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Department of Polymer Science
Hattiesburg, MS 39406-0076

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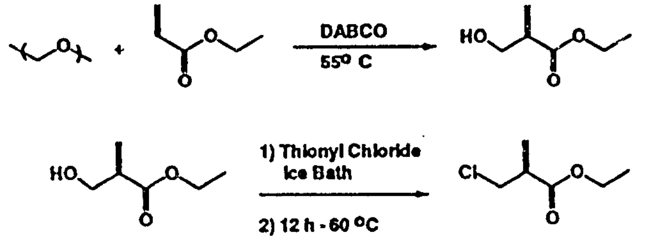
Multifunctional Acrylic Ether Monomers, Their Polymers, and Polymerizable Epoxide Derivatives from Simple α-Substitution of Alkyl Acrylates

Robert D. Thompson, Thomas H. Barclay and Lon J. Mathias
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

Introduction

Our group has been exploring the synthesis of 1,1- disubstituted monomers and their polymers obtained via the DABCO catalyzed hydroxymethylation of alkyl acrylates[1]. Previous work in this area has involved complicated or low yield syntheses[2,3]. We are using a simple, clean synthetic technique using paraformaldehyde and neat substrate to produce alkyl α(hydroxymethyl)acrylates, albeit in yields of only 25-30%. Conversion of the hydroxymethyl group with thionyl chloride gives a reactive allyl chloride which allows a wide range of ether forming reactions to be applied (see below).



The ether linkage is inherently more stable than the ester linkage and is much more flexible. While previous research has concentrated on the kinetics of the polymerization of these monomers as 1,1-disubstituted ethylenes, we are studying these materials with regard to their utility as optical materials (high refractive index polymers), liquid-crystalline monomers (fluoroalkyl ethers)[4], anti-cancer agents (cyclopolymer similar to DIVEMA)[5] and wood-polymer composites (as an impregnation monomer)[6]. Several of the alkyl ethers of ethyl α-(hydroxymethyl)acrylate have been reported, including the ethyl, propyl, isopropyl, dodecanyl,[7] and phenyl[8] ethers. The kinetics of polymerization and ceiling temperatures were also reported. The methyl ether, surprisingly, has not been described yet in the literature. Based on the interesting physical properties of the polymer of methyl α-(hydroxymethyl)acrylate[1] (a monomer we do not now study due to severe vesicant properties), we have synthesized the methyl ether of ethyl α-(hydroxymethyl)acrylate and describe here the properties of the monomer and polymer along with those of ethyl α-(benzyloxymethyl)acrylate.

Experimental

Methanol, paraformaldehyde, 1,4-diazabicyclo[2.2.2.]octane (DABCO) and ethyl acrylate were used as received from Aldrich Chemical Company. Triethylamine (Aldrich) was dried over calcium hydride for 24 hours then distilled into a dry vessel which was stoppered and stored. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. Monomer syntheses were monitored by gas chromatography using a Hewlett-Packard 5890 Gas Chromatograph equipped with an FID detector, 95% dimethyl/5% diphenyl polysiloxane column and HP 3396a Integrator, or by ^{13}C NMR with Bruker AC-300 NMR spectrometer.

Monomer Syntheses

Ethyl α-(chloromethyl)acrylate (ECMA) has been synthesized by our group before from ethyl α-(hydroxymethyl)acrylate[9]. We have modified this procedure due to several recent findings. We have found that when the crude reaction solution is used from the ethyl α-(hydroxymethyl)acrylate (EHMA) synthesis, a chloromethyl by-product is produced from reaction of thionyl chloride with the acetal byproducts of the EHMA reaction. We have also discovered that a chlorosulfite intermediate is involved in the conversio of EHMA to ECMA which is very long-lived relative to other chlorosulfit intermediates. This chlorosulfite apparently degrades in the injector of th gas chromatograph during monitoring of the reaction giving false evidenc of complete conversion to ECMA. If water is used to wash traces of thiony chloride from the solution, a violent reaction can occur. Therefore, w recommend the procedure below with monitoring by NMR.

Ethyl α-(chloromethyl)acrylate

Ethyl α-(hydroxymethyl)acrylate (77.67 g, 0.596 mol) and a teflon-coatec magnetic stir bar were added to a three-neck round-bottom flask in an ic bath. Nitrogen was blown in one neck, while the opposite one wa connected by a hose to a base solution to trap HCl gas. Thionyl chlorid (78.03 g, 0.656 mol) was added slowly to the flask. After complet addition, the solution was allowed to warm to room temperature. Th solution was then refluxed for one hour to allow conversion of th chlorosulfite intermediate to the primary chloride. Reaction progress wa monitored by ^{13}C NMR since the chlorosulfite apparently decomposes in th gas chromatograph to ECMA, making it very difficult to measure th conversion of chlorosulfite to ECMA by GC. Excess thionyl chloride wa removed by rotary evaporation. Vacuum distillation gave 99% ethyl α-(chloromethyl)acrylate (85% yield).

Ethyl α-(methoxymethyl)acrylate

Methyl alcohol (4.6 g, 0.113 mol), ethyl α-(chloromethyl)acrylate (8.37 g, 0.056 mol), and a teflon-coated magnetic stir bar were placed in a 100 mL single-neck round-bottom flask. The flask was placed in an ice bath and its contents stirred. Triethylamine (11.6 mL, 0.160 mol) was added to the flask slowly via addition funnel. The solution was allowed to come to room temperature and stirred for an additional 8h. The triethylamine/HCl salt and excess triethylamine were extracted by washing with 1 wt-% aqueous HCl solution (three times with 10 mL each). The organic layer was separated and the aqueous layer was back-extracted with methylene chloride. Organic layers were combined and dried with magnesium sulfate. Cuprous chloride was added as a free-radical inhibitor, and solvent and excess reactants were removed by rotary evaporation. The product was then vacuum distilled to yield 98% ethyl α-(methoxymethyl)acrylate (41% yield).

Ethyl α-(benzyloxymethyl)acrylate

Benzyl alcohol (4.15 mL, 0.040 mol), triethylamine (3.5 mL, 0.0[illegible] mol), and ECMA (2.88 g, 0.019 mol) were added to a 50 mL round-bottom flask. A calcium sulphate filled drying tube was attached and the reactants allowed to stir at 68° C for 21 h. 40 mL of ethyl ether were added and the mixture shaken vigorously with 20 mL of 1% HCl (three times), then separated to remove triethylamine/HCl and excess triethylamine. Cuprous chloride was added as inhibitor, and the ethyl ether removed by rotary evaporation. The product was then vacuum distilled to yield 98% ethyl α-(benzyloxymethyl)acrylate (69% yield).

Typical Polymerization Conditions

Ethyl α-(methoxymethyl)acrylate Bulk polymerizations were carried out by heating monomer samples containing 1% AIBN at 50-70 °C under dry nitrogen gas. Polymerization was complete in under 5 h.

Ethyl α-(benzyloxymethyl)acrylate. A mixture of 1% AIBN dissolved in neat monomer was heated at 55 °C overnight; yd 96%.

Results and Discussion

Ether Substituted Acrylates

Both the benzyl and methyl ethers polymerized relatively rapidly, giving high conversions in short times. The intrinsic viscosity of a typical methyl ether polymer was 0.6 dL/g, which would correspond to molecular weight of several hundred thousand if it were poly(methyl methacrylate). As far as we know this is the first report of the methyl ether derivative of this type of of monomer being synthesized and polymerized. The benzyl ether polymer has not been fully characterized yet, and only preliminary results are given here. Both polymers have glass transition temperatures around 65 °C, which is approximately 25 °C lower than the phenoxymethyl substituted polymer[8] which possesses one less CH_2 unit. DSC's were conducted to 160 °C with no signs of degradation. ^{13}C NMR spectra of the polymers (Figure 1) confirm expected structures for these polymers. Several of the peaks in the spectrum of the methyl ether polymer indicate tacticity, but the assignment of the peaks to configurational sequences has not been made. Note the sharpness of the quaternary peak. This is most likely due to the "protection" of the carbon nucleus by the four carbons attached. The methylene backbone carbon, on the other hand, "sees" many more electronic environments that are not able to average into a single, sharp peak, thus leading to a broad resonance. Further characterization of these monomers is being conducted along with evaluation of their polymerization and copolymerization capabilities.

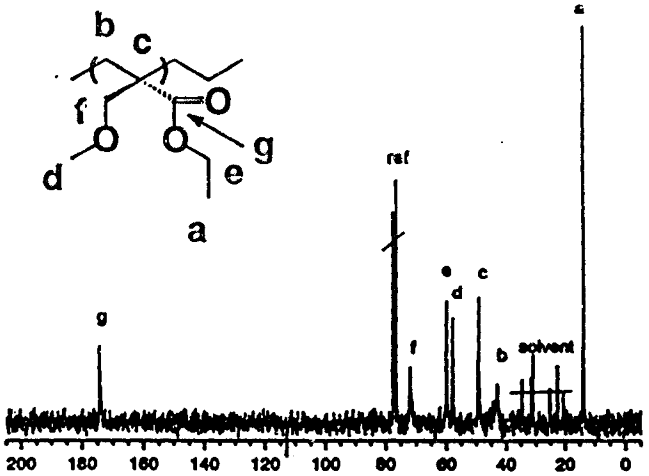


Figure 1. ^{13}C NMR of poly[ethyl α-(methoxymethyl)acrylate].

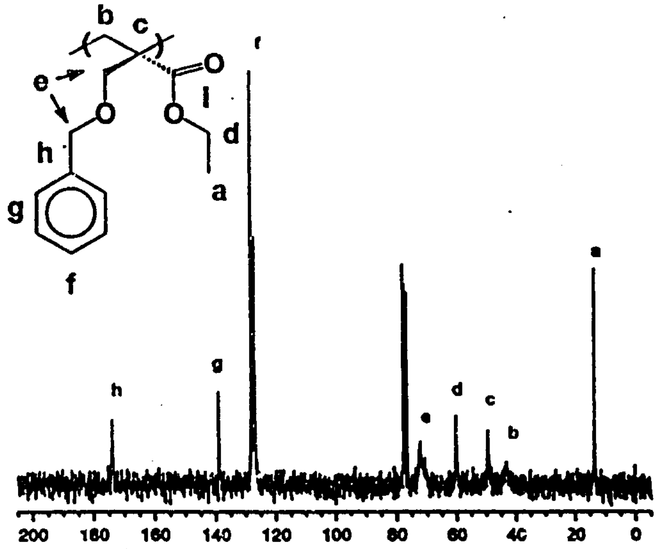
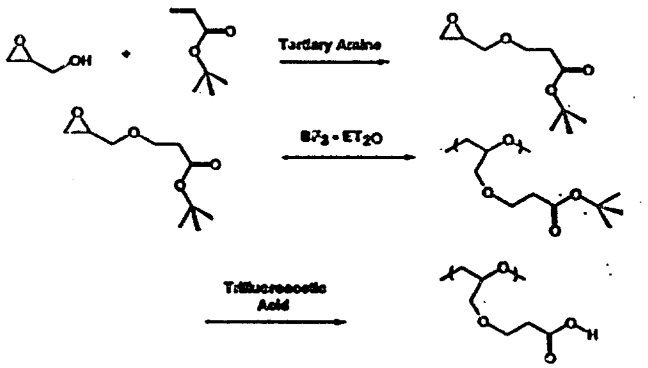


Figure 2. ^{13}C NMR of poly[ethyl α-(benzyloxymethyl)acrylate

Ester Functionalized Epoxide

In the course of attempting to find an alternate synthetic route to functionalized acrylates, we have also discovered a facile route to t-butyl ester derivatives of epoxides which offer potential for synthesis of novel ester and acid functionalized ethylene oxide polymers (see below).[10]



Synthesis of this monomer is straightforward, and involves simply mixing t-butyl acrylate and glycidol with tertiary amine catalyst. The reaction occurs at room temperature with no noticeable exotherm. The only major side-reaction appears to be polymerization of glycidol. Amines are used as catalysts for ring-opening of epoxides and therefore this reaction competes with the Michael addition to the acrylic monomer. The three different amines used as catalyst were DABCO, DBU, and triethylamine. All three caused excess consumption of the glycidol during reaction. Attempts to use this technique with ethyl acrylate led to what appeared to be a highly branched polymer. The solution appeared to have gelled but after two days in methylene chloride, it became completely soluble. We believe that alcoholysis of the ester group by the glycidol occurred which (after ring-opening) produced more hydroxyl groups which can then attack more ester groups leading to the highly branched material. The t-butyl ester apparently hinders nucleophilic attack sufficiently to avoid alcoholysis of the ester group. No attempt has been made to deprotect the esters although we have demonstrated ring-opening polymerization of this monomer.

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