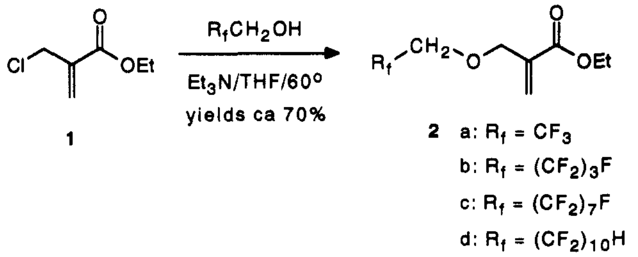
New Hydrophobic and Liquid-Crystalline Fluoroalkyl Ether Derivatives of Ethyl α-(Hydroxymethyl)acrylate: Monomer Synthesis and Polymerization

Introduction. Polymers rich in fluorine generally have high thermal stability, chemical and oxidative resistance, and a low refractive index. They are used, for example, in nonstick cookware, fabric treatments, lubricating oils and greases, car finishes, contact lenses, and optical fibers.[1] A key property of such polymers is their low surface energy. Illustrative is the surface free energies of single-carbon fragments which decrease in the order $-CH_2 > -CH_3 > -CF_2 > -CF_3$.[2] Such a low surface energy prevents sticking and adhesion, polymer blending and degradation, and attack or solvation by aqueous solutions and most organic solvents. 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.[3] In addition, a recent report describes the ability of semifluorinated alkyl methacrylates [e.g., $F(CF_2)_{12}(CH_2)_4O_2CC(CH_3){=}CH_2$] to form apparent liquid-crystal gels that can be converted directly to polymers photochemically.[4] We wanted to combine the properties of fluorocarbon segments with those of methacrylate groups in a new family of monomers which would provide increased stability, flexibility, and solvent resistance and perhaps a modified or improved ability to form liquid-crystalline phases.

Most of the fluoroacrylate monomers reported in the literature were prepared by esterification of a fluoroalcohol with acryloyl chloride,[5] although a novel synthesis from perfluoroketones reportedly works well.[6,7] In addition, several fluoroalkyl acrylates and methacrylates are available commercially (PCR, Inc., P.O. Box 1466, Gainesville, FL 32602; Polysciences, Inc., 400 Valley Road, Warrington, PA 18976; and Aldrich Chemical Company, Inc., 1001 West St. Paul Avenue, Milwaukee, WI 53233). We have developed a new synthetic approach to substituted methacrylates which involves synthesizing ethyl α-(chloromethyl)acrylate (ECMA) and then substituting with various nucleophiles.[8] The monomers readily polymerize using AIBN to give homopolymers and copolymers. This paper describes the synthesis of four new fluoroether monomers, their thermal and photochemical radical polymerization, and characterization of the obtained polymers. Most interesting is the ability of one new monomer to form polymerizable mesophases.

Experimental Section. Ethyl α-(hydroxymethyl)acrylate (EHMA) and ECMA were prepared using the previously published procedures.[8] The alcohols used (trifluoroethanol, 1*H*,1*H*-perfluorobutanol, 1*H*,1*H*-perfluorooctanol, and 1*H*,1*H*,11*H*-eicosafluoroundecanol) were purchased from Aldrich and PCR and used as obtained.

General Procedure for the Synthesis of the Fluoroether Acrylate Monomers. To a stirring mixture of the fluoroalcohol (83 mmol) and triethylamine (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 vacuum filtered and the THF evaporated under reduced pressure. The residue was passed through a silica gel column with chloroform as eluent. The chloroform was evaporated under reduced pressure. Vacuum distillation of the residue gave monomers as clear liquids except for **2d** which was a waxy solid. Yields ranged from 69 to 71%.



General Polymerization Procedure. Neat monomer (usually ca. 2.5 g) was mixed with AIBN (0.1 mol %) and the mixture 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 **2a** was dissolved in warm chloroform, while **2b–d** were dissolved in 1,1,2-trichlorotrifluoroethane, and the products slowly precipitated into cold hexanes. The precipitate was filtered and dried under vacuum. Yields ranged from 69 to 84%.

Results and Discussion. Conversion of the CH_2OH group of the readily available ethyl α-(hydroxymethyl)acrylate (EHMA) to the more reactive CH_2Cl group makes substitution and ether formation 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. Facile substitution of ECMA probably involves a combination of alcohol activation by Et_3N and high ECMA reactivity due to allylic attack giving a 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.

The ^{13}C NMR spectra of the monomers clearly show the absence of the methylene carbon (CH_2Cl) at 61.0 ppm and the presence of a triplet or quartet at 67.7 ppm (OCH_2CF_3) plus a singlet at 68.6 ppm ($=CCH_2O$) indicating the formation of the ether. All the monomers obtained were liquids except for **2d**, which was a waxy solid at room temperature.

Bulk polymerizations of the monomers at 50–70 °C with AIBN proceeded smoothly. After reprecipitation of the polymers into hexanes, they were characterized by FTIR, NMR, and intrinsic viscosity. The FTIR spectra 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} in the polymer. Figure 1 shows solution ^{13}C NMR spectra of monomer **2a** (trace A) and its polymer (trace B) in $CDCl_3$. These clearly show disappearance of the double bond carbons of the monomer at 126.2 and 136.2 ppm and appearance of the backbone α and β carbons at 49.4 and 42.5 ppm, respectively. The solid-state ^{13}C CP/MAS spectra (traces C and D) correspond to the polymers obtained from monomers **2c** and **2d** and show no residual vinyl carbons. The backbone α and β carbons are at ca. 49 and 39–41 ppm, respectively, while the broad peak at 109.1 ppm is due to the fluorocarbon groups. Representative carbon positions and peaks are indicated on the structure and the solution spectrum in Figure 1; peaks in the solid-state spectra are broadened and shifted somewhat but correlate with the solution peaks.

The intrinsic viscosity values measured at 32 °C for polymers obtained from **2a–d** were 0.49, 0.44, 0.24, and 0.25 dL/g, respectively, in $CHCl_3$ (**2a**) or 1,1,2-trichlorotrifluoroethane (**2b–d**). These values confirm that rea-

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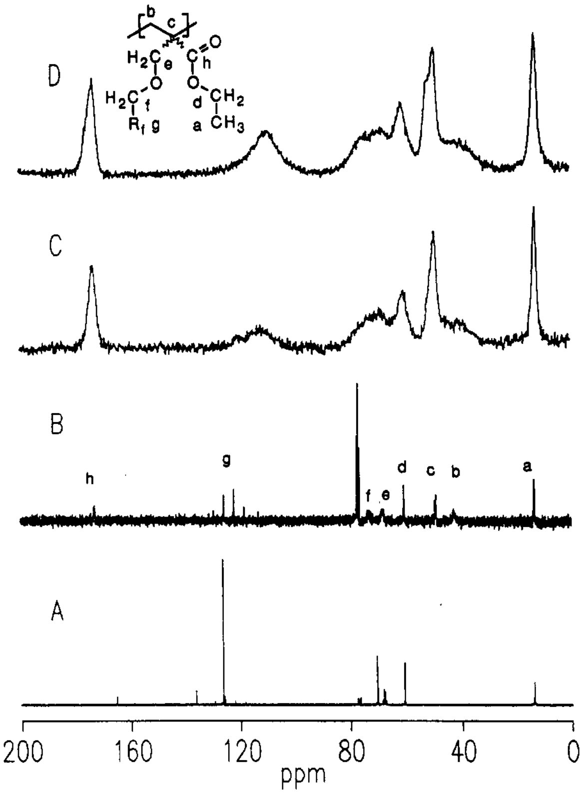

Figure 1. Solution ^{13}C NMR spectra of monomer **2a** (trace A) and its polymer (trace B) and ^{13}C CP/MAS spectra of polymers from **2c** and **2d** (traces C and D, respectively).

sonably high molecular weight polymers were obtained in good yields. Films could be solvent-cast which were optically transparent, and all four polymers showed excellent bulk sample flexibility at room temperature. Initial DSC analysis indicates no strong glass transitions for any of these materials, behavior similar to many fluoroalkyl acrylate polymers.[9]

Most interesting was the ability of **2d** to form liquid-crystalline phases. DSC analysis showed a clearing transition at 32 °C on heating (10 °C/min under N_2); the mesophase reformed at ca. 24 °C. On cooling from the isotropic melt under a polarizing optical microscope, this monomer showed a smectic B type liquid-crystalline texture similar to those seen for semifluorinated alkanes.[10] Photopolymerization in the mesophase did not disrupt the liquid-crystalline phase at conversions up to 40%. In addition, the clearing temperature was raised to 78 °C. Similar behavior was observed for the semifluorinated methacrylates, which also maintained their mesophases and showed increased clearing temperatures of ca. 40 °C for the polymers.[4] The pure polymer of **2d** did not show liquid crystallinity when isolated after polymerization in solution. Preliminary polymerization rate studies under photoinitiation show a unique behavior for this monomer in the liquid-crystalline phase. Especially noteworthy are the very long lifetimes of the propagating radicals after stopping photolysis: molecular weights and conversion continue to grow for tens of hundreds of seconds. Additional study of these and related monomers is underway with respect to polymer properties and especially the polymerization kinetics in the liquid-crystalline state.

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Chetan P. Jariwala, Per-Erik G. Sundell,
Charles E. Hoyle, and Lon J. Mathias*

Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39406-0076

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