Facile and Inexpensive Synthesis of α,β,β′-Deuterated Liquid Crystalline and Classical Acrylate Monomers

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Received May 14, 2001

Revised Manuscript Received October 16, 2001

Neutron scattering, associated with selective deuterium labeling, has long been recognized as a very powerful tool for studying the backbone conformation of both "classical"[1,2] and liquid crystalline polymers.[3−6] Over the years, the systems being investigated have become more and more chemically and structurally complex (elastomers, polyelectrolytes, block copolymers, brushes of polymers, etc.), so new methods of deuterium incorporation at well-defined positions in more "sophisticated" or functionalized monomers are needed. In the course of our work on liquid crystalline polymers, we developed the synthesis of backbone-deuterated mesomorphic polymethacrylates and polyacrylates. Although it is relatively easy and inexpensive to prepare perdeuterated $^2H_5$-methacrylic acid derivatives from perdeuterated acetone using classic textbook chemistry,[7,8] there is no well-established simple route for the synthesis of $^2H_3$-acrylic derivatives.[9] To push further our recent studies on nematic acrylate elastomers[10] as model systems for artificial muscle actuators, we became interested in gaining specific structural information, such as the order parameters of the backbone and the mesogenic group using FTIR and the backbone conformation using SANS. Most of the studies we were planning were based on easy access to selectively deuterated acrylate elastomers.

In our quest for a simple and inexpensive route for the synthesis of $^2H_3$-acrylic acid derivatives, we became aware of a recent paper by Pitlik and Townsend[11] which described the synthesis of multiply labeled (i.e., ^{13}C and ^2H) carbohydrates. In their synthesis, the preparation as intermediates of selectively deuterated acrylic acid derivatives was described, the key step being a Wittig reaction between a phosphonium salt and commercially available deuterated formaldehyde (as a 20% solution in D_2O). Making use of this key reaction, we have developed a very simple, efficient, and inexpensive route for the preparation of $^2H_3$-labeled liquid crystalline acrylate monomers and explored the possibility of synthesizing "classical" or simple acrylate monomers such as benzyl 1,2,2-$^2H_3$ acrylate, which could find application in the synthesis of backbone-deuterated poly(acrylic acid) after deprotection.

Multistep routes designed to prepare typical deuterated side-on and side-end liquid crystalline acrylate monomers are presented in Schemes 1−3, and the synthesis of benzyl $^2H_3$-acrylate is outlined in Scheme 4.

The first step in the synthesis of deuterated side-on and side-end liquid crystalline acrylate monomers involved the transformation of a terminal carbon−carbon double bond to a terminal hydroxyethyl group using borane chemistry.[12] The hydroboration reaction, using 9-borabicyclo[3.3.1]nonane (9-BBN), was followed by an oxidation step to obtain the hydroxy function using *m*-chloroperbenzoic acid as oxidant as proposed by Pelter.[13] The gentle reaction conditions used are well adapted to the presence of ester groups in the starting material, thus avoiding most of the side reactions produced when using the classical H_2O_2/NaOH oxidation route and base-sensitive compounds.

The hydroxy-functionalized liquid crystalline compounds were then esterified[14] with bromoacetic acid in the presence of dicyclohexylcarbodiimide and pyrrolidinopyridine to give the bromoesters.

These bromoesters were reacted with triphenylphosphine at room temperature to give, by a Arbuzov reaction, the phosphonium salts which were used in the next step without further purification.

Treating these phosphonium salts dissolved in dry THF with the ^2H-labeled formaldehyde (as a commercial 20% solution in D_2O) in the presence of solid potassium carbonate at room temperature produced the expected $^2H_3$-labeled acrylates.

Similarly, reacting the triphenylphosphonium salt of benzyl bromoacetate with $^2H_2$-formaldehyde in dry THF in the presence of K_2CO_3 produced the benzyl $^2H_3$-acrylate in good yield and high level of deuteration.

For all the monomers synthesized, the level of deuterium incorporation was determined by proton NMR to be better than 95% and slightly different for the α and β positions. Deuteration at the β and β′ positions was better than 98%, while it was around 96% for the α position. This difference originates from the chemistry, the β and β′ deuterium atoms coming from the deuterated formaldehyde via the Wittig reaction and the α deuterium atom by fast exchange between the hydrogen in α of the phosphonium group and D_2O prior to the Wittig reaction. (^1H NMR spectra for all the deuterated monomers synthesized are presented in the Supporting Information.)

In conclusion, we have described a very simple, inexpensive, but efficient synthesis of $^2H_3$-labeled acrylate monomers. The deuterated side-on liquid crystalline monomers will be used in the synthesis of new macroscopically oriented nematic elastomers. Making use of the specific labeling, FTIR and SANS experiments will be performed in order to obtain structural information about these new materials which are promising models of "artificial muscles".[10]

Experimental Section

Materials and Techniques. 2,5-Dihydroxybenzoic acid, 4-bromo-1-butene, 3-bromo-1-propene, 4-butyloxybenzoic acid, 4-pentylcyclohexylcarboxylic acid, bromoacetic acid, benzyl bromoacetate, triphenylphosphine, *N*,*N*-dicyclohexylcarbodiimide, and pyrrolidinopyridine were used as received from Aldrich. 3-Chloroperbenzoic acid (pract.,70%) and 9-BBN (as a 0.5 M solution in THF) were from Fluka. Formaldehyde-$^2H_2$

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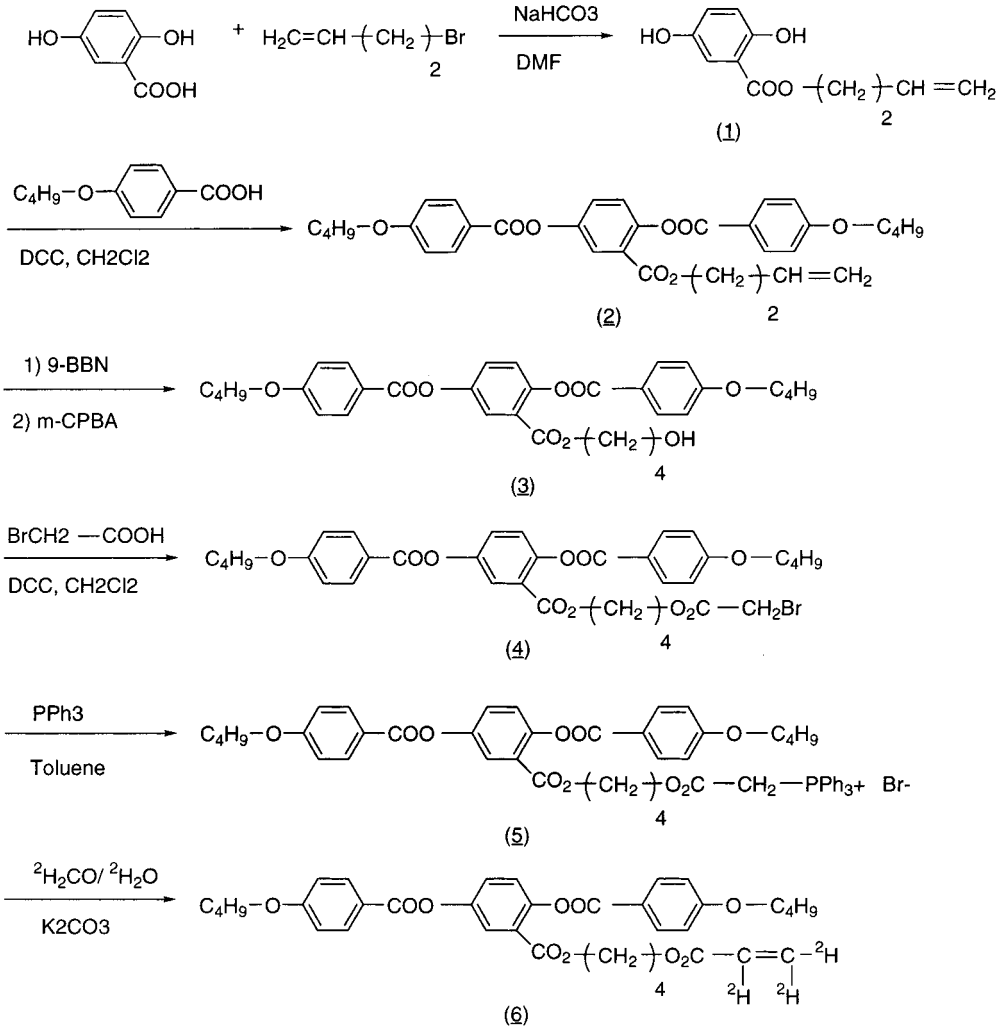
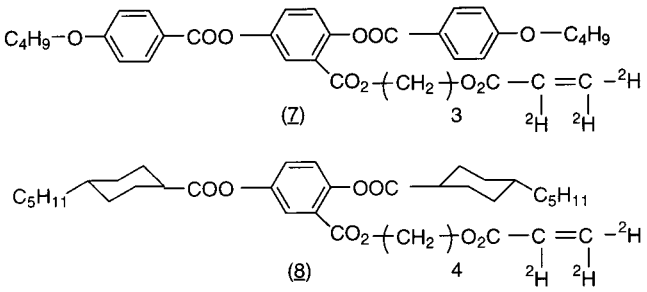
10.1021/ma010838m CCC: $22.00
Published on Web 12/13/2001

Scheme 1. Side-On Liquid Crystalline Monomer Synthesis



Scheme 2. Structure of Other Synthesized Side-On Monomers



was from Isotech Inc. or Aldrich (as a 20% solution in ^2H_2O). All other reagents and solvents were commercially available and used as received.

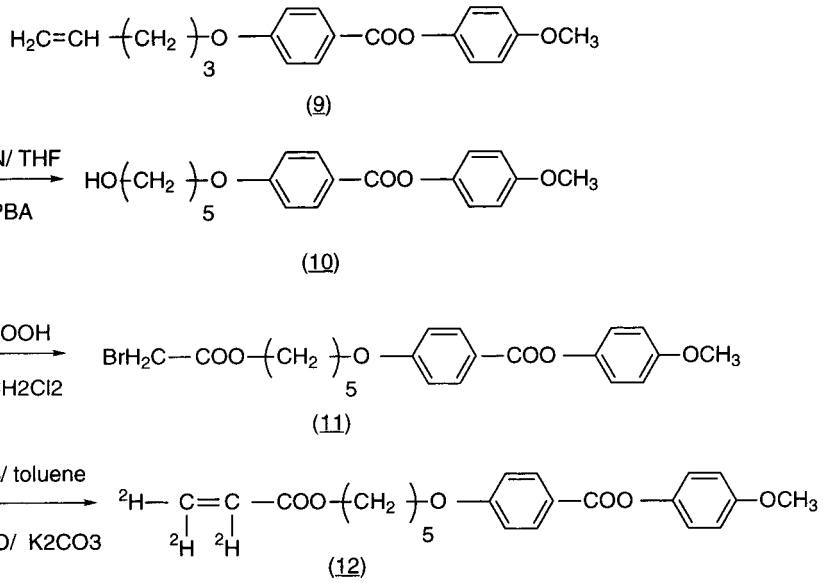
Textures and transition temperatures for the synthesized compounds were observed by polarizing optical microscopy using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP 82 heating stage (K = crystal; N = nematic phase; I = isotropic phase).

^1H NMR spectra (δ, ppm) were recorded on either a Bruker 300 MHz or 400 MHz spectrometer. All spectra were recorded in $CDCl_3$. Elemental microanalyses were performed at Service de Microanalyse (I.C.S.N.-CNRS, Gif, France).

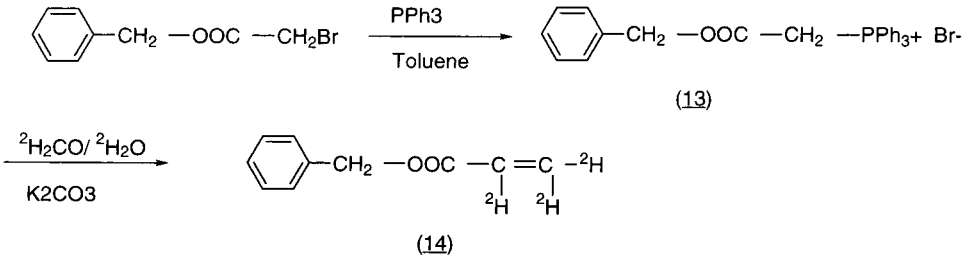
Synthesis of (4″-((α,β,β′-$^2H_3$)-acryloyloxy)butyl) 2,5-Di-(4′-butyloxybenzoyloxy)benzoate (6). (But-3′-enyl) 2,5-dihydroxybenzoate (**1**): To a stirred solution of 2,5-dihydroxybenzoic acid (3.08 g, 20 mmol) in DMF (30 mL) was added solid $NaHCO_3$ (4.95 g, 58.5 mmol). The mixture was stirred at 70 °C for 1 h. 4-Bromo-1-butene (2.7 g, 20 mmol) was then added, and the reaction was maintained at 70 °C for 7 h. The reaction mixture was cooled, diluted with water (100 mL), and extracted twice with 60 mL of a 50:50 hexane/ethyl acetate mixture. The organic phases were washed twice with water (100 mL) and dried over Na_2SO_4. After evaporation of the solvents, the solid residue was purified by column chromatography on a short column of silica gel with diethyl ether as eluting solvent; yield 3.75 g (18 mmol, 90%) of white solid (K 53 °C I).^1H NMR: 2.52 (m, 2H, $-CH_2-CH=$), 4.37 (m, 2H, $-CO_2-CH_2-$), 5.19 (m, 2H, $=CH_2$), 5.84 (m, 1H, $-CH=CH_2$), 6.8 (d, 1H, arom), 7 (m, 1H, arom), 7.2 (m, 1H, arom), 10.4 (s, $-OH$). Anal. Calcd ($C_{11}H_{12}O_4$): C (63.45%), H (5.80%). Found: C (63.47%), H (5.79%).

(But-3″-enyl) 2,5-di(4′-butyloxybenzoyloxy)benzoate (**2**): A solution of **1** (3.75 g, 18 mmol), 4-butyloxybenzoic acid (7.7 g, 39.6 mmol), *N*,*N*-dicyclohexylcarbodiimide (8.77 g, 42.5 mmol), and pyrrolidinopyridine (0.6 g, 4 mmol) in 180 mL of dichloromethane was stirred at room temperature for 24 h. The *N*,*N*′-dicyclohexylurea was removed by filtration, and the filtrate was washed with water (200 mL), a 5% acetic acid solution (150 mL), water (200 mL), and dried over Na_2SO_4. After evaporation of the solvent, the crude product was recrystallized twice from ethanol and dryied under vaccuum to give 7.5 g (13.3 mmol, 74%) of white solid (K 101 °C N 114 °C I). ^1H NMR: 1 (t, 6H, $-CH_3$), 1.53 (m, 4H, $-CH_2-CH_3$), 1.83 (m, 4H, $-CH_2-CH_2-CH_3$), 2.26 (m, 2H, $-CH_2-CH=$), 4.05 (t, 4H, $O-CH_2-$), 4.21 (t, 2H, $-CO_2-CH_2-$), 5 (m, 2H, $H_2C=CH-$), 5.68 (m, 1H, $-CH=CH_2$), 6.98 (d, 4H, arom), 7.25 (m, 1H, arom), 7.45 (m, 1H, arom), 7.88 (d, 4H, arom), 8.1 (m, 4H, arom). Anal.

Scheme 3. Side-End Liquid Crystalline Monomer Synthesis



Scheme 4. Deuterated Benzyl Acrylate Synthesis



Calcd ($C_{33}H_{36}O_8$): C (70.69%), H (6.47%). Found: C (70.75%), H (6.25%).

(4″-Hydroxybutyl) 2,5-di(4′-butyloxybenzoyloxy)benzoate (**3**). To a stirred solution of **2** (7 g, 12.5 mmol) in 100 mL of dry THF kept under argon was added via syringe 9-BBN as a 0.5 M solution in THF (27.5 mL, 13.75 mmol). The mixture was stirred overnight at room temperature under argon.

The solution was then cooled in an ice/water bath, and solid *m*-chloroperbenzoic acid (*m*-CPBA) (12.4 g, of commercial (70%) acid) was added slowly in small portions. After stirring at room temperature overnight, the reaction mixture was diluted with water (200 mL) and extracted twice with dichloromethane. The organic phases were washed thoroughly with a saturated sodium bicarbonate solution (4 × 250 mL) and water (250 mL) and then dried over Na_2SO_4. After evaporation of the solvent, the solid residue was purified by recrystallization from ethanol to give 6.4 g (11 mmol, 88%) of white solid (K 79 °C N 104 °C I). (Alternatively, the compound might be purified by column chromatography on silica gel using a 50/50 hexane/ethyl acetate mixture.) ^{1}H NMR: 1 (t, 6H, $-CH_3$), 1.53 (m, 8H), 1.81 (m, 4H, $-O-CH_2-CH_2-$), 3.52 (t, 2H, $HO-CH_2-$), 4.05 (m, 4H, $-O-CH_2-$), 4.2 (m, 2H, $-CO_2-CH_2-$), 6.98 (d, 4H, arom), 7.26 (m, 1H, arom), 7.45 (m, 1H, arom), 7.88 (d, 1H, arom), 8.15 (m, 4H, arom). Anal. Calcd ($C_{33}H_{38}O_9$): C (68.49%), H (6.61%). Found: C (68.30), H (6.64).

(4″-(Bromoacetyloxy)butyl) 2,5-di(4′-butyloxybenzoyloxy) benzoate (**4**): A solution of **3** (2.89 g, 5 mmol), bromoacetic acid (0.76 g, 5.5 mmol), *N*,*N*-dicyclohexylcarbodiimide (1.13 g, 5.5 mmol), and pyrrolidinopyridine (0.08 g, 0.55 mmol) in 50 mL of dichloromethane was stirred at room temperature for 12 h. The *N*,*N*-dicyclohexylurea was removed by filtration, and the filtrate was washed with water (100 mL), a 5% acetic acid solution (100 mL), and water (100 mL) and dried over Na_2SO_4. After evaporation of the solvent, the crude product was recrystallized twice from ethanol to give 2.6 g (3.7 mmol, 75%) of white solid (K 101 °C I (79 °C monotropic N)). ^{1}H NMR: 1 (t, 6H, $-CH_3$), 1.56 (broad m, 8H), 1.81 (m, 4H, $-O-CH_2-CH_2-$), 3.79 (s, 2H, $Br-CH_2-$), 4.05 (m, 6H, $CH_2-CO_2-CH_2$, $-O-CH_2-$), 4.2 (m, 2H, $-CO_2-CH_2-$), 6.99 (m, 4H arom), 7.26 (m, 2H, arom), 7.46 (m, 1H, arom), 7.88 (d, 1H, arom), 8.15 (m, 4H, arom). Anal. Calcd ($C_{35}H_{39}BrO_{10}$): C (60.09%), H (5.61%). Found: C (60.14%), H (5.55%).

((4″-(Bromoacetyloxy)butyl) 2,5-di(4′-butyloxybenzoyloxy) benzoate) triphenylphosphonium bromide (**5**): To a solution of **4** (3 g, 4.29 mmol) in toluene (15 mL) was added in one portion triphenylphosphine (1.2 g, 4.58 mmol), and the reaction mixture was stirred at room temperature for 48 h. The white solid which has precipitated was removed by filtration and washed with hexane. Drying under vacuum provided **5** (4.02 g, 4.18 mmol) (97%), which was used for the Wittig reaction without further purification or characterization.

(4″-((α,β,β′-$^2H_3$)-Acryloyloxy)butyl) 2,5-di(4′-butyloxybenzoyloxy)benzoate (**6**). Phosphonium salt **5** (2 g, 2.08 mmol) was dissolved in dry THF (50 mL). Anhydrous potassium carbonate (0.29 g, 2.1 mmol) and $^2H_2$-formaldehyde (as a 20% solution in ^2H_2O) (2 mL) were added, and the reaction mixture was stirred at room temperature overnight. The THF was evaporated under reduced pressure, and the residue was dissolved in dichloromethane (60 mL). The organic phase was washed with water (100 mL) and brine (2 × 100 mL) and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with a 80/20 hexane/ethyl acetate mixture as eluting solvent followed by two recrystallizations from ethanol to give 0.81 g (1.27 mmol, 61%) of white solid (K 77 °C N 86.5 °C I). ^{1}H NMR: 1 (t, 6H, $-CH_3$), 1.55 (m, 8H), 1.81 (m, 4H, $-O-CH_2-CH_2-$), 4.06 (m, 6H, $-O-CH_2$, $=CD-CO_2-CH_2-$), 4.2 (m, 2H, $-CO_2-CH_2-$), 5.78 (s, O.O1H, $HC=CH$), 6.07 (s, 0.04H, $=CH-CO_2$), 6.34 (s, 0.01H, $HC=CH$), 6.98 (m, 4H, arom), 7.25 (m, 1H, arom), 7.46 (m, 1H, arom), 7.88 (d, 1H, arom), 8.15 (m, 4H, arom). Anal. Calcd ($C_{36}H_{37}{}^2H_3O_{10}$): C (68.01%), H (5.86%). Found: C (68.18%), H (5.88%).

Using the same synthetic scheme, (4″-((α,β,β′-$^2H_3$)-acryloyloxy)propyl) 2,5-di(4′-butyloxybenzoyloxy)benzoate (**7**) and (4″-

((α,β,β′-$^2H_3$)-acryloyloxy)butyl) 2,5-di(5′-pentylcyclohexylcarboxyloxy)benzoate (**8**) were prepared.

7 (K 75 °C N 100 °C I). ^{1}H NMR: 1 (t, 6H, −CH_3), 1.52 (m, 4H, −CH_2−CH$_3$), 1.85 (m, 6H, −O−CH$_2$−CH_2−, −CO$_2$−CH$_2$−CH_2−), 4 (m, 6H, −O−CH_2−, −CH_2−O$_2$C−CD═), 4.26 (m, 2H, −CO$_2$−CH_2−), 6.98 (m, 4H, arom), 7.26 (m, 1H, arom), 7.47 (m, 1H, arom), 7.88 (d, 1H, arom), 8.15 (m, 4H, arom). Anal. Calcd ($C_{35}H_{35}O_{10}{}^2H_3$): C (67.61%), H (5.67%). Found: C (67.42%), H (5.74%).

8 (K 81 °C I (45 °C monotropic N)). ^{1}H NMR: 0.88 (t, 6H, −CH$_3$), 0.98 (m, 4H), 1.27 (m, 18H), 1.54 (m, 4H), 1.84 (m, 8H), 2.15 (m, 4H), 250 (m, 2H), 4.20 (m, 2H, −CH_2−O$_2$C−CD═), 4.29 (m, 2H, −CO$_2$−CH_2−), 7.04 (d, 1H, arom), 7.25 (m, 1H, arom), 7.64 (d, 1H, arom). Anal. Calcd ($C_{38}H_{53}O_8{}^2H_3$): C (70.88%), H (8.29%). Found: C (70.63%), H (8.29%).

Synthesis of (4′-Methoxyphenyl) 4-(5″-((α,β,β′-$^2H_3$)-Acryloyloxy)pentyloxy)benzoate (12). (4′-Methoxyphenyl) 4-(5″-hydroxypentyloxy)benzoate (**10**): To a stirred solution of 4′-methoxyphenyl 4-(pentenyloxy)benzoate (**9**) (1 g, 3.2 mmol) in 25 mL of dry THF kept under argon was added via syringe 9-BBN as a 0.5 M solution in THF (7 mL, 3.5 mmol). The mixture was stirred overnight at room temperature under argon. The solution was cooled in an ice/water bath, and solid *m*-chloroperbenzoic acid (3.2 g of commercial (70%) acid) was added slowly in small portions. After stirring at room temperature overnight, the reaction mixture was diluted with 100 mL of water and extracted twice with dichloromethane. The organic phase was washed thoroughly with a saturated sodium bicarbonate solution (4 × 100 mL) and water and then dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using a 50/50 hexane/ethyl acetate mixture as eluting solvent to give 0.96 g (2.9 mmol, 90%) of white solid (K 102 °C I). ^{1}H NMR: 1.64 (m, 4H, HO−CH$_2$−CH_2−CH_2−), 1.88 (m, 2H, −O−CH$_2$−CH_2−), 2.15 (broad m, 1H, *H*O−), 3.7 (m, 2H, HO−CH_2−), 3.81 (s, 3H, CH_3−O−), 4.05 (m, 2H, −O−CH_2−), 6.95 (m, 4H, arom), 7.1 (m, 2H, arom), 8.12 (m, 2H, arom). Anal. Calcd ($C_{19}H_{22}O_5$): C (69.07%), H (6.71%). Found: C (68.66%), H (6.65%).

(4′-Methoxyphenyl) 4-(5″-(bromoacetyloxy)pentyloxy)benzoate (**11**): A solution of **10** (0.86 g, 2.6 mmol), bromoacetic acid (0.4 g, 2.86 mmol), *N*,*N*-dicyclohexylcarbodiimide (0.59 g, 2.86 mmol), and pyrrolidinopyridine (0.042 g, 0.28 mmol) in a mixture of dichloromethane (50 mL) and THF (20 mL) was stirred at room temperature for 12 h. The *N*,*N*-dicyclohexylurea was removed by filtration, and the filtrate was washed with water (100 mL), a 5% acetic solution (100 mL), water (100 mL), and dried over Na_2SO_4.

After evaporation of the solvent, the residue was recrystallized from ethanol to give 0.62 g (1.37 mmol, 53%) of white solid (K 53 °C I). ^{1}H NMR: 1.6 (m, 2H, −O−CH$_2$−CH$_2$−CH_2−), 1.81 (m, 4H, −O−CH$_2$−CH_2−CH$_2$−CH_2−), 3.81 (s, 3H, −O−CH_3), 4.06 (m, 2H, −O−CH_2−), 4.22 (m, 2H, −CO$_2$−CH_2−), 6.94 (m, 4H, arom), 7.1 (m, 2H, arom), 8.12 (d, 2H, arom). Anal. Calcd ($C_{21}H_{23}BrO_6$): C (55.88%), H (5.13%). Found: C (56.84%), H (5.35%).

(4′-Methoxyphenyl) 4-(5″-((α,β,β′-$^2H_3$)acryloyloxy)pentyloxy)-benzoate (**12**): **11** (0.55 g, 1.21 mmol) was dissolved in toluene (5 mL). Triphenylphosphine (0.35 g, 1.31 mmol) was added, and the reaction mixture was stirred for 2 days. Toluene was evaporated under reduced pressure, and the solid residue was dissolved in 30 mL of dry THF.

Anhydrous potassium carbonate (0.18 g, 1.3 mmol) and $^2H_2$CO (as a 20% solution in ^2H_2O) (1.5 mL) were added, and the reaction mixture was stirred at room temperature overnight.

The THF was evaporated under reduced pressure, and the residue was dissolved in dichloromethane (50 mL). The organic layer was washed with brine (2 × 50 mL) and water (50 mL) and dried over Na_2SO_4.

After evaporation of the solvent, the residue was purified by column chromatography on silica gel with a 70/30 hexane/ethyl acetate mixture as eluting solvent to yield, after recrystallization from ethanol, 0.24 g (0.62 mmol, 50%) of white solid (K 69 °C I (45 °C monotropic N)). ^{1}H NMR: 1.6 (m, 2H, −O−CH$_2$−CH$_2$−CH_2−), 1.84 (m, 4H, −O−CH$_2$−CH_2−CH$_2$−CH_2−), 3.81 (s, 3H, −OCH_3), 4.05 (m, 2H, −O−CH_2−), 4.2 (m, 2H, −CO$_2$−CH_2−), 6.94 (m, 4H, arom), 7.12 (m, 2H, arom), 8.12 (m, 2H, arom).Anal. Calcd ($C_{22}H_{21}{}^2H_3O_6$): C (68.19%), H (5.46%). Found: C (68.69%), H (5.38%).

Synthesis of Benzyl (α,β,α′)-$^2H_3$-Acrylate (14). Benzyl bromoacetate triphenylphosphonium bromide (**13**) (0.92 g, 2 mmol) was dissolved in dry THF (48 mL). Anhydrous potassium carbonate (0.28 g, 2 mmol) and $^2H_2$CO (as a 20% solution in ^2H_2O) (2.4 mL) were added, and the reaction mixture was stirred at room temperature overnight.

The THF was evaporated under reduced pressure, and the residue was dissolved in dichloromethane (60 mL). The organic layer was washed with brine (2 × 100 mL) and water (100 mL) and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with a 80/20 hexane/ethyl acetate mixture as eluting solvent to yield 0.25 g (1.51 mmol, 75%) of liquid. ^{1}H NMR: 5.2 (s, 2H, −CO$_2$−CH_2−), 7.35 (m, 5H, arom). Anal. Calcd ($C_{10}H_7{}^2H_3O_2$): C (72.69%), H (4.27%). Found: C (72.73%), H (4.06%).

Acknowledgment. Part of this work was performed at the University of Colorado during a visit of P. Keller to Professor D. M. Walba's group. Work performed there was supported by NSF Materials Research Science and Engineering Centers (Grant DMR 98-09555).

Supporting Information Available: ^{1}H NMR spectra for all the deuterated monomers synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA010838M