Syntheses, Polymerization, and Characterization of Novel Semifluorinated Methacrylates, Including Novel Liquid Crystalline Materials

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Received January 19, 1993; Revised Manuscript Received March 18, 1993

ABSTRACT: Ethyl α-(chloromethyl)acrylate was converted to a variety of new ether derivatives using triethylamine-catalyzed reaction with commercially available fluoroalkyl alcohols. Rapid, high-conversion polymerization of neat monomers occurred with 2,2′-azobis(isobutyronitrile) at 50–70 °C. Monomers and polymers were characterized by FTIR, both solution- and solid-state ^{13}C NMR spectroscopy, differential scanning calorimetry, optical microscopy, viscosity, gel permeation chromatography (GPC), and X-ray analysis. Weight-average molecular weights (M_w) estimated by GPC ranged from 3.02×10^5 to 7.59×10^5. Additionally, *tert*-butyl α-(hydroxymethyl)acrylate (tBHMA) was converted to α-(chloromethyl)acryloyl chloride in one step. This reactive intermediate allows incorporation of identical ester and ether moieties (e.g., trifluoroethyl) or mixed ester–ether units consisting of, for example, perfluoroalkyl ether units with either hydrophilic esters (based on oligomers of ethylene oxide) or lipophilic esters such as longer alkyl and *tert*-butyl derivatives. Polymers containing longer alkyl and *tert*-butyl ester units had M_w(GPC) values ranging from 3.98×10^4 to 6.0×10^4. Monomers with a semifluorinated ether group containing ten CF_2 units were found to form highly ordered smectic B-like mesophases, which were confirmed by optical microscopy and X-ray analysis. Especially interesting was the persistence of the order in polymers obtained by polymerization in the mesophase. For example, the ethyl ester polymer showed much sharper X-ray peaks when obtained by in situ polymerization (in the monomer liquid crystal phase) than polymer reprecipitated from solution. Analogous diacrylates were synthesized by reacting the chloromethyl acid chloride with various diols followed by ether formation with fluoroalcohols. Most interesting was the ability of the mono- and diacrylate compounds incorporating ethylene oxide ester units to form liquid crystalline phases similar to that of the ethyl ester monomer. All the polymers containing ten CF_2 units in the side chain exhibited a single first-order transition by DSC (48–58 °C) which corresponds to melting of the side chain crystals independent from the main chain behavior.

Introduction

Polymers rich in fluorine generally have properties very different from those of other polymers, e.g., good thermal stability, low refractive index, and chemical and oxidative resistance. Poly(tetrafluoroethylene) (PTFE) is the premier commercial fluorocarbon polymer mainly because it is insoluble in most solvents and degrades only above ca. 450 °C. The properties exhibited by such fluoropolymers are directly due to the high C–F bond energy (540 kJ/mol) and short bond length (0.132 nm). Moreover, the C–F bond strength *increases* with the extent of adjacent carbon fluorination; thus, the longer the fluoroalkyl group, the higher is its stability.

Fluoropolymers have low coefficients of friction and antiadhesive properties causing them to repel water, oil, and dirt. This combination of properties makes them useful in nonstick cookware, fabric treatments, lubricating oils and greases, car finishes, contact lenses, and optical fiber claddings.[1,2] A key property in such applications is their low surface energy. Illustrative are the surface free energies of carbon fragments which decrease in the order $CH_2 > CH_3 > CF_2 > CF_3$.[3] Thus, PTFE has a critical surface tension of 18.5 dyn/cm while poly(perfluoroalkyl methacrylates) have surface tensions of 3–5 dyn/cm.[4] Such low surface energy prevents sticking and adhesion, polymer swelling and solvation, and attack or degradation.

The forces causing such low surface energies also can lead to molecular-level phase separation. For example, linear semifluorinated alkanes such as $F(CF_2)_{10}(CH_2)_{10}H$ form lamellar liquid crystals consisting of sheets of extended chain molecules lined up more or less perpendicular to the plane surface.[5] In addition, a recent report describes the ability of semifluorinated alkyl methacrylates [e.g., the methacrylate ester of $F(CF_2)_{12}(CH_2)_4OH$] to form liquid crystal (LC) gels that can be converted directly to polymer gels photochemically.[6]

Most of the fluoroalkyl acrylate monomers reported in the literature have been prepared by transesterification with a fluoroalkyl alcohol or by reaction of the latter with acryloyl chloride.[7] A novel synthesis from perfluoroketones reportedly also works well to give branched chain fluoroalkyl acrylates.[8,9] Several fluoroalkyl acrylates and methacrylates are available commercially.[10] Recently, Otsu and co-workers[11] reported polymerization of methyl α-((fluoroalkoxy)methyl)acrylates synthesized via a procedure similar to that reported earlier by us.[12] This new synthetic approach to substituted methacrylates uses a key intermediate, ethyl α-(chloromethyl)acrylate (ECMA, 1 in Figure 1), and involves substitution with various nucleophiles[13] of the highly reactive allyl halide. The multifunctionality of ECMA and its analogs allows ready incorporation of a perfluoroalkyl ether with various hydrocarbon esters. This combination also allows facile determination of the effects of structural changes on polymerization and polymer properties and makes processability, solubility, and flexibility a combined function of the nature of the perfluoroalkyl ether and hydrocarbon ester segments of the molecule.

In a previous communication[12] we reported the synthesis and polymerization of four new fluoroalkyl ether monomers based on ECMA. We also described the ability of the ethyl ester monomer with a semifluorinated ether group containing ten CF_2 units to form a highly ordered smectic B-like mesophase in which polymerization was possible. In this paper, we report the detailed analysis of these and related monomers along with the synthesis and polymerization of amphiphilic mono- and diacrylates containing oligo(oxyethylene) groups.

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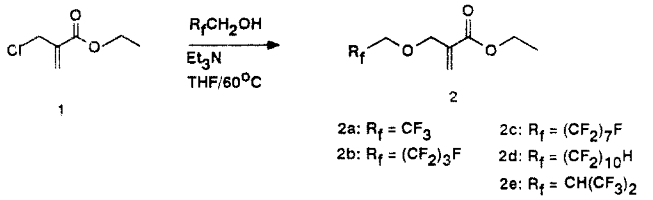

Figure 1. Synthetic scheme for the monomers derived from ECMA.

Experimental Section

Ethyl α-(hydroxymethyl)acrylate (EHMA), ECMA,[13] and t-BHMA[14] were prepared using previously published procedures. The fluoroalcohols, trifluoroethanol (TFE), 1*H*,1*H*-heptafluorobutanol, 1*H*,1*H*-pentadecafluorooctanol, 1*H*,1*H*,11*H*-eicosafluoroundecanol (EFU), and hexafluoroisopropyl alcohol (HFIP), were purchased from Aldrich and PCR Chemical Co. and used as obtained. Infrared spectra were taken on a Perkin-Elmer FTIR 1600 spectrometer using sodium chloride sample plates. ^{1}H and ^{13}C solution-state NMR spectra were obtained on Bruker AC-200 and AC-300 spectrometers. Solid-state spectra were obtained on a Bruker MS-200 for polymers insoluble in common deuterated solvents. Thermal transitions were measured on a Du Pont 9900 thermal analyzer using a Model 910 DSC cell at a heating rate of 10 °C/min under a nitrogen flow. Optical textures were determined using a Nikon microscope with a Mettler FP5/52 programmable hot stage. X-ray data were obtained on a Siemens XPD-700P using Cu Kα radiation. The molecular weights of the polymers were estimated by gel permeation chromatography in THF solvent (GPC, Waters μ-Styragel columns, Waters 410 differential refractometer) relative to polystyrene standards.

General Procedure for the Synthesis of Monomers 2a–e Derived from ECMA. To a stirring mixture of the fluoroalcohol (83 mmol) and triethylamine (TEA, 8.40 g, 83 mmol) in 50 mL of dry tetrahydrofuran (THF) was added ECMA (12 g, 80 mmol) in one portion. The reaction was slightly exothermic and was allowed to stir at ambient temperature for 30 min. The solution was then heated at 60 °C for 12 h before being cooled in the freezer (−5 °C). The precipitate was removed by filtration and the THF evaporated under reduced pressure. The residue was passed through a basic alumina column with chloroform as eluent. The chloroform was evaporated under reduced pressure. Vacuum distillation of the residue gave monomers **2a–c** and **2e** as clear liquids; **2d** was obtained as a waxy solid at room temperature. Yields ranged from 69 to 71%. Representative analyses of the monomer **2c** are as follows: FTIR (cm^{-1}): 2984, 1713, 1636, 1466, 1394, 1200, 1143, 1025, 959, 825; ^{1}H NMR ($CDCl_3$) δ 1.2 (t, 3H, CH_3), 3.93 (t, 2H, CH_2CF_2), 4.15 (q, 2H, CH_2CH_3), 4.27 (s, 2H, CCH_2O), 5.79 and 6.25 (s, 2H, $C{=}CH_2$); ^{13}C NMR ($CDCl_3$) δ 13.68 (CH_3), 60.74 (t, CH_2CF_2), 70.86 (CCH_2O), 103–118.5 (CF_2's), 126.07 ($C{=}CH_2$), 136.44 ($C{=}CH_2$), 165.32 ($C{=}O$).

Synthesis of α-(Chloromethyl)acryloyl Chloride (4). In a 50-mL one-neck round-bottom flask t-BHMA (5 g, 31.64 mmol) and excess thionyl chloride were added and stirred at ambient temperature for 24 h. Most of the thionyl chloride was evaporated in the rotary evaporator, and vacuum distillation of the residue gave α-(chloromethyl)acryloyl chloride (4) as a clear liquid in 60% yield. FTIR (cm^{-1}): 3107, 2966, 1742, 1637, 1407, 1284, 967, 896; ^{1}H NMR ($CDCl_3$) δ 4.26 (s, 2H, CH_2Cl), 6.41 and 6.74 (s, 2H, $CH_2{=}C$); ^{13}C NMR ($CDCl_3$) δ 41.53 (CH_2Cl), 136.14 ($CH_2{=}C$), 141.14 ($C{=}CH_2$), 166.78 ($C{=}O$).

Synthesis of Monomer 5. To a stirring mixture of TFE (4.75 g, 47.48 mmol) and TEA (4.79 g, 47.48 mmol) in 20 mL of dry THF at 10 °C 4 (3 g, 21.58 mmol) was slowly added in one portion (the reaction was exothermic). The mixture was stirred at 10 °C for 1 h before raising the temperature to 55 °C and stirring for another 12 h. The mixture was diluted with 50 mL of CH_2Cl_2 and extracted with 3 × 25 mL aliquots of water. The organic layer was separated, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. Vacuum distillation of the residue gave the pure monomer as a clear liquid in 63% yield. FTIR (cm^{-1}): 2965, 1767, 1648, 1281, 1166, 1119, 971; ^{1}H NMR ($CDCl_3$) δ 3.85 (q, 2H, $OCOCH_2CF_3$), 4.33 (s, 2H, CCH_2OCH_2), 4.51 (q, 2H, $CH_2OCH_2CF_3$), 5.01 and 6.43 (s, 2H, $C{=}CH_2$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 60.55 (q, $OCOCH_2CF_3$), 68.2 (q, $CH_2OCH_2CF_3$), 70.24 (CCH_2OCH_2), 114.64–131.09 and 115.66–132.01 (two q, $^1J_{C-F}$ = 275 Hz, CF_3's), 129.19 ($C{=}CH_2$), 134.7 ($C{=}CH_2$), 163.62 ($C{=}O$).

Synthesis of Monomers 6a–c. In 15 mL of dry THF the appropriate alcohol (30.34 mmol) and TEA (3.07 g, 30.34 mmol) were added. To this stirring mixture 4 (4.21 g, 30.34 mmol) was slowly added at 10 °C in one portion. The reaction mixture was stirred at this temperature for 12 h before diluting with 50 mL of CH_2Cl_2 and extracting with 3 × 50 mL aliquots of water. The organic layer was separated, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give the corresponding alkyl α-(chloromethyl)acrylate as a liquid; yield 75%.

The second step involved reaction of this intermediate (used without further purification) with the fluoroalcohol. To a mixture of fluoroalcohol (11.69 g, 22 mmol) and TEA (2.22 g, 22 mmol) in 25 mL of THF was added the appropriate chloromethyl intermediate (22 mmol). The reaction was slightly exothermic. The mixture was stirred at ambient temperature for 30 min before raising the temperature to 60 °C and stirring for 12 h. This mixture was diluted with 50 mL of CH_2Cl_2 and extracted with 3 × 50 mL aliquots of water. The organic layer was separated, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was passed through a basic alumina column using chloroform as eluent. Solvent evaporation under reduced pressure gave the monomers as viscous liquids in 65–75% yield.

Analysis of monomer **6a**: FTIR (cm^{-1}): 2921, 1714, 1637, 1468, 1212, 1147, 971; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.46 (t, 3H, CH_2CH_3), 1.24–1.64 (m, 16H, alkyl), 3.98 (t, 2H, OCH_2CF_2), 4.13 (t, 2H, OCH_2CH_2), 4.32 (s, 2H, $=CCH_2O$), 6.00 (t of t, $^2J_{H-CF}$ = 56 Hz, 1H, HCF_2CF_2); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.64, 25.94, 28.55, 29.27, 29.52, 31.9 (alkyls), 65.09 (OCH_2CH_2), 67.7 (t, OCH_2CF_2), 70.92 ($=CCH_2O$), 103–118 (fluoroalkyls), 126.42 ($CH_2{=}C$), 136.34 ($CH_2{=}C$), 165.46 ($C{=}O$).

Analysis of monomer **6b**: FTIR (cm^{-1}): 2977, 2866, 1716, 1639, 1450, 1211, 1138, 1038, 956; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.16 (t, 3H, CH_3), 3.46–4.7 (m, 8H, OCH_2CH_2O), 3.97 (t, 2H, CH_2CF_2), 4.26–4.31 (m, 4H, $OCH_2O{=}$ and OCH_2CH_2O), 5.86 and 6.34 (s, 2H, $CH_2{=}C$), 6.01 (t of t, $^2J_{H-CF}$ = 56 Hz, 1H, HCF_2CF_2); ^{13}C NMR ($CDCl_3$) δ 14.99 (CH_3), 63.99, 66.63, 68.96, 69.78, 70.67, 70.85 ($OCH_2C{=}$ and OCH_2CH_2O), 67.75 (t, CH_2CF_2), 103.2–118 (fluoroalkyls), 127.03 ($CH_2{=}C$), 135.9 ($CH_2{=}C$), 165.3 ($C{=}O$).

Analysis of monomer **6c**: FTIR (cm^{-1}): 2978, 1713, 1642, 1454, 1366, 1219, 1149, 955, 843; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.47 (s, 9H, $C(CH_3)_3$), 3.98 (t, 2H, CH_2CF_2), 4.28 (s, 2H, $=CCH_2O$), 5.7 and 6.23 (s, 2H, $CH_2{=}C$), 6.03 (t of t, $^2J_{H-CF}$ = 56 Hz, 1H, HCF_2CF_2); ^{13}C NMR ($CDCl_3$) δ 27.9 ($C(CH_3)_3$), 67.7 (t, CH_2CF_2), 71.0 ($=CCH_2O$), 81.3 ($C(CH_3)_3$), 103.10–118 (fluoroalkyls), 125.77 ($CH_2{=}C$), 137.55 ($CH_2{=}C$), 164.65 ($C{=}O$).

Synthesis of Diacrylates 7a and 7b. To a stirring mixture of the appropriate diol (10.75 mmol) and TEA (21.5 mmol) in 20 mL of dry THF at 10 °C was slowly added 4 (3 g, 21.5 mmol). This mixture was stirred for 4 h, diluted with 50 mL of CH_2Cl_2, and extracted with 3 × 50 mL aliquots of water. The organic layer was separated, dried with anhydrous sodium sulfate, and evaporated under reduced pressure to give the intermediate product as a liquid; crude yields 80–85%.

These intermediates were used without further purification. The appropriate bis[α-(chloromethyl)acrylate] (10.7 mmol) was then added to a stirring mixture of EFU (11.42 g, 21.5 mmol) and TEA (2.15 g, 21.5 mmol) in 20 mL of dry THF at ambient temperature. The reaction was exothermic. The mixture was stirred at ambient temperature for 1 h before raising the temperature to 60 °C and allowing it to stir for another 4 h. The mixture was diluted with 100 mL of CH_2Cl_2 and extracted with 3 × 50 mL aliquots of water. The organic layer was separated, dried with anhydrous sodium sulfate, and evaporated under reduced pressure. In the case of diacrylate **7a**, the residue obtained was a solid which was recrystallized once from methanol to give the pure diacrylate in 50% yield. The diacrylate **7b** was obtained as a waxy solid and was purified by passing it through a basic alumina column using CH_2Cl_2 as an eluent. The CH_2Cl_2 was evaporated under reduced pressure to give the waxy solid in 57% yield.

Analysis of **7a**: FTIR (cm^{-1}): 2931, 2848, 1701, 1460, 1218, 1143; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.28–1.67 (m, 16H, alkyl), 3.99 (t, 4H, OCH_2CF_2), 4.14 (t, 4H, CH_2OCO), 4.33 (s, 4H, $=CCH_2O$), 5.86 and 6.32 (s, 4H, $CH_2{=}C$), 6.03 (t of t, $^2J_{H-CF}$ =

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Figure 2. Synthetic scheme for α-(chloromethyl)acryloyl chloride.

56 Hz, 2H, HCF_2CF_2); ^{13}C NMR ($CDCl_3$) δ 25.9, 28.5, 29.18, 29.39 (alkyl), 65.08 ($OCOCH_2$), 67.25 (t, OCH_2CF_2), 70.93 ($=CCH_2O$), 104.1–118 (CF_2's), 126.61 ($CH_2=C$), 136.2 ($C=CH_2$), 165.47 ($C=O$).

Analysis of **7b**: FTIR (cm^{-1}): 2884, 1719, 1637, 1202, 1149; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.62, 3.7, and 4.29 (m, 20H, $=CCH_2O$ and OCH_2CH_2O), 3.98 (t, 4H, OCH_2CF_2), 5.86 and 6.32 (s, 4H, $CH_2=C$), 6.03 (t of t, $^2J_{H-CF}$ = 56 Hz, 2H, HCF_2CF_2); ^{13}C NMR ($CDCl_3$) δ 63.98, 68.98, 70.63, 70.86 ($=CCH_2O$ and OCH_2CH_2O), 67.76 (t, OCH_2CF_2), 103–118 (CF_2's), 127.05 ($CH_2=C$), 135.9 ($CH_2=C$), 165.28 ($C=O$).

General Polymerization Procedure. Neat monomer (usually ca. 2.5 g) was mixed with AIBN (0.1 mol %), and the mixture was purged with nitrogen for 30 min. The mixture was then heated at 50–70 °C for 12 h under N_2. The viscous polymer solidified on cooling to a clear transparent mass. Polymer from **2a** was dissolved in warm chloroform, while those from **2b–e** were dissolved in 1,1,2-trichlorotrifluoroethane and that from **5** was dissolved in THF. Each was slowly precipitated into cold hexanes. The precipitate was filtered and dried under vacuum; yield 69–84%.

Monomers **6a** and **6b** were polymerized in α,α,α-trifluorotoluene (TFT). To 1 mL of TFT, monomer (0.5 g) and AIBN (0.5 mol %) were added, and the mixture was purged with nitrogen for 30 min. This mixture was then heated at 55 °C for 24 h before slowly pouring into hexanes (**6a**) or methanol (**6b**). The precipitate was vacuum filtered and dried; yield 90%.

Monomer **6c** was polymerized in bulk by placing the monomer (ca. 1 g) in a round-bottom flask along with AIBN (0.5 mol %). This mixture was purged with nitrogen for 30 min and then heated at 55 °C for 7 days under a nitrogen flow. After every 24-h period, additional AIBN (0.1 mol %) was added to the flask. The final mixture was dissolved in THF and slowly poured into hexanes. The precipitate was vacuum filtered and dried; yield 15%.

The diacrylates **7a** and **7b** were polymerized in THF. To 5 mL of THF was added the diacrylate (ca. 0.5 g) along with AIBN (1 mol %). This mixture was purged with nitrogen for 45 min and then heated at 55 °C for 48 h. This mixture was poured in hexanes, and the precipitate was vacuum filtered and dried; yield 95 and 85%, respectively.

Results and Discussion

Monomer Synthesis and Characterization. Conversion of the CH_2OH group of the readily available EHMA to the more reactive CH_2Cl group makes substitution and ether formation extremely easy. Though the fluoroalcohols are not very nucleophilic, displacement of the chlorine of ECMA was fast and clean with Et_3N as base and catalyst. Such facile substitution probably involves a combination of alcohol activation by Et_3N and high ECMA reactivity (possibly through allylic attack) to generate the more stable C–O bond from the C–Cl group. Thus, the synthesis of the fluoroether acrylates **2** from ECMA **1** occurred easily and in excellent yields while preserving the ethyl ester group. The ^{13}C NMR spectra of the monomers clearly show the absence of the methylene carbon (CH_2Cl) at 41.0 ppm and the presence of a quartet at 67.7 ppm (OCH_2CF_3) plus a singlet at 68.6 ppm ($=CCH_2O$), indicating the formation of the ether. Monomer from HFIP showed a multiplet at ca. 77 ppm [$OCH(CF_3)_2$] and a quartet at 122 ppm (CF_3, $^1J_{H-CF}$ = 285 Hz) in the ^{13}C NMR spectrum. All the ethyl ester monomers obtained were liquids except for **2d**, which was a waxy solid at room temperature.

Similarly, t-BHMA was converted in a one-pot process to **4** by reacting with excess thionyl chloride (Figure 2). Initial reaction converts the CH_2OH group to the CH_2Cl group. Liberated HCl cleaves the *tert*-butyl group, and the CO_2H group thus generated is converted to the acid chloride. The ^{13}C NMR spectrum of **4** (trace A in Figure 4) shows the absence of the CH_2OH at 61.6 ppm and the presence of a singlet at 41.5 ppm (CH_2Cl). Cleavage of the *tert*-butyl group is demonstrated by the absence of the *tert*-butyl methyl peak at 27.8 ppm and quaternary carbon peak at 80.7 ppm. The intermediate **4** was converted to **5** in good yield by reacting with 2 equiv of TFE (Figure 3). This was confirmed by the ^{13}C NMR spectrum (trace B in Figure 4), which shows the disappearance of the methylene carbon at 41.5 ppm (CH_2Cl) and the appearance of two quartets at 60.5 and 68.1 ppm (CH_2CF_3) plus a singlet at 70.2 ppm ($=CCH_2$). The two CF_3 groups are seen as two quartets at 122.5 and 123.5 ppm with coupling constants $^1J_{F-C}$ of 275 Hz, typical for one-bond carbon–fluorine coupling.

Monomers **6a–c** were synthesized from intermediate **4** via a two-step process. Since preferential substitution at the acid chloride moiety was desired, **4** was reacted first with decyl alcohol, 2-(2-ethoxyethoxy)ethanol, or *tert*-butyl alcohol at 10 °C in the presence of TEA as an acid scavenger and catalyst to give the corresponding esters. ^{13}C NMR spectra of these intermediates clearly show formation of only ester groups by the presence of the carbon attached to the ester oxygen at 63.9–70.0 ppm for $OCH_2CH_2CH_2$ and OCH_2CH_2O or at 81.1 ppm for $OC(CH_3)_3$ plus the retention of the methylene carbon at 41.2 ppm (CH_2Cl). The second step involved substitution of the chlorine (without further purification) by $H(CF_2)_{10}CH_2OH$ in the presence of TEA under conditions similar to those used for ECMA substitution. This gave the crude monomers **6a–c** (Figure 3), which were purified by column chromatography. Their ^{13}C NMR spectra (see Figure 5 for that of **6b**) clearly show loss of the methylene carbon at 41.2 ppm (CH_2Cl) and appearance of a singlet at 70.9 ppm ($CH_2OCH_2CF_2$), a triplet at 67.7 ppm ($CH_2OCH_2CF_2$), and the fluoroalkyl carbons in the region 103–118.5 ppm, confirming formation of the fluoroalkyl ether. Similarly, the diacrylates were prepared by reacting **4** first with 1,10-decanediol or tetraethylene glycol to give the diesters and then with $H(CF_2)_{10}CH_2OH$ to incorporate the semifluorinated ether groups of **7a** and **7b** (Figure 3). Their structures were confirmed by ^{13}C NMR spectra which showed peaks in the same region as monomers **6a** and **6b** with the noticeable absence of terminal methyl peaks in the region 13.9–14.9 ppm.

Monomers **2a–c**, **2e**, **5**, and **6a–c** were liquids, monomer **2d** and diacrylate **7b** were waxy solids at room temperature, and the diacrylate **7a** was obtained as a powder after attempted recrystallization from methanol. Differential scanning calorimetry (DSC) of monomers **2d**, **6a–c**, **7a**, and **7b** showed only broad endotherms during the heating cycle. The transition temperatures were taken as the maximum point of the endotherm on the first heating cycle. The broad transitions are presumably due to the presence of small amounts of lower and higher homologs of $H(CF_2)_{10}CH_2OH$ which were present in the commercial material obtained.

Liquid Crystallinity in Mono- and Diacrylates. Semifluorinated alkanes (roughly half fluoroalkyl and half hydrocarbon) form smectic B-like phases due to their amphiphilic nature and display identical textures to those seen here for many of the derivatives containing the $H(CF_2)_{10}CH_2O$ moiety.[15] Optical microscopy, DSC, and X-ray analysis showed that the smectic B-like LC phase for the semifluorinated alkanes has a bilayered structure where the molecules are interdigitated and tilted with respect to the bilayer normals.[5] Raman spectroscopy[16,17]

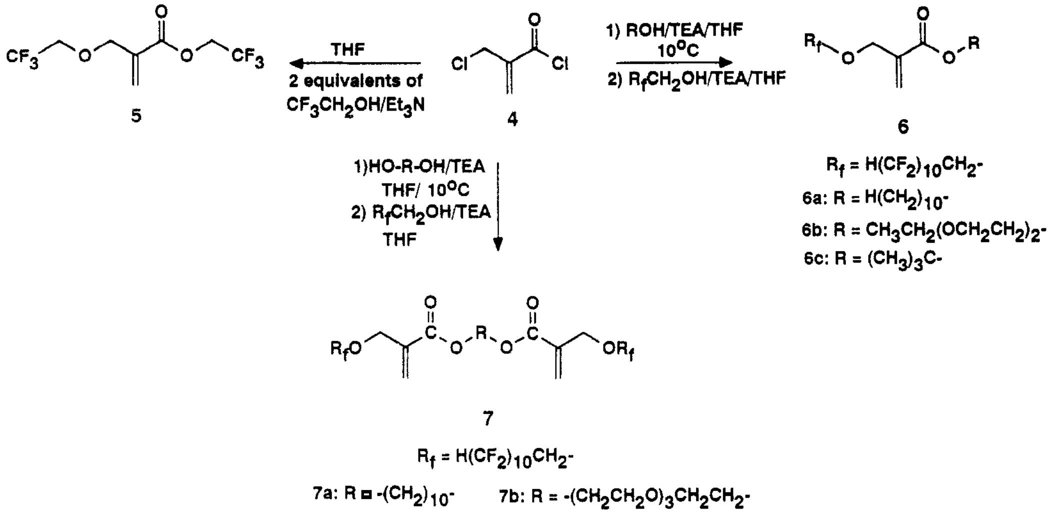

Figure 3. Synthetic scheme for the monomers and diacrylates derived from α-(chloromethyl)acryloyl chloride.

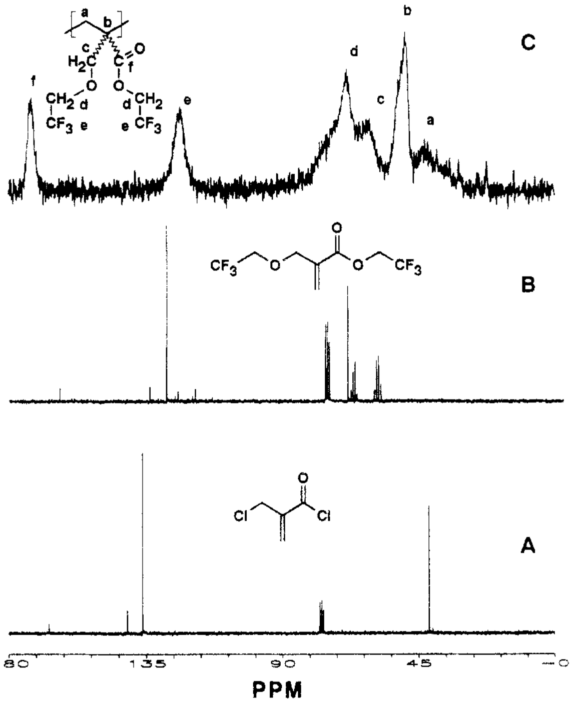

Figure 4. ^{13}C NMR (CDCl$_3$) spectra of intermediate **4** (trace A) and monomer **5** (trace B), and solid-state ^{13}C NMR of **5** polymer (trace C).

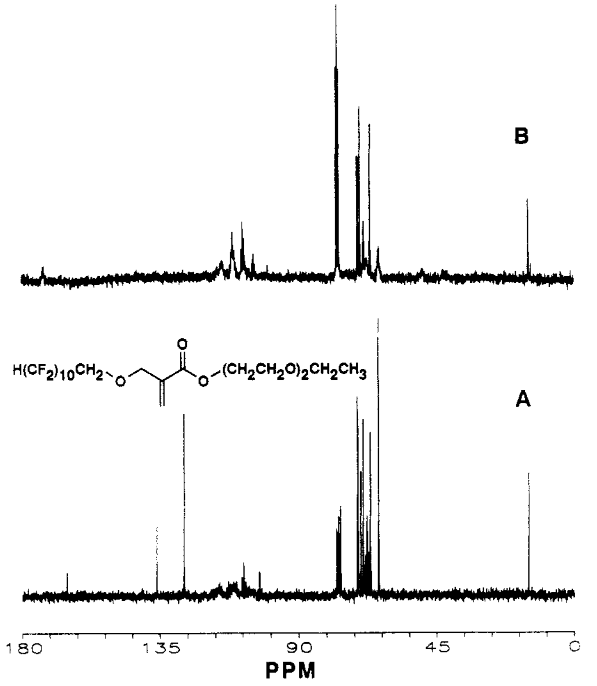

Figure 5. ^{13}C NMR (CDCl$_3$) spectra of monomer **6b** (trace A) and its polymer (trace B).

and solid-state ^{13}C NMR[18] data show that above the melt, the fluorocarbon segments retain some rigidity while the hydrocarbon segments are disordered and have liquid like conformational freedom. Based on optical microscopy and DSC results, derivatives **2d**, **6a**, **6b**, and **7b** were found to possess liquid crystalline phases.

The endothermic transition at 32.3 °C for monomer **2d** during the first DSC heating cycle (Figure 6) corresponds to the transition from the smectic to the isotropic phase (S → I). A supercooling of the I → S transition of ca. 8 °C is seen for the exotherm on the corresponding cooling cycle. Observation under the polarizing microscope of the as-synthesized monomer **2d** at room temperature (Figure 7) shows a mosaic texture characteristic of smectic B-like liquid crystals.[19] When this sample was heated to 32 °C, transition to the isotropic phase occurred and subsequent cooling from this phase gave a viscous, birefringent fluid displaying the same characteristic texture seen on the heating cycle.

Monomer **6a** shows an endotherm at 13.5 °C with a shoulder at 20 °C during the heating cycle (trace 3 in Figure 6) which is resolved into two distinct exotherms on cooling (trace 4 in Figure 6). Although the transition at 13.5 °C was not characterized by optical microscopy (due to limited cooling programmability on our microscope), this transition is thought to be the crystalline → smectic transition while the transition at 20 °C is attributed to the S → I transition. These transitions were reproducible on subsequent heating and cooling cycles. The S → I transition for monomer **6b** occurs at 26.6 °C on the heating cycle while the I → S transition in the cooling cycle shows a supercooling of 5.5 °C. The transitions from the crystal to the mesophase for the LC monomers **6a** and **6b** are believed to be below −50 °C as no transition was seen by DSC despite cooling to −50 °C.

Monomers **6a** and **6b** display optical textures characteristic of smectic B-like phases when placed between a glass plate and cover slip, and they can be made to flow by applying pressure on the cover slip. The optical micrograph of monomer **6b** (Figure 8, obtained by cooling the sample from the isotropic phase and quickly observing under the microscope) shows a lancet texture, also characteristic of smectic B-like phases. Although, amphiphilic molecules containing perfluoroalkyl segments and oligomers of ethylene oxide were synthesized earlier,[20] the occurrence of smectic ordering in such materials has

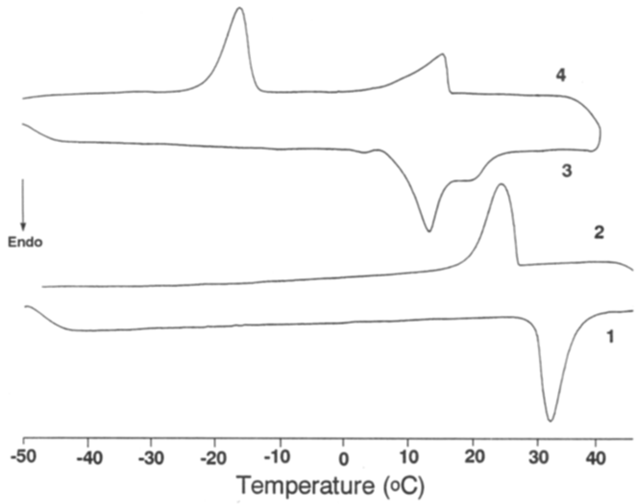

Figure 6. DSC scans of **2d**, first heating (trace 1) and cooling cycle (trace 2); and **6a**, first heating (trace 3) and cooling cycle (trace 4).

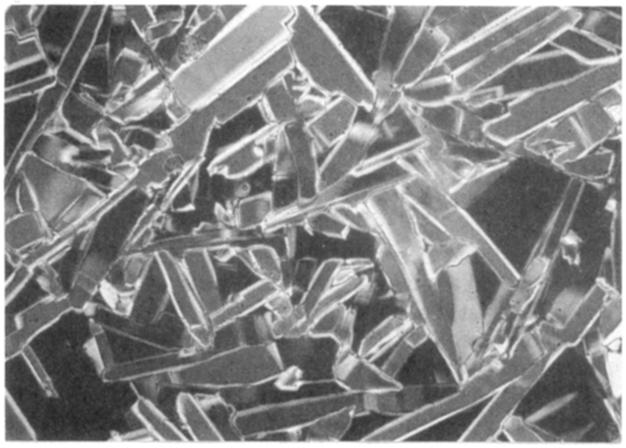

Figure 7. Smectic B-like mosaic texture of monomer **2d** as observed under a polarizing microscope.

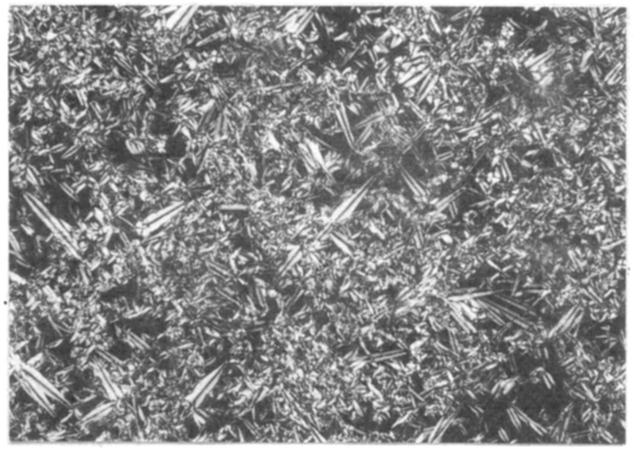

Figure 8. Smectic B-like texture with lancets of monomer **6b** as observed under a polarizing microscope.

not been reported in the literature to the best of our knowledge. Monomer **6c** (*tert*-butyl ester) shows a broad endothermic transition at 13.1 °C, although phase assignments accompanying this transition have not yet been made.

The diacrylate **7a** containing ten methylene units in the center diol unit shows a broad endothermic peak at 78.6 °C in the heating cycle which corresponds to the crystal–isotropic transition temperature seen at 79 °C by optical microscopy. No LC phase was observed for this compound. The DSC cooling cycle shows an exotherm which is attributed to the formation of crystalline spherulites as seen by optical microscopy. Linear triblock semifluorinated alkanes [$F(CF_2)_n(CH_2)_m(CF_2)_nF$] show a single endotherm above room temperature attributable to crystalline melting but also do not form liquid crystalline phases.[21] However, incorporation of tetraethylene oxide units in the center of **7b** allows greater mobility and decreased crystalline packing to the point that **7b** exhibits LC behavior. A broad DSC endotherm is observed centered at 41.9 °C with a shoulder at 48.8 °C in the heating cycle which corresponds to the S → I seen at 52.5 °C by optical microscopy as a much finer grained smectic B-like texture compared to those seen for monomers **2d** and **6b**. When heated above 52.5 °C, this phase is transformed to an isotropic liquid. For these diacrylates, subsequent heating and cooling cycles were not identical due to spontaneous thermal polymerization and cross-linking.

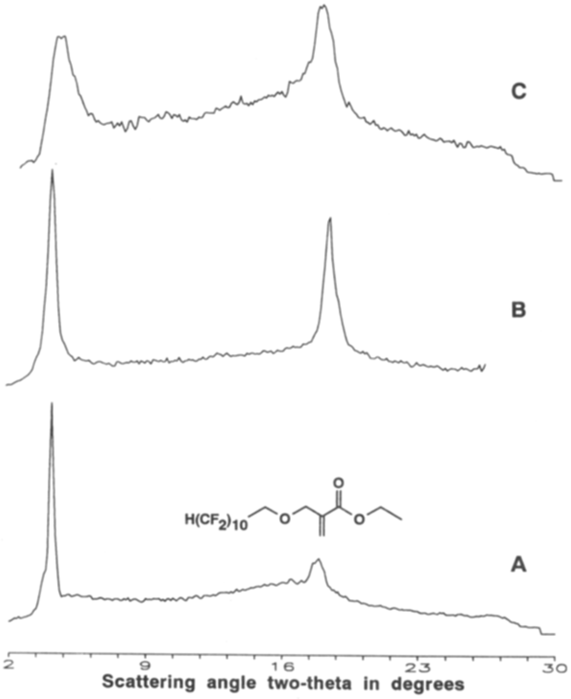

Figure 9. X-ray diffraction pattern at room temperature of monomer **2d** (trace A), its polymer polymerized in the mesophase (trace B), and material polymerized in the isotropic phase and precipitated (trace C).

The LC phases of monomer **2d** and diacrylate **7b** were confirmed by X-ray analysis done at room temperature by placing the sample in a quartz capillary, heating to the isotropic phase, and then allowing it to cool into the mesophase. Figure 9 (trace A) shows the two reflections seen in the powder diffraction pattern of monomer **2d**. The sharp reflection occurring at low angles corresponds to a lamellar thickness of 21.01 Å, in good agreement with the value of 20.9 Å estimated for the molecular length of the monomer by computer modeling. The wide-angle reflection centered at 4.92 Å is attributed to the intermolecular distance between CF_2 chains. X-ray analysis of the monomers **6a** and **6b** was not possible on our instrument due to the S → I transitions occurring below room temperature. The diffraction pattern of **7b** shows three reflections. The smallest angle reflection represents arrangement of the molecules in lamellar layers with a thickness of 23.8 Å. The weak reflection occurring at 9.5 Å may be the second-order peak for this structure while the reflection at 4.95 Å corresponds to intermolecular distances.

The combined analytical methods used confirm formation of liquid crystalline domains for the compounds

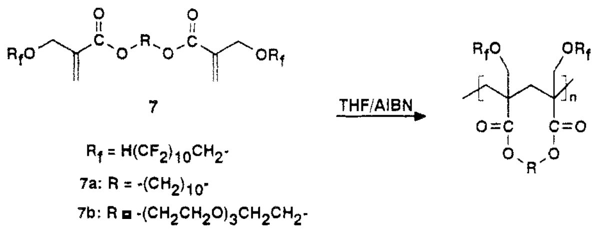

Figure 10. Polymerization scheme for the cyclopolymers.

2d, **6a**, **6b**, and **7b**. The questions of whether similar behavior could occur in the polymer and if polymerization were possible in the LC phase are addressed below.

Polymer Synthesis and Characterization. Monomers **2a–e** and **5** were polymerized in bulk at 50–70 °C using AIBN to give high conversion to polymers over an 8–12-h period. After reprecipitation of the polymers into hexanes, they were characterized by FTIR, NMR, intrinsic viscosity, GPC, DSC, and optical microscopy. As reported in a previous communication describing **2a–d**, the FTIR spectra of the polymers showed no residual monomer as seen from the absence of the vinyl stretch at 1637 cm^{-1} and shifting of the carbonyl peak of the monomer from 1717 to 1734 cm^{-1}. Solution-state ^{13}C NMR spectra (in $CDCl_3$) clearly showed disappearance of the monomer double-bond carbons (at ca. 126 and 136 ppm) and appearance of broad peaks for the backbone α and β carbons at ca. 49 and 41–43 ppm, respectively. Representative carbon positions and peaks are indicated on the structure and on the solid-state spectrum of the polymer obtained from **5** in Figure 4. The broad peak at 109.1 ppm is due to the trifluoromethyl groups.

Bulk polymerization of monomers **6a** and **6b** gave insoluble but swellable polymers due (apparently) to the presence of trace amounts of ether dimers formed from the bisacid chloride ether of intermediate **4** which was not removed by distillation.[22] These gels could be easily swollen in hydrocarbon and fluorocarbon solvents, indicating that they were lightly cross-linked. Soluble polymers were obtained from **6a** and **6b** by solution polymerization in α,α,α-trifluorotoluene; such conditions favor cyclopolymerization of the ether diacrylates.[23] The reaction mixture was homogenous after heating for 24 h, and precipitation into hexanes or methanol gave the polymers in 88–90% yield. Comparing the ^{13}C NMR spectra of monomer **6b** and its polymer (traces A and B, respectively, in Figure 5) reveals no residual vinyl peaks of the monomer at 127.03 and 135.9 ppm and the appearance of backbone α and β carbons at ca. 49 and 39 ppm. Monomer **6c** was polymerized in bulk for 7 days at 55 °C using AIBN as initiator. Purification by precipitation from hexanes gave 15% of the polymer; the rest was unreacted monomer. Characterization of this polymer by FTIR and NMR techniques showed the absence of residual vinyl peaks.

Bulk polymerization of the diacrylates **7a** and **7b** gave as expected highly cross-linked polymers as indicated by the absence of vinyl peaks in the solid-state ^{13}C NMR spectra and by the inability of these polymers to swell in common organic solvents. However, solution polymerization of the diacrylates **7a** and **7b** in THF (as shown in Figure 10) gave a slightly viscous, soluble product. Precipitation of these materials into hexanes and vacuum drying gave the polymers in ca. 90% yield. The polymer obtained from **7a** did not redissolve completely but could be easily swollen in solvents like $CHCl_3$ and THF, indicating a low cross-link density. This polymer must therefore have a high degree of cyclization. The polymer obtained from **7b** was completely soluble. Apparently, the more flexible oligo(oxyethylene) central spacer favors intramolecular attack (versus intermolecular) of the growing free radical to give the cyclic units almost exclusively. The FTIR spectra of both polymers showed disappearance of the vinyl peak at 1637 cm^{-1}. The formation of the cyclopolymer from **7b** was confirmed by its solution-state ^{13}C NMR spectrum which showed the absence of vinyl groups at ca. 127 and 136 ppm and the presence of broad backbone carbon peaks at 42.9 and 49.8 ppm. The cyclopolymerization of the diacrylate **7b** is analogous to that previously reported for oxybisacrylates (such as the ether dimer of tBHMA). The flexible sp^3-hybridized linkages connecting the acrylate units favor formation of cyclopolymers containing pyran units in the backbone.[23] Triethylene glycol dimethacrylate under dilute conditions has also been reported to give soluble cyclopolymers.[24] The cyclopolymerizability of monomers **7a** and **7b** may be enhanced through lipophobic association of the perfluoroalkyl segments, which would bring the acrylate units into close proximity.

Table I. Viscosity and Molecular Weights of Polymers

polymer from	intr visc (dL/g) at 32 °C	M_w	M_n	M_w/M_n
2a	0.49[a]	759 000	413 000	1.84
2b	0.44[b]			
2c	0.24[b]			
2d	0.25[b]	677 000	333 000	2.04
2e	0.28[c]	302 000	186 000	1.62
5	0.41[d]	220 000	149 000	1.47
6a	0.08[e]	49 000	39 000	1.24
6b	0.09[e]	60 000	45 000	1.31
6c	0.09[e]	39 800	32 300	1.23
7b	0.03[e]	15 000	12 000	1.25

[a] In chloroform. [b] In 1,1,2-trichlorotrifluoroethane. [c] In THF. [d] In THF/TFE (80:20). [e] Inherent viscosity in 1–3% solution in THF or THF/TFE.

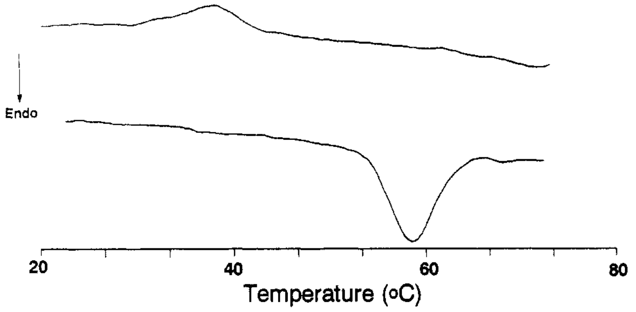

Figure 11. DSC scans of polymer obtained from **2d**, first heating (bottom trace) and first cooling cycle (top trace).

High molecular weight (MW) polymers were obtained from monomers **2a–e** and **5** as indicated by the intrinsic viscosity values and by the estimated MWs obtained by GPC (Table I) despite substitution in the α-methyl position by the relatively large fluoroalkyl ether groups. However, solution-polymerized samples of monomers **6a** and **6b** containing larger alkyl ester groups gave low-MW polymers as seen from the inherent viscosity and GPC data. This may be due to a decrease in the rate constants for propagation and termination, similar to the small rate constants reported for dialkyl itaconates.[25,26] Comparison of the viscosity and GPC values for the polymers obtained from **2d** versus **6c** (Table I) show that the monomer with the ethyl ester substituent gave a polymer with M_w of 677 000, much higher than the M_w value of only 39 800 obtained for the polymer with the *tert*-butyl ester substituent obtained under the same conditions. The low reactivity of monomer **6c** may be due to steric hindrance caused by the bulky *tert*-butyl substituent which reduces the rate of propagation, causing a reduction in both conversion and molecular weight.

Table II. DSC Transition Temperatures and Enthalpies Obtained for Six Monomers and Their Corresponding Polymers

		first heating		first cooling		second heating
monomer	T (°C)	ΔH [J/g (kJ/mol)]	T (°C)	ΔH [J/g (kJ/mol)]	T (°C)	ΔH [J/g (kJ/mol)]
2d	32.3	29.7 (19.0)	24.4	−27.7 −(17.8)	31.8	26.6 (17.07)
polymer	59.0	9.2 (5.9)	38.3	−3.0 −(1.9)	59.1	3.6 (2.3)
6a	20.0		15.0	−12.2 −(9.3)		
polymer	49.2	8.0 (6.1)	28.2	−3.9 −(3.0)	43.6	3.2 (2.4)
6b	26.4	17.8 (13.0)	21.4	−15.6 −(11.4)	26.5	14.5 (10.6)
polymer	49.3	8.3 (6.1)	24.8	−2.9 −(2.1)	43.9	4.1 (3.0)
6c	13.1	11.6 (8.2)	8.8	−11.9 −(8.4)	13.5	12.0 (8.4)
polymer	65.0	1.2 (0.9)		no exotherm		no endotherm
7a						
polymer	56.7	2.3 (3.1)		no exotherm		no endotherm
7b						
polymer[a]	63.7	4.0 (5.6)	42.3	−2.4 (−3.3)	59.6	2.3 (3.3)

[a] Measured enthalpies were divided by 2 to give values per "reactive" segment for the dimer polymers that are more comparable to the other values listed.

Optically transparent films which showed excellent flexibility at room temperature could be solvent-cast for polymers obtained from **2a–e** and **5**. Polymers obtained from **6a–c** were brittle and slightly opaque. Polymers from **6b** and the diacrylate **7b** (each containing ethylene oxide and fluoroalkyl groups) could be dissolved in warm $CHCl_3$ or CH_2Cl_2 at 1–3 wt % and cooled to room temperature to give slightly opaque, solvent-swollen gels with large zero-shear viscosities. Upon heating, these gels were transformed back into transparent, low-viscosity solutions. Optical microscopy of the gels showed birefringence and a microfibrillar morphology which disappeared on heating. This behavior was not seen in the other polymers described here, although a similar phenomenon has been known to occur in binary mixtures of semifluorinated alkanes with hydrocarbon or fluorocarbon solvents.[27]

DSC analysis of the polymers showed no observable glass transitions even after quenching in liquid nitrogen, although side chain crystallization was observed for the longest fluoroalkyl ether polymers. A previous report on 1,1-dihydroperfluoroalkyl acrylate polymers indicated that glass transition temperatures decreased with increasing length of the side chain up to groups with 8 or 10 CF_2 units which displayed side chain crystallinity as shown by first-order transitions in the DSC.[7] Similarly, reprecipitated samples of the four polymers containing 10 CF_2 units in the side chain (**2d** and **6a–c**) showed an endothermic first-order transition by DSC. This behavior is similar to that displayed by polymers containing linear alkyl side groups with greater than 8–12 carbons which show side chain crystallization independent of the backbone.[28] A representative DSC scan for the polymer obtained from **2d** (Figure 11) shows an endothermic peak at 58 °C on the first heating cycle (bottom trace). A 21 °C supercooling of this transition is seen for the exotherm of the corresponding cooling cycle (top trace). Quantitative DSC data obtained for these four polymers containing 10 CF_2 units (Table II) show that the enthalpy change (ΔH) associated with the exotherm of the first cooling cycle is much less than that of the endotherm of the first heating cycle.

The missing enthalpy must be due to incomplete "recrystallization" of the side chains (from the melt) which have difficulty in packing due to restricted mobility of the closely-bound polymer backbone. For the polymer from **6c**, the bulkiness of the *tert*-butyl group completely blocks crystallization of the ether-linked fluoroalkyl group, due to either very slow backbone mobility or complete steric inhibition of crystalline packing.

The cyclopolymers of monomers **7a** and **7b** show a broad heating endotherm (55–70 °C) which was much reduced on subsequent heating cycles. The transition temperatures and the enthalpy change are comparable with those for side chain melting of the linear polymers, while the broadness of the transitions may be due to even greater degrees of restricted backbone motion which inhibits formation of well-defined crystallites. In fact, the polymer obtained from **7a** (lightly cross-linked) showed no "recrystallization" of the fluoroalkyl side groups when cooled from the isotropic melt.

Optical microscopy of the polymers obtained from **2a–c** and **5** does not show birefringence and is consistent with the DSC data which show an absence of first-order transitions due to crystallization. Polymers **2d** and **6a–c** containing ten CF_2 units showed birefringence and exhibited a fine-grained texture. Heating these samples above their melting point and then cooling at 10 °C/min does not induce birefringence even after annealing for 1–2 days at 10–15 °C below their melting points. However, applying pressure to the glass slide produces shear birefringence which only disappears on subsequent heating. Recent reports on polymers of perfluoroalkyl fumarates, methacrylates, and acrylates indicate that, while acrylate and methacrylate polymers with perfluorooctyl and perfluorodecyl ester units form highly ordered smectic B or smectic A phases, the corresponding fumarate polymers were amorphous.[29,30] The behavior of the fumarate polymers was attributed to decreased main chain flexibility which inhibits formation of the ordered structures. The reduced ability of the polymers described here to form ordered LC domains (as opposed to the smectic B-like phase formed by the corresponding monomers) is thought to be due to low mobility caused by a combination of inherent rigidity of the main chain and tight coupling of the fluoroalkyl side groups to the backbone by a short spacer.

History-dependent differences in crystallization behavior were confirmed by X-ray powder diffraction data of the polymer of **2d** after reprecipitation (trace C in Figure

9). Two diffuse peaks are seen at scattering angles (2θ) of 4.3 and 17.8° corresponding to Bragg spacings of 20.5 and 4.97 Å, respectively. The 20.5-Å spacing indicates that there is well-ordered lateral packing of the side chains and correlates well with the calculated value of 20.9 Å obtained from computer modeling. However, both peaks are diffuse compared to those of the monomer in the LC phase, indicating a lower degree of lateral order for the polymer. Photopolymerization of monomer **2d** in the mesophase in a quartz capillary (at 20 °C, initiated with Irgacure 651) gave a polymer sample with *increased* order as shown by the X-ray diffraction pattern of the as-polymerized polymer (trace B; FTIR analysis of this sample indicates almost quantitative conversion to polymer). The sharpness of both peaks (at 4.3 and 18.2° in trace B) suggests that the lateral order of the LC phase of the monomer was maintained in the polymer during polymerization.[31] In fact, the increase in the side chain packing peak (18.2°, 4.97 Å) seems to indicate *enhanced* lateral packing order in the polymer compared to the monomer. This is reasonable, given the higher S → I transition temperature for the polymer; that is, the monomer LC phase is very close to its upper stability limit at room temperature (analysis temperature for the X-ray diffraction determination) while the polymer is considerably below its transition and should therefore have more ordered side chain crystallites.

Conclusions

We have developed facile syntheses of hydrophobic and hydrolytically stable fluoroalkyl ether monomers from ECMA in high yields. Rapid free radical homopolymerization of these monomers seems to result from a balance between reduced polymerizability due to steric effects (caused by fluoroalkyl groups) and increased chain-end and/or monomer reactivity due to electronic effects (caused by the CH_2O group). Such behavior seems to be general for a variety of derivatives of the family of α-(hydroxymethyl)acrylates. Conversion of tBHMA to the intermediate **4** makes available a multifunctional intermediate which allows synthesis of novel amphiphilic monomers with controlled hydro- and lipophobicity (by substitution with various perfluoroalkyl ether and ester groups) along with variable lipophilicity or hydrophilicity by incorporation of groups such as longer alkyl groups or oligomers of ethylene oxide. Incorporation of two large substituents in the monomers **6a** and **6b** gave polymers with low MW possibly due to a greater sterically-induced decrease in propagation rate. This effect was even more pronounced in the *tert*-butyl ester monomer, which reacted only after prolonged polymerization with increased amounts of initiator. Additionally, the incorporation of the 10 CF_2 units in the ether pendent group can result in novel lamellar LC phases as seen by the formation of a highly ordered smectic B-like phase for some of the monomers. While polymers from these monomers do not show LC behavior, they do exhibit side chain crystallization independent of the main chain behavior and the order of the LC phase can be locked in by in situ photopolymerization. The amphiphilic monomers described here also have potential applications as polymeric surfactants, as compatibilizers in blends, as surface modifiers, and for generating hydrophobically modified water-soluble polymers.[32-34]

Acknowledgment. We are grateful to the National Science Foundation (Grant DMR-9111903) for partial support of this project and to the Department of Defense for an instrumentation grant through the Office of Naval Research for the purchase of our Bruker MSL-200 spectrometer. Partial support of C.P.J. by the Department of Chemistry and Biochemistry is greatly appreciated.

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