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Perfluorocyclobutyl Liquid Crystalline Fluoropolymers. Synthesis and Thermal Cyclopolymerization of Bis(trifluorovinyloxy)-α-methylstilbene

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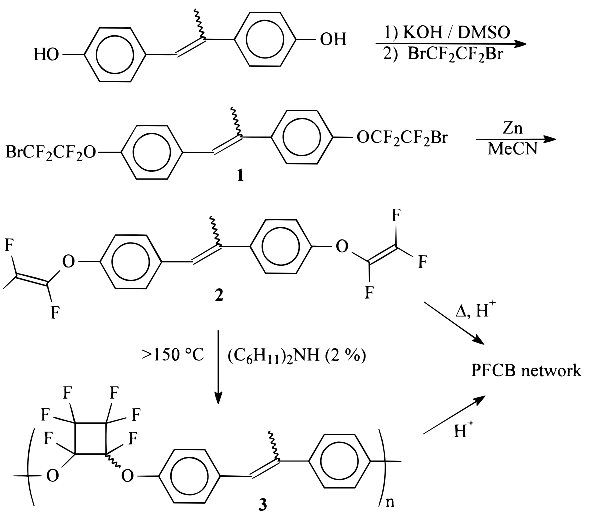
The cyclopolymerization of aromatic trifluorovinyl ether (TFVE) monomers has been established as a versatile route to a unique class of linear and network fluoropolymers containing the perfluorocyclobutyl (PFCB) linkage.[1−5] Polymerization proceeds by a thermal—radical-mediated—step-growth mechanism and provides well-defined polymers containing known fluoroolefin end groups.[2,3] Semifluorinated PFCB polymers, in general, combine the thermomechanical properties of polyaryl ethers with fluorocarbon segments and exhibit excellent processability, optical transparency, high-temperature performance, and low dielectric constants.

The typically well-defined polymer chemistry and range of controlled properties offered by TFVE cyclopolymerization prompted us to pursue the synthesis of liquid crystalline (LC) fluoropolymers based on a new TFVE monomer containing the α-methylstilbene linkage. The mesogenic behavior of α-methylstilbene has been studied in a variety of polymer architectures where most recent attention has been devoted to LC epoxy thermosets.[6−8] Semifluorinated liquid crystalline compounds consisting of small molecules[9] as well as side chain LC polymers[10−14] are also known. The incorporation of low surface energy electronegative fluorocarbon groups in liquid crystals may impart a large influence on a combination of properties such as the bulk permittivity and surface organization in film and coating applications.[9,10] Here we report the synthesis and characterization of the first liquid crystalline polymer containing the PFCB linkage and our initial efforts in probing the anisotropy as a function of semifluorinated step-growth polymer dimensions.

Synthesis. Bis(trifluorovinyl) ether monomer **2** was prepared from dihydroxy-α-methylstilbene (DHαMS, Dow Chemical) in two steps by established procedures (Scheme 1).[1−2,15] Fluoroalkylation of DHαMS to ether intermediate **1** proceeded in rather low isolated yield (50%) due to the formation of a protic byproduct ($-OCF_2CF_2H$) which plagues TFVE monomer chemistry in general.[1,2] Although this method has become quite general for bis- and tris-phenolic precursors, other synthetic methods involving Grignard[2] and aryllithium[5] reagents, which enables the delivery of the TFVE group directly to a variety of substrates, have also been developed. A high trans (*E* isomer) content was retained from the starting bis(phenol) and gave 99% trans olefin in monomer **2**.[15]

Scheme 1



Polymerization was accomplished by simply heating neat monomer **2** in an inert atmosphere at temperatures above 150 °C.[16] Cyclopolymerization of aromatic TFVE groups has been shown to be regioselective, giving 95+% 1,2-disubstituted hexafluorocyclobutane units.[1] An equal amount of cis and trans 1,2-disubstitution is also typically observed.[1,2] Exothermic cyclodimerization was detected just above 130 °C by DSC (25−350 °C at 10 °C/min) for monomer **2** and gave $\Delta H = -34$ kca/mol and $E_a = 24$ kcal/mol. Kinetic parameters were calculated by the *n*th-order model and were found to be consistent with other TFVE thermal cyclopolmerizations.[17] Linear cylcopolymerization was confirmed by ^{19}F NMR[15] and FTIR spectroscopy. For example, the FTIR spectra clearly show the disappearance of the fluoroolefin stretch at 1830 cm^{-1} and formation of the characteristic PFCB vibration at 970 cm^{-1}.

However, unlike traditional TFVE monomer thermolysis, cyclopolymerization of **2** was accompanied by cross-linking at high temperature due to the reactive isopropenyl group. Heating above 300 °C resulted in an insoluble polymer, and a second DSC scan gave a reproducible $T_g = 110$ °C for the network. Upon monitoring the polymerization by GPC and NMR, we found that the isopropenyl group provides a branching mechanism leading to broad molecular weight distributions and ultimate gelation even at much lower temperatures. After heating for 5 h at 155 °C, new aliphatic signals in the ^1H and ^{13}C NMR spectra appeared, and M_w/M_n (7200/3200) values increased from 2.3 to 20 (107900/5500) over 2 h. The absence of new fluorocarbon signals in the ^{19}F NMR spectrum indicated that the trifluorovinyl groups do not participate in branching. After bulk polymerization[16] for 2 h, integration of the clearly resolved vinyl groups and cyclobutyl fluorine signals gave a 91% fluoroolefin conversion and an average degree of polymerization (DP) of 10 ($M_n = 4200$). An average DP(n) = 10 is predicted by Carother's equation ($1/(1 - \rho)$, for ρ the fractional functional group conversion) and is consistent with the cylcopolymerization selectivity of aromatic trifluorovinyl ether groups.

Since unsaturated fluorocarbons can contain trace quantities of HF, the branching chemistry at 155 °C was thought to be due to acid-catalyzed vinyl addition via

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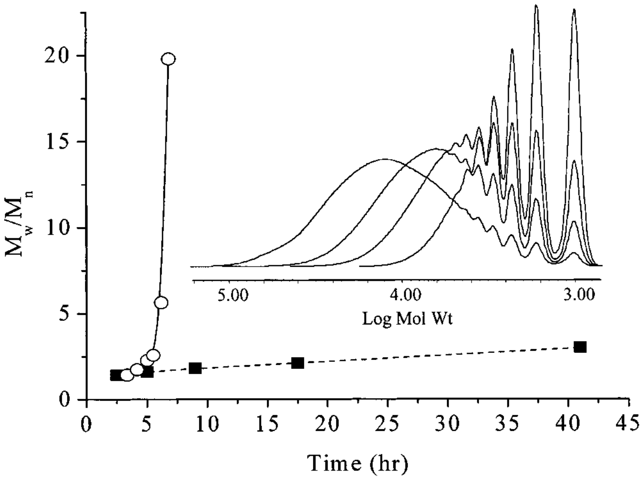

Figure 1. Molecular weight distributions vs polymerization time at 155 °C for **2** with (squares) and without (circles) dicyclohexylamine and linear polymer growth (inset) for the former.

stabilized benzylic and tertiary carbocation intermediates, similar to that known for isopropenyl acid-catalyzed polymerization.[18] To test this hypothesis, cyclopolymerization was performed in the presence of dicyclohexylamine (2%) as a proton scavenger. Under identical conditions, the polymerization containing the amine gave linear PFCB polymer **3** with $M_n = 7200$ and $M_w/M_n = 2.1$ after 17.5 h at 155 °C while pure monomer without the base gelled in less than 10 h. Figure 1 shows the plot of M_w/M_n for the bulk polymerization of pure monomer **2** (circles) and **2** containing the amine stabilizer (squares). Clearly, branching begins in less than 5 h without stabilization, while in the presence of the amine, linear step-growth polymerization proceeds and affords **3** with ideal molecular weight distributions after 17 h (Figure 1, inset). Further polymerization for a total of 41 h gave polymer **3** with $M_n = 14\,100$ ($M_w/M_n = 3$) and a $T_g = 76$ °C (DSC, 10 °C/min).

Liquid Crystalline Order. Our initial approach to explore mesophase formation in PFCB polymer **3** relied on the ability of TFVE polymerization to provide precise oligomers with intact terminal groups by a simple heat/quench cycle. Initially we focused on unstabilized oligomers with distributions ranging from $n = 1$ to 5. At these low conversions, very little branching chemistry has occurred (by GPC), and the primary structure consists of the classical mesogenic α-methylstilbene group bridged by a flexible PFCB aryl ether linkage.

Polarized optical microscopy and ^{2}H NMR experiments were carried out in an attempt to detect mesophase formation during these initial stages of cyclopolymerization.[19] Polarized optical microscopy detects birefringence resulting from anisotropy of the refractive indices $\Delta n = n_{\mathrm{II}} - n_{\mathrm{I}}$, where n_{II} and n_{I} are the parallel and the perpendicular components of the refractive index n, with respect to the director of the mesophase.[20] Further characterization of the nature of the phase can be obtained from the observed patterns due to characteristic deformations. The ^{2}H NMR measurements were used to detect the order signature.[21,22] In an ordered phase, the signal due to nuclei with spin number $I \geq 1$ will spilt to $2I$ lines due to the nonaveraged quadruple interactions. For ^{2}H nuclei, $I = 1$; therefore, for an oriented material the isotropic line will split into two lines. The line shape corresponds to the dynamics of the molecule and to its interaction with the magnetic field.[23]

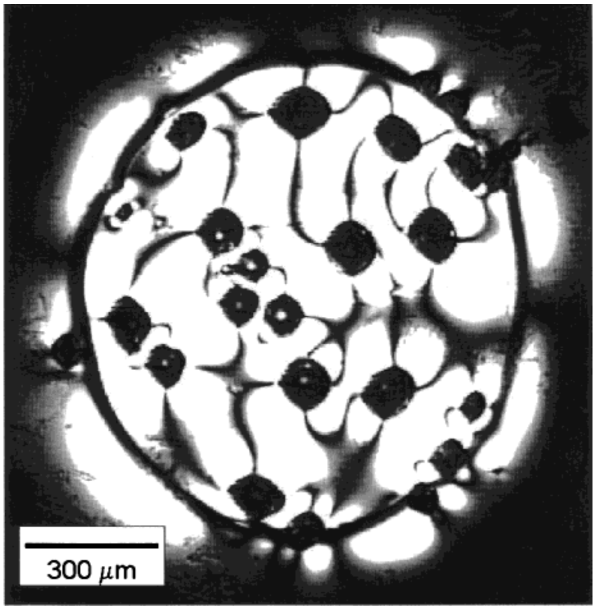

Figure 2. Polarized optical micrographs of polymer **3** at room temperature, indicating nematic textures under slight shear induced by the cover slide (circle image).

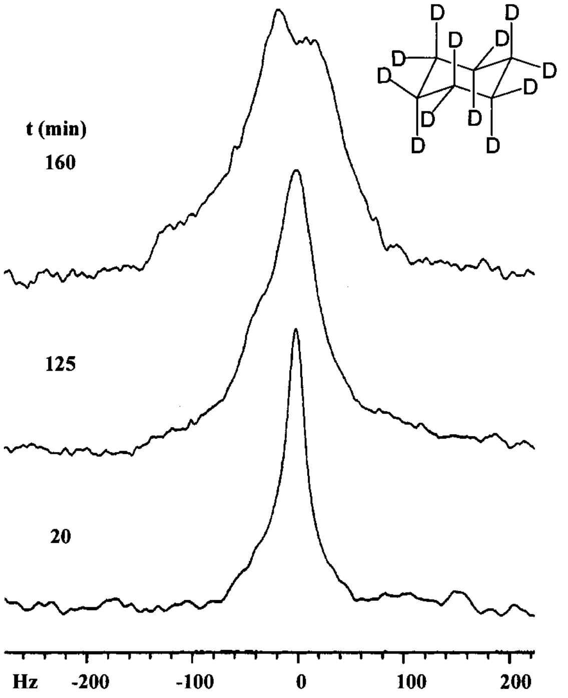

Figure 3. ^{2}H NMR spectrum of cyclohexane-d_{12} probe during oligomerization of **2** vs polymerization time at 155 °C.

Pure monomer **2** does not exhibit optical birefringence. However, upon thermal advancement from 155 °C for 30 min, oligomers with $n = 1-5$ were obtained, and a faint transmitted light suggesting mesophase formation was observed. Further polymerization resulted in an increase in intensity of the transferred light. The patterns obtained following gentle shear of the samples are shown in Figure 2. These textures are consistent with a nematic phase, and the slight shear was essential in order to obtain the patterns, which decay with time. This decay is characteristic of either a shear-aligned polymer or of homeotropic liquid crystallinity.

The signature of inherent ordering without shear was detected by ^{2}H NMR using cyclohexane-d_{12} (~0.5 wt %) as a probe molecule.[21] The spectrum was recorded at room temperature following periodic heating of the neat oligomer mixture at 155 °C and quenching to room temperature. The spectrum of the sample containing monomer before heating consists of a single isotropic line. Upon heating at 155 °C for 20 min, the appearance of coexisting isotropic lines and a powder pattern corresponding to the ordered phases was revealed (Figure 3). With further heating, the powder pattern became the dominant feature. The spectra suggest that nonisotropic phases are formed although the order parameter cannot be directly inferred without further studies. The appearance of the powder pattern suggests that the birefringent textures that were observed under shear correspond to a homeotropic liquid crystalline phase. The powder nature of the observed spectrum indicates that the LC does not align in the magnetic field. This is consistent with the high viscosity and ensuing branched structure of the unstabilized mesophase.

We have shown that a polydispersed PFCB polymer containing the α-methylstilbene linkage forms a lyotropic phase. A detailed study of branching mechanism, potential photodefinability, and liquid crystalline order as a function of PFCB fluoropolymer dimensions (by fractionization) with and without branching effects is currently underway using the techniques described here in combination with small-angle X-ray scattering.

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Supporting Information Available: Text giving analytical information, synthetic procedures, and characterization data for **1**−**3**, including DSC data for the thermal polymerization of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Intermediate **1** (0.22 mol) was added dropwise to 0.1 L of anhydrous acetonitrile and 0.46 mol of Zn at 80 °C, refluxed for 18 h, extracted, and flashed over alumina in hexanes to provide **2** (58%); mp (DSC) 17 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.17 (trace, s, cis Me), 2.23 (3H, s, trans Me), 6.78 (1H s, trans H_v), 7.08 (2H, d, $J = 3.2$ Hz), 7.09 (2H, d, $J = 3.2$ Hz), 7.32 (2H, d, $J = 8.7$ Hz), 7.48 (2H, d, 8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): 17.6 (trans Me), 26.8, 115.8, 126.4, 127.5, 130.7, 135.0 (ddd, $CF{=}CF_2$, $^1J = 110$ Hz, $^2J = 156$, 90 Hz), 135.5, 136.2, 147.0 (ddd, $CF{=}CF_2$, $^1J = 62$, 276 Hz, $^2J = 273$ Hz), 153.7, 154.5. ^{19}F NMR (188 MHz, $CDCl_3$): δ −120 (2F, dd, *cis*-$CF{=}CF_2$, F_a), −127 (2F, dd, *trans*-$CF{=}CF_2$ F_b), −134 (2F, dd, $CF{=}CF_2$, F_c) ($J_{ab} = 97$ Hz, $J_{ac} = 58$ Hz, $J_{bc} = 110$). FTIR (neat): ν 3047, 1898 (w), 1830 (w, $CF{=}CF_2$), 1609, 1514, 1302 (st, br), 1166 (st, br), 843 (w). GC/MS (calcd for $C_{19}H_{12}F_6O_2$ 386 g/mol), obsd *m*/*z*: 386 (M^+), 191, 165, 152, 115, 89. Anal. Calcd for $C_{19}H_{12}F_6O_2$ (found): C, 59.07 (58.91); H, 3.14 (3.14).

(16) Degassed monomer **2** was heated above 155 °C for up to 41 h. The THF soluble polymer was obtained as a slightly yellow solid in essentially quantitative yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.16 (s, cis Me), 2.21 (s, *trans* Me), 6.42 (s), 6.73 (s), 6.86 (br, m), 7.13 (br, d), 7.21 (br, d), 7.29 (br, d), 7.45 (br, d). ^{13}C NMR (75 MHz, $CDCl_3$) 17.4, 26.6, 105.9 (m, cyclobutyl-F_6), 109.3 (m, cyclobutyl-F_6), 112.7 (m, cyclobutyl-F_6), 115.4, 117.9, 118.2, 121.4, 125.9, 126.6, 127.2, 127.5, 128.4, 129.6, 134.9, 137.8, 140.6, 140.9, 151.0, 151.7. ^{19}F NMR (188 MHz, $CDCl_3$): δ trifluorvinyl end groups at −119 (2F, dd, *cis*-$CF{=}CF_2$, F_a), −126 (2F, dd, *trans*-$CF{=}CF_2$ F_b), (2F, dd, $CF{=}CF_2$, F_c) ($J_{ab} = 97$ Hz, $J_{ac} = 58$ Hz, $J_{bc} = 110$); broad cyclobutyl-F_6 at −127.2, −127.6, −128.3, −128.4, −129.0, −129.6, −130.2, −130.5, −130.8 (total cyclobutyl-F. FTIR (neat): ν 3021, 1608, 1515, 1319, 1217, 970 (cyclobutyl-F_6), 775.

(17) For a series of four TFVE monomers (including **2**), *n*th-order DSC analysis gave a range of $E_a = 22-25$ kcal/mol and $-\Delta H = 17-18$ kcal/mol TFVE group.

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