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Ester Derivatives of α-(Hydroxymethyl)acrylates: Itaconate Isomers Giving High Molecular Weight Homopolymers

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Introduction. Monomers based on α-(hydroxymethyl)acrylate offer great versatility for functionalization and polymer formation. Earlier work in this area involved complicated or low-yield monomer syntheses.[1,2] Insertion of formaldehyde at the α-position of acrylic esters catalyzed by DABCO (1,4-diazabicyclo[2.2.2]octane) produces alkyl α-(hydroxymethyl)acrylates in yields of 30–50%.[3] Conversion of the alcohol group to ester moieties with acid chlorides has been demonstrated by us and others;[4,5] the acid chlorides, however, are expensive or not available for some acids, are difficult to keep, and often undergo side reactions. Conversion of the hydroxymethyl group to the allyl chloride offers an alternative method for functionalization as shown for various ether derivatives[6] which display surprisingly good polymerizability (although to only moderate molecular weight polymer) in light of the low reactivity or nonreactivity of acrylates with α–alkyl substituents larger than methyl.[7] We describe here several synthetic approaches to the ester derivatives (especially using the PTC method) that are isomers of itaconate diesters[8] but with the ester group β to the vinyl moiety reversed in the bonding sequence.[9]

General Procedures for the Synthesis of the Monomers. Ethyl α-(Chloromethyl)acrylate (ECMA). ECMA was synthesized from purified ethyl α-(hydroxymethyl)acrylate (EHMA) isolated from the crude reaction solution from the synthesis of the hydroxymethyl monomer. Conversion to the chloromethyl derivative involved refluxing in excess thionyl chloride for ca. 3 h followed by evaporation of residual thionyl chloride. Gas chromatographic (GC) analysis of the reaction mixture does not give correct identification of key impurities and intermediates; we therefore recommend monitoring by NMR. Washing twice with water followed by vacuum distillation gave a 99% pure product in ca. 80% yield.

Representative Acid Chloride Procedure. Into the solution of EHMA (5 g, 38 mmol) and pyridine (3.95 g, 50 mmol), was added benzoyl chloride (7 g, 50 mmol) with 30 mL of CCl_4 at 0 °C. After 30 min of additional stirring, the CCl_4 was evaporated under vacuum and the reaction mixture was poured into 100 mL of ice water and neutralized with a 5% Na_2CO_3 solution. The solution was extracted twice with 100 mL of $CHCl_3$, and the combined $CHCl_3$ solutions were dried with $CaCl_2$. Evaporation of the $CHCl_3$ and double vacuum distillation of the product gave a colorless liquid in 50% yield.

Representative Phase-Transfer-Catalyzed Ester Procedure. ECMA (3.46 g, 23.3 mmol), sodium formate (4.46 g, 65.6 mmol), Aliquat 336 (Aldrich; 0.13 g, 0.32 mmol), and 20 mL of CH_2Cl_2 were added to a 50-mL round-bottomed flask. The mixture was stirred at room temperature until all ECMA reacted as monitored by GC. The solution was filtered, and the CH_2Cl_2 was evaporated under reduced pressure. Vacuum distillation of the residue gave monomers as colorless liquids except for the stearate ester which was a solid isolated by washing with cold methanol. Yields were 97–98% of >98% pure products before distillation; it is important to remove residual catalyst by extraction, chromatography, or distillation for reproducible polymerizability.

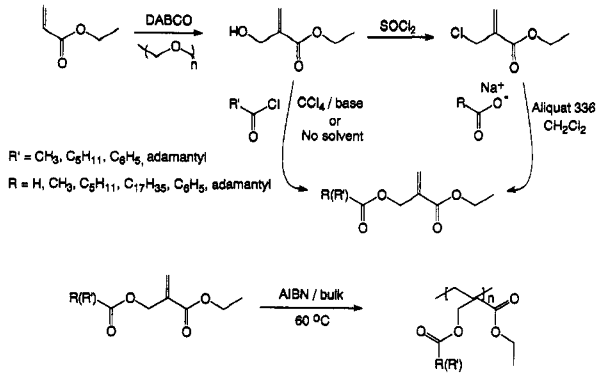

Figure 1. Overall reaction scheme showing formation of α-(hydroxymethyl)acrylate (EHMA), the corresponding chloromethyl derivative (ECMA), their conversion to the various ester derivatives through PTC or acid chloride reaction, and radical polymerization.

Synthesis of Trifluoroacetate Derivative. EHMA (10.52 g, 80.8 mmol) and a Teflon-coated magnetic stirbar were added to a 100-mL round-bottomed flask in an ice bath under a dry nitrogen purge. Trifluoroacetic acid (30 mL, 0.389 mol) and trifluoroacetic anhydride (12 mL, 85.0 mol) were added dropwise to the flask. The solution was allowed to warm to room temperature and stirred for 18 h; GC analysis showed complete reaction of the EHMA. Excess reagents were removed by rotary evaporation, and vacuum distillation gave 98.5% pure ethyl α-[(trifluoroacetoxy)methyl]acrylate in 90% yield.

General Polymerization Procedure. Neat monomer was mixed with AIBN (0.25–0.5 wt %) in a septum-sealed flask which was subjected to three freeze–evacuate–thaw procedures and placed in a 60 °C oil bath. Polymers were dissolved in acetone or CH_2Cl_2 and precipitated into methanol except for the acetate derivative which was precipitated from $CHCl_3$ into hexanes; yields ranged from 45 to 80% after drying under vacuum at 60 °C.

Results and Discussion. Three procedures were used for the synthesis of ester derivatives of EHMA. Two are illustrated in Figure 1 along with polymer formation. The first involved the reaction of the alcohol group of EHMA with acid chlorides with or without added base (pyridine or triethylamine). Typical isolated yields ranged from 50 to 80%, although some derivatives were difficult to purify due to residual acid chloride codistillation (benzoyl and adamantyl esters). In addition, acid chlorides are expensive and prone to gradual hydrolysis and degradation. This led us to attempt a phase-transfer-catalyzed reaction with simple acid salts in two-phase systems.

Reaction of ECMA in CH_2Cl_2 was carried out at room temperature with solid sodium salts of a variety of organic acids in the presence of Aliquat 336, a quaternary ammonium chloride phase-transfer catalyst (Aldrich Chemical Co.). This mild procedure gave essentially quantitative formation of high-purity products after filtration; final purification (usually by distillation) gave monomers that polymerized more reproducibly.

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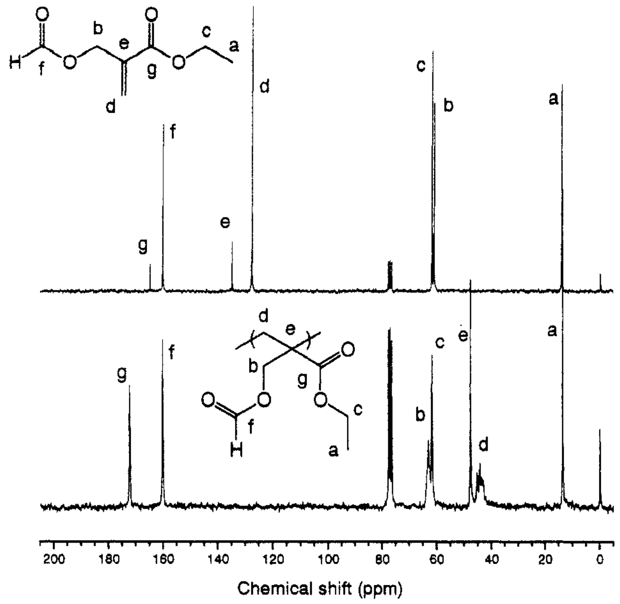

Figure 2. ^{13}C-NMR spectra of the formate monomer and polymer in $CHCl_3$.

The third esterification method involved direct reaction of EHMA with a mixture of trifluoroacetic acid and its anhydride. This approach gave essentially quantitative conversion to the pure ester which, however, was susceptible to gradual hydrolysis and side reactions. This method, along with the acid chloride method, has disadvantages of expense and difficulty of product purification that are generally overcome by the phase-transfer procedure. While formation of the trifluoroacetate was not possible with the sodium salt (probably due to low nucleophilicity of the anion because of the electron-withdrawing fluorine atoms), other monomers (such as the benzoyl and adamantanoyl derivatives) gave higher purity products under much milder conditions using PTC. In fact, such mild conditions allowed formation of derivatives for which the corresponding acid chlorides do not exist (e.g., the formate monomer).

The monomers were polymerized in bulk at 60 °C using AIBN. Polymerization times for these ester derivatives ranged from hours to days although rates were sometimes fast; e.g., the hexanoate completely solidified in ca. 2 h (but to a completely soluble polymer). The ^{13}C-NMR spectra of a typical monomer and its polymer are given in Figure 2. Disappearance of vinyl carbons and appearance of the backbone peaks (at ca. 45 and 47 ppm) are consistent with vinyl polymerization; multiple peaks seen for the backbone CH_2 suggest that tacticity information is present; we have not further analyzed these data.

Molecular weights of the polymers obtained were high, usually with bimodal distributions. Intrinsic viscosities were determined at 30 °C using Cannon–Ubbelohde microviscometers, initial polymer concentrations of ca. 0.5–0.85 g/dL in tetrahydrofuran (THF), and extrapolated least-squares fits of reduced and inherent viscosity values to zero concentration (correlation coefficients of >0.996). Intrinsic viscosities of the alkyl ester derivatives were between 2 and 2.5 dL/g, with corresponding SEC *number-average* molecular weights (based on polystyrene standards) of (4–7) × 10^5. These polymers showed bimodal distributions with significantly higher *peak* molecular weights of (2–2.1) × 10^6 due to the Trommsdorff effect (to be discussed further in the full paper); we cannot rule out the possibility that the high molecular weights obtained are due in part to chain transfer giving branching from the pendent ester or α-CH_2O groups. The trifluoroacetate gave a viscosity of 0.84 dL/g and an estimated molecular weight of 280 000, again with a shoulder on the high side of the SEC trace. The bulky adamantanoyl group apparently retarded propagation somewhat, resulting in polymer with a viscosity of 0.5 dL/g and an estimated molecular weight of 300 000.

DSC analysis of the polymers showed a progressive decrease in T_g as the length of the side chain increased, from 77 °C for the formate to 15 °C for the hexanoate. Values for the trifluoroacetate and benzoate were 69 and 130 °C, respectively. The adamantanoate derivative showed a much higher T_g (214 °C), as expected.[10] The stearate polymer did not display a T_g but did show side-chain melting at 40 °C.

Overall, the approaches outlined here provide entry to a wide variety of ester derivatives of the highly reactive α-(hydroxymethyl)acrylates. The phase-transfer procedure is especially useful, occurring at ambient temperature and in high yield to give easily purified products. Most important is the ready conversion of these ester-containing side-chain monomers to very high molecular weight polymers in comparison to ether derivatives (which we[6] and others[11] have found to give relatively low molecular weight products [<100 000] under similar polymerization conditions) and other 1,1-disubstituted monomers such as itaconates. These monomers and polymers offer multifunctionality *and* high molecular weight not easily available with other systems.

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