Liquid Crystalline Perfluorocyclobutyl Aryl Ether Polymers Containing Oligophenylene Mesogens

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Introduction. Poly(*p*-phenylene)s (PPP) are highly extended linear macromolecules due to their rigid structure, and as a result, unmodified PPP is an insoluble and intractable material.[1] Structural modifications of PPPs have been explored vigorously, and successful examples exist.[2,3] Topologically, two strategies have been created to improve its solubility while retaining notable optoelectronic and mechanical properties either by docking a solubilizing side chain or by enchainment of a solubilizing segment into the PPP backbone.[3−6] For the latter approach in particular, the synthesis can be generalized as the condensation polymerization between oligophenylene component and soluble (e.g., aliphatic) segment. The polycondensation takes place usually via nucleophilic substitution or aryl−aryl cross-coupling reactions. For example, Kallitsis et al. described the synthesis of soluble aromatic−aliphatic polyethers bearing oligophenylene segments in the main chain.[4,5] These processable blue-light-emitting polymers with high fluorescence quantum yield can be used as the active layers in polymer light-emitting devices (PLED). Goodson et al. reported a rod−coil block copolymer composed of rigid oligophenylene units and oligo(ethylene glycol) segments as flexible blocks via Suzuki coupling.[6]

In this Communication, we describe a new strategy to access processable oligophenylene segmented polymers through thermal cyclodimerization of aromatic trifluorovinyl ether monomers to perfluorocyclobutyl (PFCB) polymers (Scheme 1). Previous work in our lab on the preparation of PFCB polymers containing the rigid α-methylstilbene mesogen resulted in the first PFCB liquid crystalline polymers.[7] A wide variety of PFCB materials have been developed due to facile functional group transformation starting from versatile and commercially available bromo intermediate, *p*-Br−C_6H_4−OCF=CF_2.[8] The synthesis and polymerization of a series of bis(trifluorovinyl ether)-substituted oligophenylene monomers offers a new strategy toward semifluorinated high-temperature thermotropic liquid crystalline polymers.

Results and Discussion. a. Monomer Synthesis. Recent interests in oligophenylene-containing polymers with improved processability and notable optoelectronic and mechanical properties led us to a new approach toward soluble PPP materials. Our strategy has been to incorporate the oligophenylene unit

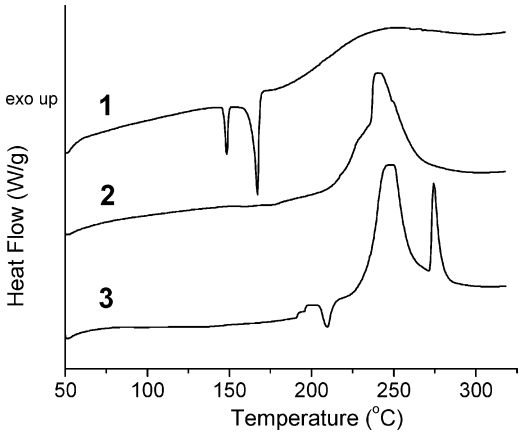
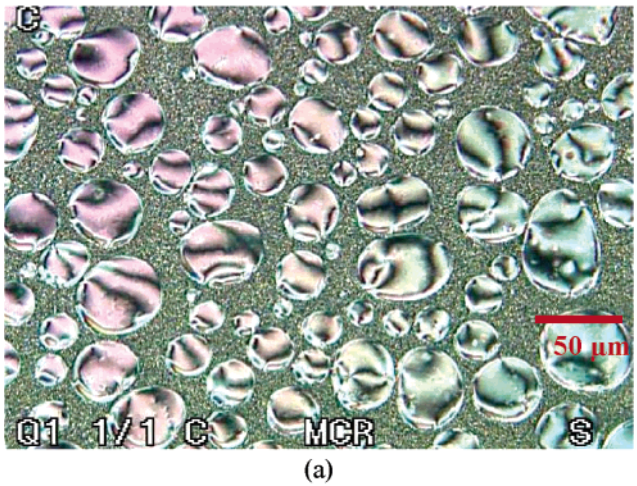
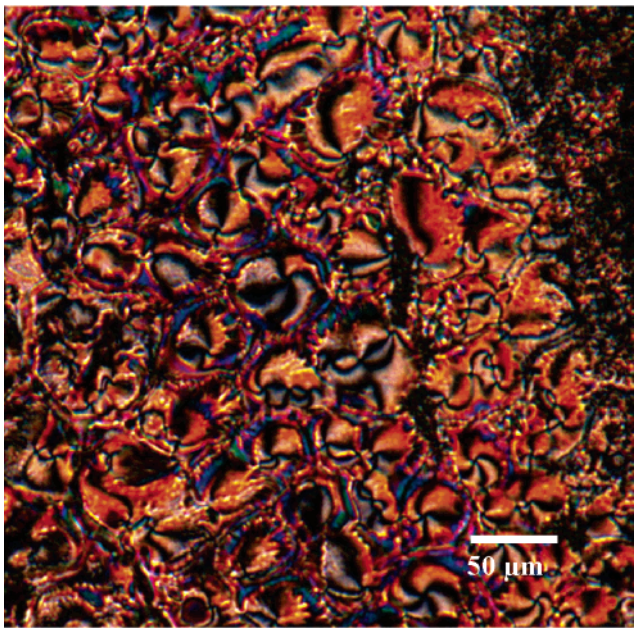


Figure 1. Polymerization of monomers **1**−**3** by DSC (10 °C/min).



(a)



(b)

Figure 2. Polarized optical microscope (POM) image of birefringent droplets initially formed after 15 min (a) and final texture formed after 2 h (b) for monomer **1** during polymerization at 190 °C.

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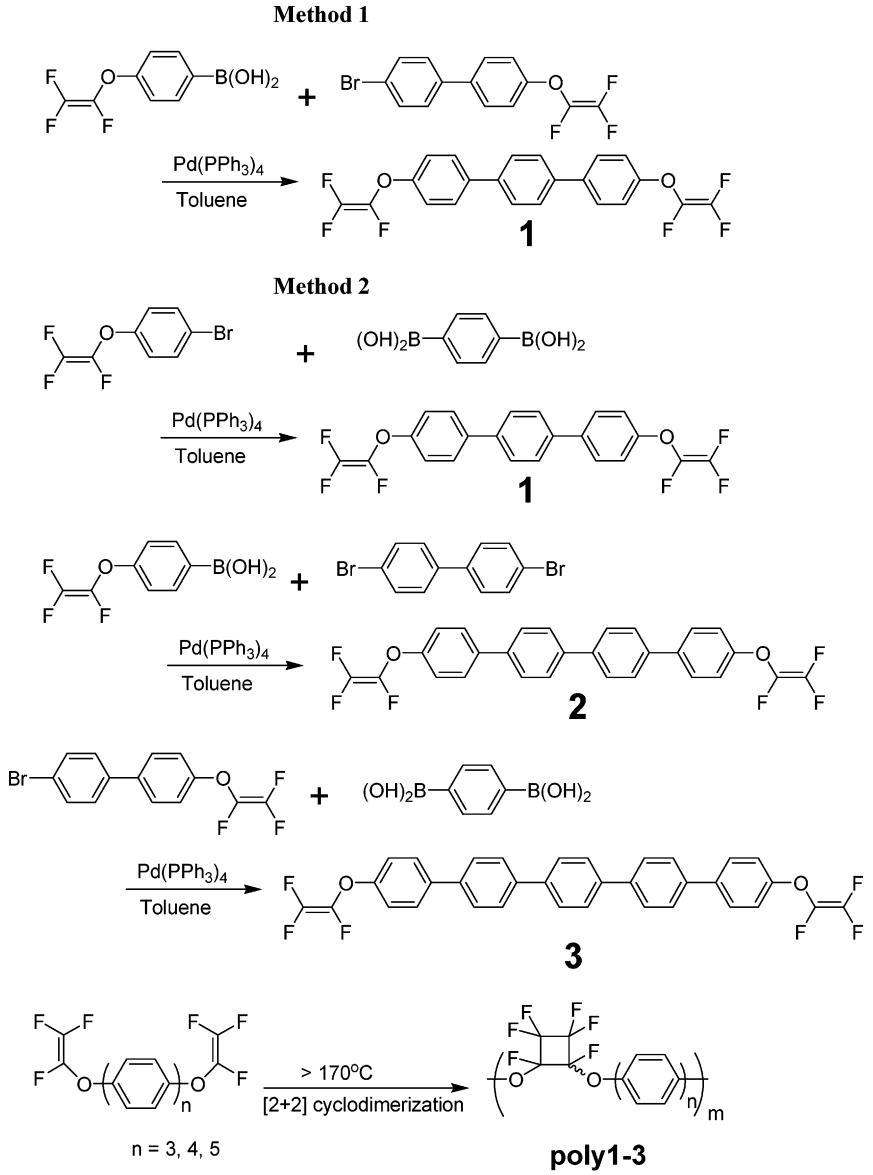
Scheme 1. Synthesis of Bis(trifluorovinyl aryl ether)-Substituted Oligophenylene Monomers (1−3) and Thermal Cyclopolymerization to Poly1−3



into a versatile class of semifluorinated aryl ether polymers containing the perfluorocyclobutyl (PFCB) linkage.[7−10] As depicted in Scheme 1, a series of oligophenylene-containing aryl trifluorovinyl ether monomers (**1**−**3**) were prepared in one step by standard Suzuki cross-coupling (SCC) procedures.[8] Monomer **1** was prepared by two different methods (Scheme 1). Although the yield for the double SCC is slightly lower than single SCC, the second method is adopted as the more practical, scalable, and cost-effective since all the starting materials are commercially available.

Compared to the parent unsubstituted oligophenylene compounds, the trifluorovinyl ether-substituted oligophenylenes exhibit dramatically enhanced solubility, thereby allowing characterization by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and solution spectroscopy. For example, monomer **1** is highly soluble in common organic solvents such as dichloromethane, chloroform, and THF; meanwhile, monomer **2** is slightly soluble in chloroform, DMSO, mesitylene, and toluene. Unfortunately, monomer **3** is not soluble in any solvents attempted. All monomers (**1**−**3**) were characterized by MALDI-TOF MS (see Supporting Information).

The melting temperatures, determined by modulated DSC studies, were also reduced dramatically resulting from the perfluorovinyl ether substitution. Monomers **1** and **2** gave mp of 168 and 226 °C, respectively (cf. parent compounds: *p*-terphenyl, mp 212 °C; *p*-quaterphenyl, mp 300 °C).[11] The UV absorbance maximum of monomers **1** and **2** (THF solution) is gradually red-shifted about 18 nm per phenyl group compared to the parent.[12]

b. Polymer Synthesis via Thermal Cyclodimerization. Originally developed at Dow Chemical,[10] perfluorocyclobutyl (PFCB) aryl ether polymers are prepared by simply heating bis(trifluorovinyl aryl ether)-containing monomers at or above 150 °C.[7−9] The thermal cyclopolymerization reaction does not require catalysts, and stereorandom 1,2-disubstituted cyclobutane rings are typically produced, resulting in transparent polymers useful for optical applications.[9]

Figure 1 exhibits the DSC data for monomers **1**−**3**. Monomer **1** exhibited a solid−solid transition at 149 °C before melting. Melting transitions were not observed for monomer **2** by unmodulated DSC. By modulated DSC, however, we found that the melting transition was embedded under the dominating

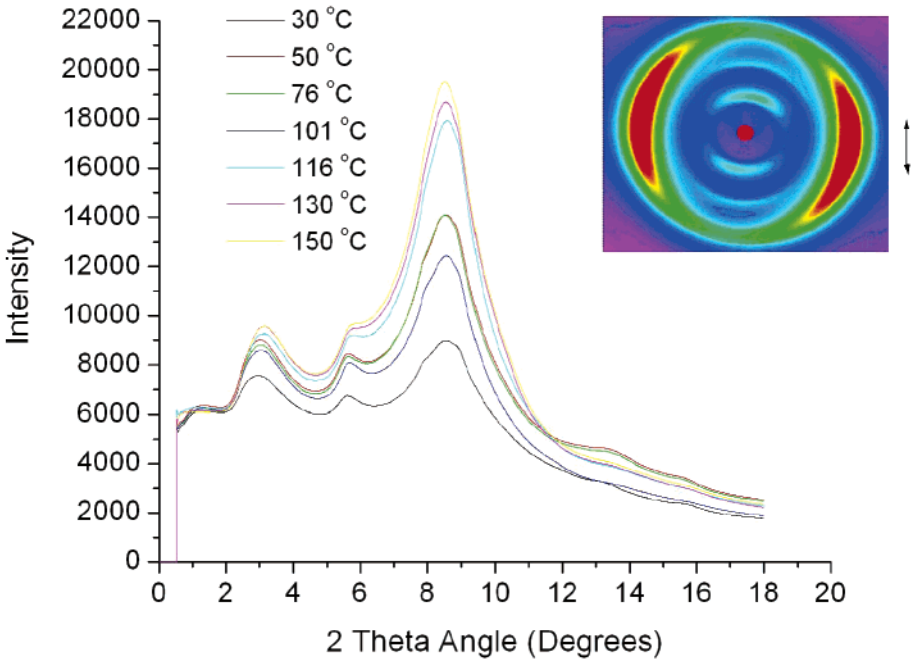


Figure 3. X-ray diffraction pattern of **poly1** collected at different temperatures and its 2D image (inset) (sample prepared at 180 °C for 120 min). The arrow shows the sample orientation induced by flow in the capillary.

exothermic peak of cyclodimerization (see Supporting Information). Monomer **3** does not exhibit a melting peak up to 325 °C and is polymerized in the solid state. Interestingly, there is an additional reproducible sharp exothermal peak at 275 °C for monomer **3**, the origin of which is unknown. Such polymerization profiles for monomers **1**−**3** are quite different from those observed for most other PFCB polymerizations. Subsequent heating cycles in the DSC for the homopolymers (**poly1**−**3**) gave no clear glass transitions. On the basis of our previous experience with the biphenyl PFCB polymer analogue (T_g = 160 °C), the terphenyl polymers should exhibit much higher T_g values.

After polymerization, **poly2** and **poly3** are intractable materials, while **poly1** was completely soluble in chloroform and mesitylene on warming. Upon cooling, the **poly1** solution in mesitylene turns milky. If allowed to stand for a few hours, the colloid becomes gel-like with thixotropic behavior. A degree of polymerization (DP) of ca. 12 was measured by ^{19}F NMR end-group analysis and corresponds to number-average molecular weight, M_n = 5100 for **poly1**. As expected, **poly1** exhibited blue photoluminescence typical of poly-*p*-phenylenes such as *p*-terphenyl in solution (see Supporting Information).

c. Polarized Optical Microscopy. The polymerization of monomer **1** was monitored in-situ via hot stage polarized optical microscopy (POM) at 190 °C. Initially, monomer **1** melted to form a clear isotropic liquid that does not exhibit birefringence. As the polymerization proceeded (at 15 min), birefringent droplets were observed (Figure 2a). The droplets further grew in size and coalesced into a continuous birefringent film with Schlieren textures, characteristic of a nematic phase. The evolution of LC morphology ceased at 57 min, presumably due to vitrification as the glass transition temperature of **poly1** reached the hot stage temperature (Figure 2b).

Isothermal polymerization was further carried out at 175, 185, 200, and 250 °C, and the induction time from the homogeneous melt to the first appearance of birefringent droplets was observed at 23, 13, 7, and 1.5 min, respectively. When heated at higher temperature, the nematic droplets appeared early due to the increased polymerization rate. However, the final textures are nearly identical in that they all show Schlieren nematic textures. In related work, Sue and Lee et al. reported liquid crystalline epoxy networks which when cured at low temperature gave higher order smectic phases and higher temperatures gave nematic textures.[13] In another LC acrylate system,[14] the morphology is tailored by the relative rates of photopolymerization and of phase separation.

The polymerization kinetics of trifluorovinyl ether monomers in the bulk have been characterized via Raman spectroscopy by measuring the disappearance of the fluoroolefin Raman signal at 1831 cm^{-1}.[15] Using these data to estimate monomer **1** conversion vs time, we found that the induction times for development of an LC phase at different temperatures all similarly point to a monomer conversion of 50% (see Supporting Information). From step growth polymerization statistics, 50% conversion represents an oligomer composition with average degree of polymerization of 2 or dimer.

d. X-ray Diffraction. Figure 3 depicts the X-ray diffraction pattern of **poly1** as a function of temperature where one-dimensional patterns are obtained by integrating over the entire detector. Three diffuse peaks are observed at 14.8, 7.8, and 5.1 Å. The inset represents the entire two-dimensional pattern obtained at 150 °C, where the direction of the 5.1 and 7.8 Å peaks is perpendicular to that of the 14.8 Å peak. This indicates that the system is in a liquid crystalline phase with orientational order and the long axis of these molecules are oriented parallel to the direction of the director. The length scale of 14.8 Å is consistent with the length of the monomers, including the aromatic groups and the PFCB ring. The lines of 5.1 and 7.8 Å are consistent with the distance between the terphenylene groups and the PFCB ring, respectively. While the X-ray studies are carried out in the presence of a magnetic field of 2.5 kG, the orientation direction of the LC was found to be independent of the direction of the magnetic field. The orientation of the LC in an X-ray capillary in a magnetic field is a combination of alignment effects of the capillary walls, the shear-induced orientation as the sample is inserted, and the effects of the magnetic field. Further studies are ongoing to resolve these factors.

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Although the peak positions remain essentially unchanged, their intensities significantly increase with decreasing temperature. The most noticeable change is observed in the peak centered at 5.1 Å. Upon closer inspection, this peak reveals two temperature dependent regions, one below and one above 100 °C, where the rate of change of the peak intensity is distinctly higher at the lower temperature range. No phase transition was detected by DSC or microscopy studies; therefore, the increase in intensity and the evolution of other features below 100 °C are indicative of increasing overall long-range orientational order of the liquid crystal. The sample is cooled to room temperature after heating and forms a quenched ordered gel, suggesting that the long-range packing has been disrupted. With increasing temperature, the mobility within the quenched state increases and the system becomes more ordered. Above the glass transition temperature, the polymer undergoes a phase transition into a nematic liquid crystal phase and persists over at least 40 °C.

Conclusions. A series of bisfunctional trifluorovinyl ether oligophenylene monomers ($n = 3-5$) were synthesized and characterized. Monomers **1**−**3** were polymerized via thermal cyclopolymerization, affording the first perfluorocyclobutyl (PFCB) aryl ether polymers containing oligophenylene units in the main chain. Terphenyl **poly1** exhibited a thermotropic nematic mesophase and was characterized by polarized optical microscopy and X-ray diffraction. Kinetic data confirmed that the LC phase begins upon formation of dimer. A glassy liquid crystalline film and gelation was obtained upon cooling to room temperature and treatment with solvent. Because of the condensate free polymerization, PFCB cyclodimerization offers a simple thermal approach to LC structures. Further evaluation of the properties and potential photonics applications of these series of polymers and their copolymerization with other trifluorovinyl ether monomers is currently ongoing.

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Supporting Information Available: Synthetic details including MALDI-TOF, ^{1}H NMR, ^{19}F NMR, and UV−vis characterization of monomers **1**−**3** and polymerization kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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