

## A Novel Class of High-Performance Perfluorocyclobutane-Containing Polymers for Second-Order Nonlinear Optics

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Recent developments in the field of organic second-order nonlinear optical (NLO) polymers have shown great promise in the application of these materials for photonic devices such as high-speed electrooptic (E–O) modulators and switches, due to their large E–O coefficients, ultrafast response times, and ease of processing into thin films.<sup>1,2</sup> It is well-known that an attractive class of second-order NLO materials are poled polymers in which noncentrosymmetric alignment of NLO chromophores is induced by an external electric field.

In the past decade, a large number of high  $\beta\mu$  chromophores have been synthesized and some of these exhibit very large macroscopic nonlinearities in guest/host poled polymers.<sup>3</sup> However, to realize a stable dipole alignment, it is a critical prerequisite to utilize high glass-transition temperature ( $T_g$ ) polymers with NLO chromophores as a side-chain, or cross-linkable polymers with NLO chromophores that were locked in the polymer network. Typically, most of these materials are synthesized either by conventional radical polymerization of chromophore-containing monomers or by step-growth condensation reactions that yield polymers, such as polyacrylates,<sup>4</sup> polyurethanes,<sup>5</sup> polyimides,<sup>6</sup> or polyquinolines.<sup>7</sup> Unfortunately, both of these strategies have major drawbacks that limit their use. In radical polymerization, the high charge-transfer chromophores often act as retarders or inhibitors to the reaction and thereby decrease the yield and molecular weight of the polymers. Besides, many of the NLO chromophores cannot survive the conditions of radical polymerization.<sup>8</sup> In the step-

growth reactions, the monomers usually need to tolerate the harsh acidic/basic conditions at high temperatures.<sup>9</sup>

Recently, perfluorocyclobutane (PFCB)-containing polymers have been studied as a unique class of fluoropolymer with a combination of excellent properties, such as low dielectric constant, good thermal stability, high glass-transition temperature, and optical transparency.<sup>10</sup> PFCB polymers are prepared by the radical-mediated thermal cyclopolymerization of trifluorovinyl ethers. The versatility of this methodology was demonstrated by developing microelectronic laminates, low dielectric coatings, and optical waveguides.<sup>11</sup> In this paper, we report a novel synthetic approach for incorporating second-order NLO chromophores into PFCB polymer for E–O applications, utilizing the well-defined nature and the unique combination of properties offered by PFCB polymers. A broad variety of NLO chromophores,<sup>12</sup> including those containing sensitive functional groups such as the tricyanovinyl acceptor, could be easily incorporated into PFCB polymers without decomposing chromophores or inhibiting polymerization (Scheme 1).

NLO chromophore-containing monomers **3a–e** were prepared in high yields (>95%) by the condensation reaction between di(trifluorovinyl ether)silyl chloride<sup>13</sup> and hydroxy-containing chromophores at ambient temperature under mild conditions<sup>14</sup> as described in Scheme 1. All of the monomers were purified by column chromatography and fully characterized using <sup>1</sup>H NMR and elemental analysis. Exothermic cyclodimerization of trifluorovinyl ether groups in these NLO chromophores are typically detected just above 140 °C by DSC (10 °C/min) with reaction profiles similar to that of general di(trifluorovinyl ether) compounds. For example, the reaction of **3c** showed a peak polymerization temperature at 243 °C and gave an enthalpy of –16 kcal/mol per perfluoroalkene linkage. Consequently, polymeri-

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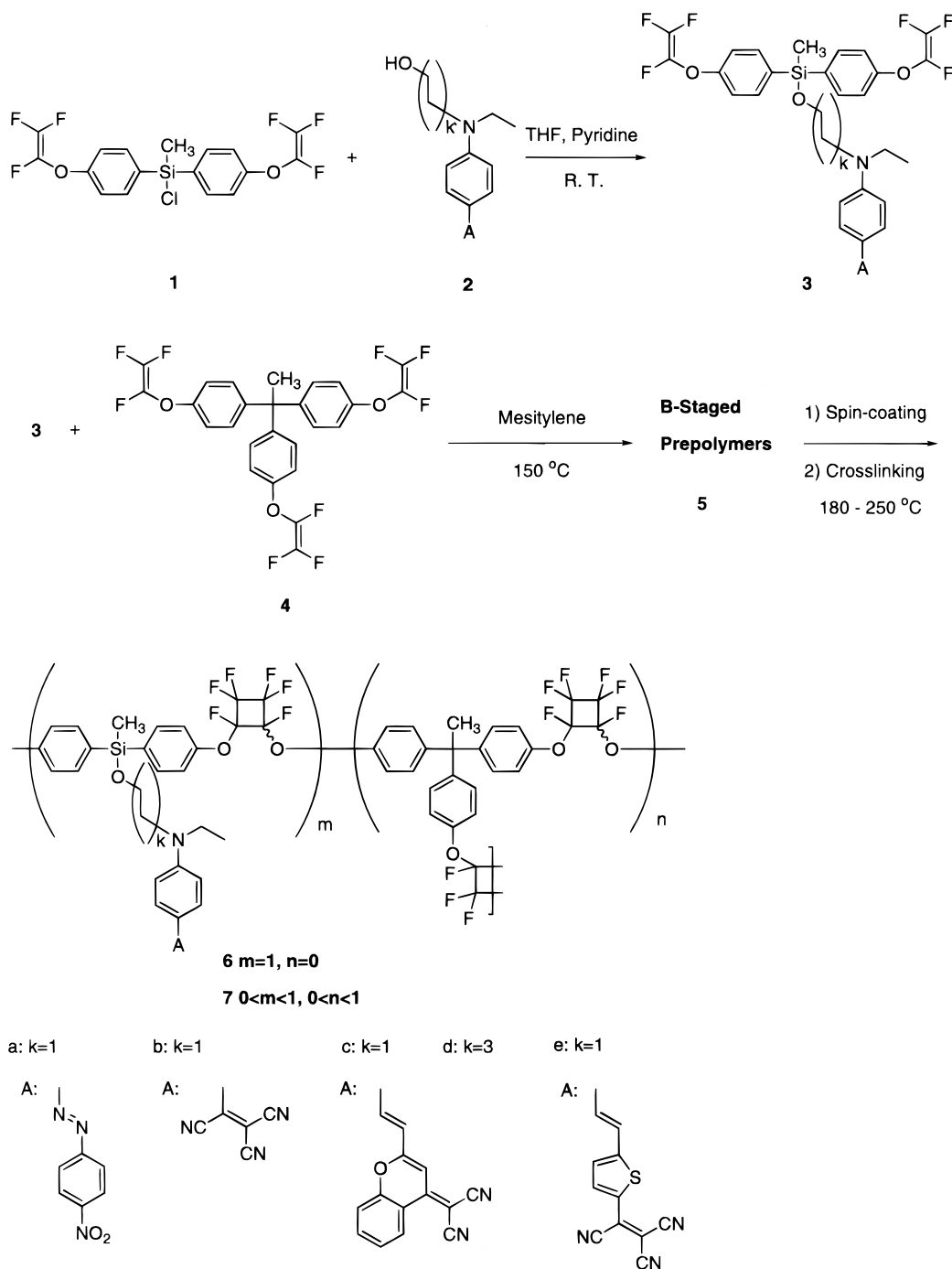
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## Scheme 1. Synthesis of Second-Order NLO PFCB Polymers



zation was accomplished by simply heating the neat monomers or the solution of monomers under an inert

(14) Typical synthetic procedure for monomer **3**: To a well-stirred solution of di(trifluorovinyl ether)silyl chloride **1** (2.0 mmol) and hydroxy-containing NLO chromophore **2** (2.0 mmol) in dry THF (20 mL) at room temperature was added dry pyridine (2.0 mmol) dropwise under a nitrogen atmosphere. The mixture was stirred at room temperature for 0.5–1.0 h, evaporated, and run through a neutral aluminum oxide column with methylene chloride as the eluent to afford the NLO chromophore-containing di(trifluorovinyl ether) monomer **3** (yield >95%). For **3e**: mp 40 °C by DSC. UV-vis:  $\lambda_{\text{max}} = 631$  nm in dioxane.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.92 (d,  $J = 4.2$  Hz, 1H), 7.47 (d,  $J = 8.4$  Hz, 4H), 7.35 (d,  $J = 9.0$  Hz, 2H), 7.14 (d,  $J = 4.8$  Hz, 1H), 7.09 (d,  $J = 7.5$  Hz, 4H), 7.03 (s, 1H), 6.97 (s, 1H), 6.56 (d,  $J = 8.7$  Hz, 2H), 3.84 (t,  $J = 6.0$  Hz, 2H), 3.52 (t,  $J = 6.3$  Hz, 2H), 3.39 (q,  $J = 7.2$  Hz, 2H), 1.15 (t,  $J = 7.2$  Hz, 3H), 0.60 (s, 3H) ppm. Elemental Anal. Calcd for  $\text{C}_{38}\text{H}_{28}\text{F}_6\text{N}_4\text{SiO}_3$ : C, 59.83; H, 3.70; N, 7.35. Found: C, 59.97; H, 3.65; N, 7.50.

atmosphere at 150–250 °C. The NLO chromophores remained intact since the polymerization process is a radical-mediated stepwise addition that is followed by a rapid ring cyclization. This is very different from the conventional radical and condensation polymerization.

The linear NLO polymers **6a–e** obtained by bulk polymerization of **3** at 180–250 °C had molecular weights ranging from 30 000 to 60 000 but relatively low  $T_g$ s in the range of 90–140 °C due to high chromophore concentrations (38–51 wt %). To adjust the chromophore loading density to a suitable level for poling studies, monomers **3** and **4** were copolymerized at 150 °C in mesitylene at a solution concentration of 35–45 wt % to yield reactive oligomer/monomer mixtures with

**Table 1. Properties of Thermoset NLO PFCB Polymers**

poly- mers	chromophore density (w/w %)	$T_g$ (°C) <sup>a</sup>	weight loss at 350 °C <sup>b</sup> (%)	$\lambda_{max}$ (nm) <sup>c</sup>	$n^d$		loss (dB/cm) <sup>d</sup>
					TE	TM	
<b>7b</b>	30	185	0.9	506	1.5855	1.5840	6.0
<b>7c</b>	25	230	0.2	502	1.5670	1.5634	2.7
<b>7d</b>	20	195	0.8	511	1.5454	1.5413	2.4
<b>7e</b>	25	192	2.4	636	1.5752	1.5711	2.9

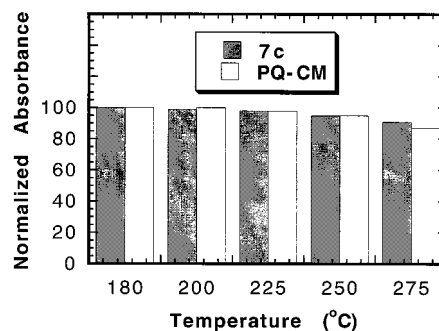
<sup>a</sup> DSC (10 °C/min) in nitrogen. <sup>b</sup> TGA (10 °C/min) in nitrogen. <sup>c</sup> In film. <sup>d</sup> At 830 nm for polymer **7b–d** and at 1300 nm for polymer **7e**.

controlled molecular weights<sup>15</sup> (Scheme 1). The B-staged prepolymers **5** possess very good solubility in the mixture of mesitylene and cyclopentanone (30–40%, w/w). Optical quality thin films can be easily prepared from these solutions. The prepolymers have low  $T_g$ s or melting points ( $T_m$ s) that allow them to be melted, reflowed, and efficiently cross-linked in thin films at 180–250 °C. All of the resulting NLO PFCB thermosets have high  $T_g$  (>180 °C) and excellent thermal stability (Table 1). Weight losses of <3% up to 350 °C were observed by thermogravimetric analysis (TGA) for all of the NLO polymers. Most importantly, these NLO PFCB thermosets possessed excellent solvent resistance, which is highly desirable for multilayer process in the fabrication of E–O devices.

To measure the stability of NLO chromophore during the cross-linking reaction, thin film samples of the NLO prepolymers were isothermally heated on a hot stage at temperatures between 180 and 275 °C under N<sub>2</sub> at 25 °C intervals for 20 min. The  $\pi$ – $\pi^*$  charge-transfer absorption band of the chromophores was used to monitor the extent of decomposition. NLO prepolymer **7c** possessed a high stability similar to that of the side-chain polyquinoline with the same NLO chromophore (Figure 1), indicating that the chromophore can tolerate the radical intermediate during the polymerization. It is noteworthy that the highly efficient tricyanovinylstyrylthiophene-based chromophore can also be incorporated into the thermoset NLO PFCB polymer **7e**.

The NLO polymers have refractive indices ranging from 1.541 to 1.586 with low birefringence (0.002–0.004) and optical loss (2–3 dB/cm) for polymer **7c,d** at 0.83  $\mu$ m and polymer **7e** at 1.3  $\mu$ m (Table 1). They were measured by the prism coupling and streak method in a Metricon system using 2–3  $\mu$ m thin films on glass

(15) Typical synthetic procedure for B-staged prepolymers **5**: A proper ratios of NLO chromophore-containing monomer **3** and 1,1,1-tris(4-trifluorovinylphenoxy)ethane monomer **4** to give a loading density of NLO chromophore in the range of 20–30 wt % were dissolved in distilled mesitylene with a solution concentration of 35–45 wt %. The mixture was stirred and heated at 150 °C under nitrogen. Samples were analyzed by GPC at given time intervals and examined for their film-forming ability. For spin-coating, the viscous solution was diluted with cyclopentanone to 30–40 wt %. For <sup>1</sup>H NMR and DSC measurements, the viscous solution was precipitated into methanol, filtered, and dried at 60 °C under vacuum for 24 h to give the B-staged prepolymers **5**. For **5e**: UV–vis:  $\lambda_{max}$  = 631 nm in dioxane. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (br, 0.45H), 7.28–7.56 (br, 2.92H), 6.88–7.24 (br, 9.53H), 6.80 (br, 0.45H), 6.52–6.62 (br, 0.45H), 3.84 (br, 0.90H), 3.52 (br, 0.90H), 3.24–3.44 (m, 0.90H), 2.12 (br, 1.65H), 1.04–1.20 (m, 1.35H), 0.60 (br, 1.35H).



**Figure 1.** Thermal stability of the B-staged NLO PFCB prepolymer **5c** and the side-chain NLO polyquinoline **PQ-CM** with isothermal heating at temperatures between 180 and 275 °C under N<sub>2</sub> at 25 °C intervals for 20 min. Normalized absorbance were plotted as a function of baking temperature.

substrates. The low optical anisotropy may be attributed to the isotropic structures of these polymers originating from the equal amount of cis and trans linkages in the 1,2-perfluorocyclobutyl ether moieties. For E–O measurements, the B-staged prepolymer solutions in mesitylene/cyclopentanone (30–40%, w/w solution, filtered through a 0.2  $\mu$ m syringe filter) were spin-coated onto an indium tin oxide (ITO) glass substrate. The films were heated in a vacuum oven at 180 °C for 0.5 h to ensure removal of the residual solvent. Thin gold electrodes (~20 nm) were sputtered on top of the resulting 1–2  $\mu$ m polymer thin films. The reactive prepolymers were advanced by heating at 190–250 °C under nitrogen. The dipole alignments in the NLO polymers were achieved by contact poling. Preliminary poling results showed that these thermoset NLO PFCB polymers possessed large  $r_{33}$ s and good temporal stability. Polymer **7e**, for example, exhibited an  $r_{33}$  value of 21 pm/V at 1.3  $\mu$ m under a poling field of 1.0 MV/cm. The  $r_{33}$  value of polymer **7e** retained ~80% of its original value at 85 °C for more than 1000 h. Further optimizations of temporal stability and E–O activity of these materials are currently under investigation.

In conclusion, we have demonstrated a new and efficient approach for synthesizing novel second-order NLO polymers by utilizing radical-mediated, stepwise cycloaddition polymerization reaction. The resulting NLO PFCB polymers exhibited excellent processability, small optical anisotropy, low optical loss, and very good thermal, nonlinear optical and mechanical properties. The extension of this method to other functional PFCB polymers for light-emitting diodes is currently in progress.

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