-tetrafluorobenzoate (3).** To a solution of 2,2,2-trichloroethanol (22 mL) was added **2** (5.19 g, 24.70 mmol) followed by concentrated sulfuric acid (0.8 mL), and the mixture was heated at 90 °C for 5 days under nitrogen. The reaction mixture was cooled and evaporated. The crude product was purified by flash chromatography

<sup>&</sup>lt;sup>†</sup> University of Washington.

<sup>&</sup>lt;sup>‡</sup> Stanford University.

<sup>\*</sup> To whom correspondence should be addressed.

eluting with 5:1 ethyl acetate/CH<sub>2</sub>CH<sub>2</sub>. Yield: 4.48 g (53%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  4.89 (s, 2H).

**2,2,2-Trichloroethyl 4-Benzyloxy-2,3,5,6-tetrafluorobenzoate (4).** Cesium carbonate (8.41 g, 25.81 mmol) was added to a rapidly stirred, cooled mixture of **3** (8.01 g, 23.46 mmol) and benzyl bromide (3.35 mL, 28.15 mmol) in dry DMF (50 mL). The mixture was allowed to warm to room temperature and stirred for 36 h. The reaction mixture was evaporated under vacuum, and the resulting residue was partitioned between water and ethyl acetate. The aqueous layer was extracted with ethyl acetate and then dried over magnesium sulfate. The crude product was purified by flash chromatography eluting with 3:1 hexane/CH<sub>2</sub>CH<sub>2</sub> to give **4** as a viscous oil. Yield: 8.64 g (85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 (m, 5H), 5.19 (s, 2H), 4.98 (s, 2H).

**4-Benzyloxy-2,3,5,6-tetrafluorobenzoic Acid (5).** To a solution of **4** (8.52 g, 19.74 mmol) in THF (25 mL) was added glacial acetic acid (25 mL), and the mixture was stirred at room temperature under nitrogen. Zinc dust (8.39 g, 128 mmol) was added, and the mixture was stirred vigorously at room temperature for 1 h. The reaction mixture was filtered, and the filtrate was poured into water (150 mL) and extracted with diethyl ether (200 mL). The combined extracts were washed with water and dried over magnesium sulfate. The crude product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then increasing polarity to ethyl acetate. Yield: 4.56 g (77%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.42 (m, 5H), 5.40 (s, 2H).

**2,2,2-Trichloroethyl 3,5-Dihydroxybenzoate (7).** To a solution of 2,2,2-trichloroethanol (30 mL) was added 3,5-dihydroxybenzoic acid (5.25 g, 34.1 mmol) followed by concentrated sulfuric acid (2 mL), and the mixture was stirred vigorously and heated at 90 °C for 48 h under nitrogen. The reaction mixture was cooled and evaporated to dryness. The crude product was purified by flash chromatography eluting with  $CH_2Cl_2$  and then increasing polarity to diethyl ether. Yield: 5.71 g (59%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (s, 2H), 7.07 (d, 2H), 6.69 (t, 1H), 5.03 (s, 2H).

2,2,2-Trichloroethyl 3,5-Bis(4-benzyloxy-2,3,5,6-tetrafluorobenzoate)benzoate (8). To a solution of 5 (4.34 g, 14.45 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (45 mL) was added 7 (1.92 g, 6.72 mmol) followed by DPTS (0.79 g, 2.69 mmol), and the mixture was stirred at room temperature under nitrogen for 15 min. DCC (3.05 g, 14.45 mmol) was then added, and the mixture was stirred for 12 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography eluting with 1:1 CH<sub>2</sub>CH<sub>2</sub>/hexane. Yield: 4.66 g (82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.94 (d, 1H), 7.43 (m, 12H), 5.42 (s, 4H), 5.01 (s, 2H). <sup>19</sup>F NMR (282 MHz, acetone- $d_6$ ):  $\delta$  –139.37, –156.01.

**2,2,2-Trichloroethyl-3,5-bis(4-benzyloxy-2,3,5,6-tetrafluorobenzoate)benzoic Acid (9).** This compound was prepared from the **8** (4.56 g, 5.37 mmol) and zinc dust (2.19 g, 33.53 mmol) in THF (20 mL) and glacial acetic acid (20 mL) following essentially the method used to prepare **5**. The crude product was purified by flash chromatography eluting with 5:1 CH<sub>2</sub>-CH<sub>2</sub>/hexane. Yield: 3.84 g (91%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (s, 1H), 8.33 (d, 2H), 7.57 (m, 4H), 7.37 (m, 10H), 7.04 (d, 4H), 5.29 (s, 4H), 4.80 (s, 2H), 1.01 (m, 9H). <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>):  $\delta$  – 139.46, –156.03.

**3,5-Bis(4-hydroxy-2,3,5,6-tetrafluorobenzoate)benzoic Acid (10).** A mixture of **9** (2.76 g, 3.84 mmol) and 10% Pd/C (0.50 g) in THF (50 mL) was degassed and stirred under H<sub>2</sub> at room temperature for 24 h. The catalyst was removed by filtration through Celite, the filtrate was evaporated, and the residue was washed with CH<sub>2</sub>Cl<sub>2</sub>. Yield: 1.91 g (93%). FTIR (KBr, cm<sup>-1</sup>): 3499, 3073, 2933, 2895, 2860, 1767, 1720, 1650, 1495, 1427, 1318, 1246, 1185, 1109, 1004, 922, 824, 736, 703. <sup>1</sup>H NMR (750 MHz, acetone- $d_6$ ):  $\delta$  7.77 (d, 2H), 7.61 (d, 1H). <sup>13</sup>C NMR (188 MHz, acetone- $d_6$ ):  $\delta$  165.59, 158.07, 150.36, 148.40, 145.00, 142.09, 139.94, 136.74, 133.55, 121.08, 98.51. <sup>19</sup>F NMR (282 MHz, acetone- $d_6$ ):  $\delta$  -140.19, -161.52.

**Polymerization of 10.** To a solution of **10** (0.15 g, 0.27 mmol) in dry dichloromethane (2 mL) and dry THF (4 mL)

was added DPTS (0. 03 g, 0.11 mmol), and the mixture was stirred at room temperature under nitrogen for 15 min. DCC (0.07 g, 0.33 mmol) was then added, and the mixture was stirred for 24 h. The reaction mixture was filtered, precipitated into methanol, and filtered to yield 0.126 g (84%) of hyperbranched polymer **11**. FTIR (KBr, cm<sup>-1</sup>): 3375, 3098, 2960, 1762, 1650, 1596, 1498, 1447, 1323, 1291, 1193, 1167, 1131, 1097, 1056, 985, 946, 746, 693. <sup>1</sup>H NMR (750 MHz, acetone- $d_6$ ):  $\delta$  8.30, 8.26, 8.23, 8.19, 7.99, 7.92, 7.85. <sup>13</sup>C NMR (188 MHz, acetone- $d_6$ ):  $\delta$  161.68, 159.02, 158.17, 152.58, 152.51, 152.34, 152.25, 148.85, 148.09, 147.46, 146.72, 143.08, 141.75, 140.28, 138.99, 133.73, 130.23, 124.05, 110.25, 100.93. <sup>19</sup>F NMR (282 MHz, acetone- $d_6$ ):  $\delta$  -137.10, -139.26, -151.28, -161.61.

Postfunctionalization of Polymer 11. To a solution of 10 (0.85 g, 1.53 mmol) in dry dichloromethane (5 mL) and dry THF (10 mL) was added DPTS (0. 18 g, 0.61 mmol), and the mixture was stirred at room temperature under nitrogen for 15 min. DCC (0.38 g, 1.84 mmol) was then added, and the mixture was stirred for 24 h. To a reaction mixture was added p-trifluorovinyloxyl benzoic acid (0.40 g, 1.84 mmol) and DPTS (0.18 g, 0.61 mmol), and DCC (0.38 g, 1.84 mmol) was then added after 15 min. After 24 h, the precipitated urea was filtered off, and the polymer was isolated by precipitation into methanol. Further purification was carried out by repetitive precipitations from CH<sub>2</sub>Cl<sub>2</sub> into methanol. Yield: 0.91 g. Polymer 12. FTIR (KBr, cm<sup>-1</sup>): 3109, 2926, 1834, 1766, 1651, 1604, 1496, 1447, 1418, 1322, 1276, 1252, 1163, 1094, 1026, 1007, 944, 906, 851, 782, 747, 666. <sup>1</sup>H NMR (750 MHz, acetone*d*<sub>6</sub>): δ 8.39, 8.30, 8.03, 7.53. <sup>13</sup>C NMR (188 MHz, acetone-*d*<sub>6</sub>):  $\delta$  161.36, 160.79, 160.02, 157.35, 151.77, 151.51, 151.45, 151.10, 147.39, 145.92, 142.37, 141.03, 133.91, 123.75, 122.66, 122.22, 116.87, 109.72, 100.00. 19F NMR (282 MHz, acetone $d_6$ ):  $\delta -119.04$ , -125.61, -136.09, -138.01, -139.37, -151.13.

Terminal Model Compound (T). This compound was prepared from the 9 (1.0 g, 1.39 mmol), pentafluorophenol (0.30 g, 1.60 mmol), DPTS (0.16 g, 0.56 mmol), and DCC (0.33 g, 1.60 mmol) in dry  $CH_2Cl_2$  (20 mL) following essentially the method used to prepare 8. The crude product was purified by flash chromatography eluting with 2:1 CH<sub>2</sub>CH<sub>2</sub>/hexane. The resulting solid (1.11 g, 1.26 mmol) and 10% Pd/C (0.25 g) in THF (15 mL) was degassed and stirred under  $H_2$  at room temperature for 24 h. The catalyst was removed by filtration through Celite, the filtrate was evaporated, and the crude product was purified by flash chromatography eluting with ethyl acetate. Yield: 0.59 g (67%). FTIR (KBr, cm<sup>-1</sup>): 3436, 3070, 2958, 2895, 2857, 1698, 1608, 1462, 1428, 1410, 1280, 1223, 1112, 1092, 908, 821, 700. <sup>1</sup>H NMR (750 MHz, acetone $d_6$ ):  $\delta$  8.30 (m, 6H), 7.99 (t, 1H), 7.89 (m, 2H), 7.73 (m, 4H). <sup>13</sup>C NMR (188 MHz, acetone- $d_6$ ):  $\delta$  161.19, 158.19, 151.51, 147.92, 146.49, 142.38, 141.91, 141.03, 139.34, 138.03, 129.46, 125.47, 122.73, 122.08, 100.33. <sup>19</sup>F NMR (282 MHz, acetone $d_6$ ):  $\delta$  -138.78, -151.54, -153.33, -158.26.

**Dendritic Model Compound (D).** This compound was prepared from the terminal model compound (**T**) (0.49 g, 0.69 mmol), benzoic acid (0.79 g, 0.83 mmol), DPTS (0.08 g, 0.28 mmol), and DCC (0.17 g, 0.83 mmol) in dry dichloromethane (2 mL) and dry THF (4 mL) following essentially the method used to prepare **8**. The crude product was purified by flash chromatography eluting with 2:1 CH<sub>2</sub>CH<sub>2</sub>/hexane. Yield: 0.53 g (84%). FTIR (KBr, cm<sup>-1</sup>): 2927, 2856, 1764, 1652, 1600, 1522, 1496, 1442, 1418, 1323, 1288, 1242, 1175, 1090, 1008, 935, 794, 703, 667, 617. <sup>1</sup>H NMR (750 MHz, acetone-*d*<sub>6</sub>):  $\delta$  8.16 (d, 2H), 7.84 (t, 1H). <sup>13</sup>C NMR (188 MHz, acetone-*d*<sub>6</sub>):  $\delta$  162.30, 162.28, 158.56, 152.64, 147.08, 145.70, 142.39, 141.05, 139.11, 136.82, 133.51, 132.09, 130.83, 128.03, 124.06, 123.60, 110.23. <sup>19</sup>F NMR (282 MHz, acetone-*d*<sub>6</sub>):  $\delta$  -139.57, -153.14, -158.28, -161.83.

**Preparation of Polymer Films.** Polymer **12** was dissolved in cyclopentanone at concentration of 30 wt %. A 1 wt % dye, DCM (4-dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran), was added to the formulation to aid in photothermal deflection spectroscopy (PDS) calibration. The solution was filtered through 0.2  $\mu$ m Teflon membrane filters. The filtered solution was spin-coated on 1 in. diameter × 0.020 in.



thick ultralow OH (<1 ppm) optical quality fused silica substrates for PDS spectral characterization. The substrates were precleaned using a Piranha process. To have good solvent resistance for multiplayer integration, it is necessary to crosslink the low loss optical polymers. The resulting polymer was cured at 200, 225, and 250 °C for 30 min each. The film cured at 200 °C was found to be slightly soluble in cyclopentanone, whereas the films that were cured at 225 and 250 °C exhibited excellent solvent resistance in common organic solvents, such as chloroform, THF, and cyclopentanone. This indicates that these films are highly cross-linked due to the reaction of the trifluorovinyl ether functional groups. However, the exact degree of cross-linking is unknown. These films also have very good adhesion to the glass and silicon substrates, and they remained colorless and transparent after curing. The thickness of the films cured at 225 °C varied from 2.1 to 2.3  $\mu$ m. Thicknesses were measured in two locations on each sample, using a Tencor Instruments Alpha-Step profilometer over small razor scratches. The films were also examined visually and at  $50-200 \times$  and judged to be of waveguide device quality, in terms of thickness and color uniformity, and complete lack of microstructure or defects.

Optical Loss Measurements.<sup>10</sup> The photothermal deflection spectroscopy (PDS) experimental test bed of this study used a 1 kW Hg (Xe) dc short arc lamp as the broadband illumination source at 12.6 Hz chopping frequency, with a  $^{1\!/_{\! 8}}$ m dual-grating monochromator. The source beam image is a vertical ellipse, which is focused through vertical entrance slits to the monochromator at a divergence nearly matching that of the monochromator (f3.7). To increase the length of interaction between the sample illuminated region and the probe beam, and thereby improve signal-to-noise, a Dove prism was used in the beam path to rotate the beam image by 90°, rendering it horizontal when focused onto the sample. A portion of the pump beam was split off and focused onto a pyroelectric detector to monitor optical power input at each wavelength via a lock-in amplifier. The probe beam was a 10 mW CW HeNe laser, attenuated to  $\sim$ 1.5 mW. The sample disk was mounted inside a special holding fixture comprised of a back plate which slightly bends the vertical centerline of the sample into the probe beam. The sample was held inside a fused silica cuvette and filled with 3M Fluorinert Liquid FC-72 as the index fluid. The cuvette was closed with an O-ring sealed lid to prevent fluid evaporation. The cuvette was placed in a custom holder on a rotational translation stage attached to a triple axis translation stage, allowing for precise alignment of the sample surface to the probe beam for maximized signal. Probe beam deflection was detected using a pn photodiode with

an op-amp drive circuit providing gain and zero offset control. A blackend razor was used in front of the detector to shadow half of the probe beam. The probe beam was 50-50 split to a replicate reference detector prior to the sample. The primary and reference detector dc signals were conditioned with a preamplifier, with the difference signal forwarded to a second lock-in amplifier. This scheme provided cancellation of probe beam pointing noise.

#### **Results and Discussion**

An  $AB_2$  type hydroxy/acid monomer was used as the starting material for polycondensation. As shown in Scheme 1, the monomer **10** was prepared by a coupling reaction between **5** and **7** (which were prepared via a series of protecting/deprotecting steps) under the DCC/DPTS esterification conditions. The benzyl ether was selected as the phenolic protecting group since it can be deprotected by catalytic hydrogenolysis under very mild conditions. Trichloroethyl ester was used as the protecting group for carboxylic acid since it can be removed in high yields by reacting with zinc in THF–AcOH.

To avoid any side reactions during the polymerization, we have employed the very mild, one-step esterification process developed by Stupp and Moore.<sup>8</sup> The hydroxy acid monomer **10** was first dissolved in THF/CH<sub>2</sub>Cl<sub>2</sub> (2: 1) together with DPTS (0.4 equiv) as the catalyst. After the addition of DCC (1.0 equiv), the solution was then stirred at room temperature for 24 h. The resulting polymer was isolated by precipitation into methanol. Further purification was carried out by repetitive precipitations from its CH<sub>2</sub>Cl<sub>2</sub> solution into methanol. The polycondensation was successful in producing a fluorinated hyperbranched polymer without any undesired byproducts. The molecular weight of the phenol terminated hyperbranched polyesters could not be determined by gel permeation chromatography (GPC) since the polymer will absorb onto the column. Thus, the ends of the peripheral branches of polymer **11** were terminated with 4-trifluorovinyloxylbenzoic acid using the same DCC/DPTS esterification condition at room temperature for 24 h to afford 12. From the FTIR spectra, the polymer exhibited no residual -OH groups after the esterification reaction. The functionalized AB<sub>2</sub>



Figure 1. Structure of the repeating units in the hyperbranched polymer 11 and the model compounds.

hyperbranched polymer **12** was highly soluble in common organic solvents, such as  $CH_2Cl_2$  and THF. The structure of the polymer was confirmed by FTIR, <sup>1</sup>H NMR, <sup>19</sup>F NMR, and <sup>13</sup>C NMR spectroscopy.

Molecular weight measurements of the hyperbranched polymer **12** using gel permeation chromatography (GPC) showed that the weight-average molecular weight ( $M_w$ ) value was 17 800 relative to polystyrene standard and with a polydispersity of 1.55. This indicates that the polymerization of the AB<sub>2</sub> hydroxy acid monomer proceeded efficiently.

For a complete understanding of the hyperbranched polymer structure, the degree of branching can be evaluated by means of NMR spectroscopy.<sup>11</sup> The degree of branching (DB) of a hyperbranched polymer is given by

$$DB = \frac{2D}{2D+L}$$

where D and L are the number of dendritic and linear units, respectively. A hyperbranched polymer takes DB values between 0 and 1, where DB = 0 and 1 imply a linear polymer structure and an ideal dendrimer structure, respectively. When considering the overall structure of the hyperbranched polymer 11, it reveals three different types of repeating units. These include the dendritic **D** structure, which contains no hydroxy group, the linear L structure, which has one hydroxy group, and the terminal T structure, which has two hydroxy groups (Figure 1). The relative percentages of **D**, **L**, and T can be evaluated using NMR spectroscopy due to peak separation from the different chemical environments in trisubstituted aromatic ester of **D**, **L**, and **T**. To assign these three subunits of the polymer, two model compounds **D** and **T** were synthesized. As compared with the quantitative <sup>13</sup>C NMR spectra of model compounds, the carbon atoms of the aromatic ring of polymer 11 split into four different peaks, which could be assigned as the linear units at 152.51 and 152.32 ppm, the dendritic unit at 152.58 ppm, and the terminal units at 152.25



**Figure 2.**  $^{13}$ C NMR (188 MHz, acetone- $d_6$ ) spectrum of the hyperbranched polymer **11**.

ppm (Figure 2). The result from these experiments shows a degree of branching of 0.50, which is in agreement with the theoretical maximum DB for a statistical growth of an  $AB_2$  polymer.<sup>11</sup>

The thermal behavior of **12** was evaluated by differential scanning calorimetry (DSC). The glass transition temperature ( $T_g$ ) of **12** was observed at 121 °C, and the exothermic cyclopolymerization of the aromatic TFVE was detected at temperatures between 200 and 260 °C (Figure 3). Thermogravimetric analysis (TGA) of **12** by heating under nitrogen at 10 °C/min showed a high thermal stability with more than 95% of its mass retained up to 470 °C.

Optical losses at 1310 nm were measured by photothermal deflection spectroscopy (PDS)<sup>10</sup> and are shown in Figure 4. The optical loss of **12** with a 4-(dicyanomethylene)-2-methyl-6-(4-(dimethylamino)styryl)-4*H*pyran (DCM) dye (1 wt %) cured at 225 °C is around 0.58 dB/cm at 1310 nm. We believe that the intrinsic optical loss of the polymer should be much lower than this value because the sample contains DCM dopant for



**Figure 3.** DSC curve of the hyperbranched polymer **12** at a heating rate of  $10 \, ^{\circ}$ C min<sup>-1</sup> in nitrogen.



**Figure 4.** Optical loss spectrum of the hyperbranched polymer **12**.

proper PDS calibration. The high C–H content of the dye may cause high absorption losses in the near-infrared (NIR) due to the vibration overtone absorption of C–H bond.

In summary, a hyperbranched polyfluorinated aromatic polyester has been prepared by a mild one-step polyesterification at room temperature using DCC/ DPTS as the condensation agents. It was then postfunctionalized with thermally cross-linkable aromatic trifluorovinyl ethers (TFVE) for optical waveguide applications. Quantitative analysis from <sup>13</sup>C NMR spectroscopy showed this polymer possessed a degree of branching of 0.50. After being thermally cross-linked, it also showed a high thermal stability up to 470 °C. The optical loss of the hyperbranched polymer is 0.58 dB/cm at 1310 nm. These unique features will make attractive approach for low-loss waveguide devices. **Acknowledgment.** Financial support from the National Science Foundation (NSF-NIRT and the NSF-STC Program under Agreement DMR-0120967) and the Air Force Office of Scientific Research (AFOSR) under the MURI Center on Polymeric Smart Skins is acknowledged. Alex K.-Y. Jen thanks the Boeing-Johnson Foundation for its support.

### **References and Notes**

- Inoue, K. Prog. Polym. Sci. 2000, 25, 453. (b) Jikei, M.; Kakimoto, M. Prog. Polym. Sci. 2001, 26, 1233. (c) Kim, Y. H.; Webster, O. J. Macromol. Sci., Polym. Rev. 2002, C42, 55.
- Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. Polym. Prepr. 1991, 32, 599. (b) Miller, T. M.; Neenan, T. X.; Zayas, R.; Bair, H. E. J. Am. Chem. Soc. 1992, 114, 1018. (c) Chapman, T. M.; Mahan, E. J. Polym. Mater. Sci. Eng. 1995, 73, 275. (d) Grieveldinger, G.; Seebach, D. Polym. Mater. Sci. Eng. 1997, 77, 134. (e) Lorenz, K.; Frey, H.; Stuhn, B.; Mulhaupt, R. Macromolecules 1997, 30, 6860. (f) Cooper, A. I.; Londono, J. D.; Wignall, G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubinstein, M.; Burke, A. L. C.; Fréchet, J. M. J.; DeSimone, J. M. Nature (London) 1997, 389, 368. (g) Yu, D.; Fréchet, J. M. J. Polym. Prepr. 1998, 39, 633. (h) Stark, B.; Steuhn, B.; Frey, H.; Lorenz, K.; Frick, B. Macromolecules 1998, 31, 5415. (i) Klug, C.; Kowalewski, T.; Schaefer, J.; Straw, T.; Tasaki, K.; Wooley, K. Polym. Mater. Sci. Eng. 1998, 77, 99. (j) Omotowa, B. A.; Keefer, K. D.; Kirchmeier, R. L.; Shreeve, J. M. J. Am. Chem. Soc. 1999, 121, 11130.
- (3) Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. J. Am. Chem. Soc. **1993**, 115, 356. (b) Mueller, A.; Kowalewski, T.; Wooley, K. L. Macromolecules **1998**, 31, 776. (c) Pitois, C.; Wiesmann, D.; M. Lindgren, M.; Hult, A. Adv. Mater. **2001**, 13, 1483. (d) Ma, H.; Jen, A. K.-Y.; Dalton, L. R. Adv. Mater. **2002**, 14, 1339.
- (4) Matsuura, T.; Ishizawa, M.; Hasuda, Y.; Nishi, S. *Macromol-ecules* 1992, 25, 3540.
- (5) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. J. Am. Chem. Soc. 1991, 113, 4583. (b) Kambouris, P.; Hawker, C. J. J. Chem. Soc., Perkin Trans. 1 1993, 2717. (c) Turner, S. R.; Voit, B.; Mourey, T. H. Macromolecules 1993, 26, 4617. (d) Wooley, K. L.; Hawker, C. J.; Lee, R.; Fréchet, J. M. J. Polym. J. 1994, 26, 187. (e) Turner, S. R.; Walter, F.; Voit, B.; Mourey, T. H. Macromolecules 1994, 27, 1611. (f) Fomine, S.; Rivera, E.; Fomina, L.; Ortiz, A.; Ogawa, T. Polymer 1998, 39, 3551. (g) Parker, D.; Feast, W. J. Macromolecules 2001, 34, 2048.
  (6) Feast, W. J.; Keeney, A. J.; Kenwright, A. M.; Parker, D.
- (6) Feast, W. J.; Keeney, A. J.; Kenwright, A. M.; Parker, D. *Chem. Commun.* **1997**, 1749. (b) Chu, F.; Hawker, C. J.; Pomery, P. J.; Hill, D. J. T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, 1627. (c) Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 10180.
- (7) Smith, D. W.; Babb, D. A. *Macromolecules* **1996**, *29*, 852. (b)
   Smith, D. W.; Babb, D. A.; Shah, H. V.; Hoeglund, A.; Traiphol, R.; Perahia, D.; Boone, H. W.; Langhoff, C.; Radler, M. *J. Fluorine Chem.* **2000**, *104*, 109.
- (8) Moore, J. S.; Stupp, S. I. Macromolecules 1990, 23, 65.
- (9) Tamborski, C.; Soloski, E. D. J. Org. Chem. 1966, 31, 746.
   (10) Pitois, C.; Hult, A.; Wiesmann, D. J. J. Opt. Soc. Am. B 2001,
- (10) Pitois, C.; Hult, A.; Wiesmann, D. J. J. Opt. Soc. Am. B 2001, 18, 908.
- (11) Holter, D.; Burgath, A.; Frey, H. Acta Polym. 1997, 48, 30.
   MA0217229