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Notes

Preparation of Soluble Poly(carbonyldioxyglyceryl methacrylate)

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Polymers containing a high density of polar substituents are of interest for a number of applications. Fluorinated and cyano polymers[1] have been investigated as piezoelectric materials, while heavily oxygenated polymers[2] and polyions[3] have been considered as components of solid electrolyte solutions.

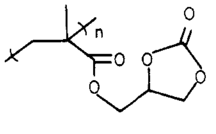
A third potential application of polar polymers is as hosts for dyes in nonlinear optical films.[4] The incorporation of strongly polar functionalities in the host media will likely increase the solubility of the dyes used as the nonlinear optically active components. Furthermore, when a suitable polymer–dye mixture is electric field poled, the dipoles in the polymers should align with the field resulting in an acentric environment in which the dye guests might tend to be nonrandomly oriented as well. A bulk noncentrosymmetric transition moment is a major requirement for the active component of second-order nonlinear optical materials.[5]

The cyclic carbonate functionality combines a relatively high dipole moment[6] and strong coordinating power with chemical stability (especially compared to the dicyanomethyl group[2]). For incorporation into hosts for nonlinear optics, it would be desirable to graft such a functional group onto an amorphous polymer of potentially high T_g that would be soluble in a volatile solvent. Therefore, polymethacrylate **1** is an attractive synthetic target.

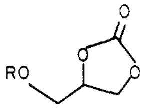
Monomer **4**, the precursor to **1**, has been previously employed in two polymerizations[7] as well as several copolymerizations.[8] However, it does not appear that soluble **1** has ever been prepared before. Indeed, one claim[7a] in the patent literature describes **1** as brittle and insoluble. In this paper we describe our synthesis of *soluble* **1** as well as its precursors from readily available starting materials.

Results

Synthesis of 3. Because of the ready availability of **2** (obtained in >97.5% purity by the base-catalyzed reaction of commercially available 3-(allyloxy)-1,2-propanediol with diethyl carbonate), we examined the Pd-mediated dealkylation of **2** to give **3**. Glycerol formation was minimized when the deallylation was carried out at ambient rather than elevated temperatures. The time needed for >90% conversion was markedly dependent on the activity of the Pd catalyst and the quantity of toluenesulfonic acid added. The yield of **3** was typically 70%, with contamination by <5% glycerol and ≤5% of **2**.



1



2, R=CH$_2$=CH—CH$_2$

3, R=H

4, R=CH$_2$=C(CH$_3$)—$\overset{\overset{O}{\|}}{C}$

Synthesis of 4. The esterification of **3** with methacryloyl chloride was first attempted in Et_2O. Problems arose because of the immiscibility of **3** with Et_2O, and a polar phase remained separated from the ethereal solution throughout the reaction. Some of the newly synthesized **4** was lost to polymerization or decomposition in this phase. Phase-separation problems were avoided when THF was used as the solvent since **3** is miscible with THF. While the crude yield of **4** was 40–50% from ether, a 77% yield was achieved with THF as the solvent.

Synthesis of 1. Monomer **4** was polymerized in toluene with AIBN as initiator. When **4** was used without chromatographic purification, the polymer was completely intractable. When THF-derived **4** was first purified by flash chromatography on neutral Al_2O_3 with Et_2O elution, the resulting polymer was soluble in Me_2SO and DMF if isolated at <50% conversion but only ≤25% soluble at 60% conversion. Compound **4** synthesized in Et_2O and purified by flash chromatography or HPLC gave a polymer that was completely soluble in Me_2SO and DMF after >50% conversion. Unfortunately, a significant amount of **4** is lost to the Al_2O_3 columns. Also, chromatography did not remove an impurity that was originally present in the methacryloyl chloride (^{1}H NMR δ 1.9, 1.7). This last impurity did not appear to affect the polymerization.

Discussion

There have been other reported syntheses of **3**, although

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all suffer from disadvantages. The direct synthesis[9] of **3** from glycerol and ethylene carbonate requires repeated distillations. Conversion[10] of 3-*O*-benzylglycerol to **3** exposes the carbonate to AcOH over a long period of time while the benzyl group is hydrogenolyzed and also uses an expensive starting material. When the (allyloxy)carbonyl group[11] is present on the precursor to **3**, its removal leaves **3** in an aqueous solution. Other approaches to **3** involve multistep sequences[12] or employ highly toxic glycidyl derivatives.[13] The present synthesis of **3** uses inexpensive starting materials and volatile solvents and results in minimal glycerol formation.

The only previous synthesis of **4** was via transesterification of **3** with methyl methacrylate followed by distillation.[7b] An advantage of the acid chloride condensation is that heating is not required and the time during which solvent- and inhibitor-free **4** must be handled is minimized. The polymerization of neat **4** to a glass occurs in a few hours at room temperature under vacuum.

A major obstacle to the preparation of tractable **1** is the high probability of cross-linking reactions. These can occur at two sites, either at di- or trimethacryloylglycerol units (due to monomer impurities) or at the tertiary 2-carbon of the glyceride. Prevention of cross-linking can be accomplished by polymerizing to low conversion or by careful monomer purification, both of which call for the sacrifice of a considerable amount of monomer. Other changes in polymerization conditions might also be effective.

In summary, a convenient synthesis of **4** has been devised and the polymerization of **4** has been examined. Soluble **1** has been obtained for the first time, although further experiments will be necessary in order to optimize the yield of tractable **1**.

Experimental Section

4-(Hydroxymethyl)-1,3-dioxolan-2-one (3). A solution of **2** (40 g) in 500 mL of MeOH was blanketed with N_2. The N_2 current was diminished, and 10% Pd on carbon (6 g) was added. (**DANGER**: The dry catalyst may ignite on prolonged contact with MeOH vapor and oxygen!) Toluenesulfonic acid hydrate (4 g) was added and the mixture was stirred at ambient temperature. Aliquots of 1 mL were periodically removed, filtered through Al_2O_3, concentrated, and assayed by NMR. After 8 h, deallylation was >95% complete. The mixture was filtered through 250 mL of neutral Al_2O_3 wet with MeOH, and the Al_2O_3 was rinsed with 700 mL of additional MeOH. The combined filtrates were concentrated at reduced pressure and the residue distilled at 130 °C and 0.2 torr on a kugelrohr (higher distillation temperatures can cause glycidol formation). Yield, 20.3 g of **3** (68%); ^1H NMR (Me_2SO-d_6) δ 3.6 (m, 2 H), 4.2–4.7 (m, 2 H), 4.9 (m, 1 H), 5.3 (t, 1 H, $J = 10$ Hz, OH); ^{13}C NMR (Me_2SO-d_6) δ 60.6, 65.8, 77.0, 155.1 (CO). (**CAUTION**: The $Pd/C/Al_2O_3$ residue should not be allowed to dry but instead should be promptly suspended in H_2O for disposal. Otherwise, the residue may smolder or ignite.

(2-Oxo-1,3-dioxolan-4-yl)methyl 2-Methyl-2-propenoate (4). A mixture of freshly distilled **3** (6.4 g, 0.057 mol), THF (90 mL), and NEt_3 (dried with KOH and distilled from P_2O_5, 8.0 mL, 0.05 mol) was mechanically stirred at 0 °C under Ar. Methacryloyl chloride (90%, 6.4 mL, 0.052 mol) dissolved in THF (30 mL) was added dropwise with stirring over 50 min, keeping the temperature below 5 °C. After 10 min of further stirring, the solution was filtered and the solids were extracted with 100 mL of Et_2O. The combined filtrates were washed with concentrated aqueous NaCl, first at pH 2 and then at pH 8, dried, filtered, and concentrated to 7.7 g of crude **4** (77%). Purification by flash chromatography on Al_2O_3, eluting with Et_2O, gave 3.5 g of **4** (35%): ^1H NMR ($CDCl_3$) δ 2.0 (m, 3 H, CH_3), 4.2–4.7 (m, 4 H), 5.0 (m, 1 H), 5.6 (m, 1 H), 6.1 (m, 1 H).

Poly[(2-oxo-1,3-dioxolan-4-yl)methyl 2-methyl-2-propenoate] (1). Monomer **4** (2.1 g) was dissolved in 80 mL of toluene and the solution was purged with Ar. Azobis(isobutyronitrile) (20 mg) was added, and the solution was stirred 43 h at 60–65 °C. The mixture was poured into 450 mL of MeOH and the polymer thus precipitated was collected, washed with MeOH, and dried under vacuum. The yield was 1.24 g of **1** as a white powder, soluble in DMF and Me_2SO, insoluble in less polar solvents (THF, CH_3CN) and H_2O: T_g 120 °C; ^1H NMR (Me_2SO-d_6) δ 0.6–2.1 (5 H), 3.8–5.3 (5 H), all very br; ^{13}C NMR (Me_2SO-d_6) δ 17 (CH_3), 44 (quaternary C), 53 (br, CH_2 in backbone), 65 (br), 66, 74, 155 (carbonate CO), 177 (ester CO); IR (KBr pellet) 2960, 1805 (carbonate CO), 1734 (ester CO), 1170. Anal. Calcd for $(C_8H_{10}O_5)_n$: C, 51.60; H, 5.41. Found: C, 51.30; H, 5.48. Molecular weight 30 000 ± 10 000 (intrinsic viscosity in DMF).

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Registry No. **1**, 109013-85-6; **2**, 826-29-9; **3**, 931-40-8; **4**, 13818-44-5; $H_2C{=}C(Me)COCl$, 920-46-7.

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Approach to the χ Function for Ternary Solutions Containing Two Polymers in a Pure Solvent

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We consider a ternary solution consisting of a pure solvent (component 0) and two monodisperse polymers (components 1 and 2) in which the partial molar volume of each component is independent of composition and pressure p. The total volume V of the solution is represented by

$$V = V_0(n_0 + P_1n_1 + P_2n_2) \tag{1}$$

where n_i and P_i are the amount in moles and the relative chain length of component i, the latter being defined by

$$P_i = V_i/V_0 \tag{2}$$

with V_i the molar volume of component i. The volume