HOMOPOLYMERIZATION OF ALKYL α- (HYDROXYLMETHYL)ACRYLATES

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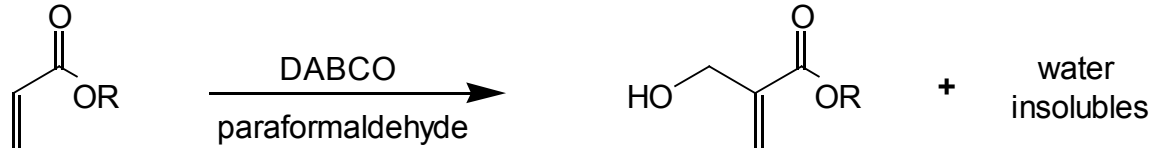

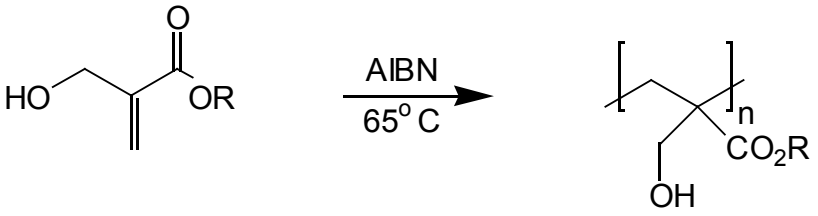

1. Synthesis of alkyl "-(hydroxymethyl)acrylates

Ethyl acrylate (285.3 g, 2.88 mol), paraformaldehyde (32.5 g, 1.08 mol) and 1,4-diazobicyclo[2.2.2]octane (DABCO, 6.5 g, 2.0% w/w) are stirred at room temperature. The reaction is monitored by gas chromatography (Note 1) and terminated after 19 days to give approximately 18% ethyl "-(hydroxymethyl)acrylate (EHMA) and 4.0% of the ether dimer, bis(ethoxycarbonyl-2-propenyl) ether.[3] The reaction may be carried out at elevated temperature (ca 60°C) to speed up conversion to ca 30-35% EHMA in 8-10 h. However, since the rate of ether formation is also increased by both higher temperatures and higher concentrations of EHMA, GC monitoring is vital to ensure maximum yield of EHMA with minimum loss to the ether dimer. If the dimer is the desired product, elevated temperature is desirable (see next procedure).

Unreacted ethyl acrylate is removed under reduced pressure and any residual paraformaldehyde is removed by filtration. The crude mixture is washed with dilute HCl and the aqueous solution extracted with diethyl ether. The combined ether fractions are dried (Na_2SO_4), added to the organic phase, concentrated in vacuo and fractionated under reduced pressure. Cuprous chloride (or any available inhibitor such as the benzoquinone or hydroquinone derivative) is added in small amounts.

Fraction 1, bp 58-59°C/0.35 mm Hg is predominately EHMA. Fraction 2, bp 100-104°C/0.2 mm Hg is predominately bis(2-carboethoxy-2-propenyl) ether. Fraction 3, bp 140-146°C/0.15 mm Hg is a mixture of acetals of EHMA and formaldehyde.

Fraction 1 is redistilled giving EHMA as a clear, free-flowing liquid. Redistilled fraction 2 gives bis(2-carboethoxy-2-propenyl) ether as a slightly viscous clear liquid. The ether dimer and diacrylate acetals are good crosslinkers[4] and must be removed from the EHMA if soluble polymers and copolymers are desired.

These monomers and dimers may be stored in the refrigerator at 0-5°C for a few days, but will spontaneously polymerize even at these temperatures. Inhibitor should be added for prolonged storage; any of the commercial acrylate inhibitors may be used including the monomethyl ether of p-hydroquinone.

Methyl "-(hydroxymethyl)acrylate (MHMA) may be prepared (not recommended) in a similar manner[5] although the monomer (or a readily-formed by-product from its synthesis) is a powerful skin irritant which causes blisters and contact dermatitis on exposure to the vapor. **CAUTION** is required in its synthesis: a good hood, butyl rubber gloves and extreme care.

2. Monomer Characterization

The alkyl "-(hydroxymethyl)acrylates are clear liquids having somewhat pungent odors. Preliminary skin irritancy tests show the pure compounds to be comparable to alkyl acrylates except for MHMA which causes contact dermatitis.

The IR spectra generally have absorption bands in the following regions: OH stretch at about 3400, carbonyl peak at 1710, and weak double bond absorption at 1610 cm-1. The 200 MHz ^{1}H NMR spectrum in $CDCl_3$ at room temperature shows alkene proton peaks at 6.2 and 5.8 ppm, the OH peak at about 4.5 ppm, and the methylene hydrogens " to the OH at 4.0 ppm (depending on concentration and dryness). The 50 MHz ^{13}C NMR spectra in $CDCl_3$ at room temperature has peaks for the carbonyl at 165 ppm, the alkene carbons at 140 and 125 ppm, and the " OH methylenes at 62 ppm. Ether by-products show an easily-seen CH_2-O peak at ca 68 peak which allows qualitative and quantitative evaluation of the amount of ether dimer present in crude or distilled monomers. Ester group hydrogen and carbon peaks appear at characteristic chemical shifts.

3. Procedure 1 (Bulk Polymerization)

Ethyl "-(hydroxymethyl)acrylate (EHMA, 2.26 g, 17.4 mmol) and 2,2'-azobis(isobutyronitrile) (AIBN, 40.0 mg, 1.7% w/w, Note 2) are sealed in a 2-dram vial equipped with a rubber septum, degassed three times using a freeze-thaw method, and then heated at 65°C for 12 h. A solid mass forms during this time. The sample is cooled, dissolved in chloroform, acetone or 1,1,1,3,3,3-hexafluoroisopropyl alcohol (HFIP, Note 3), and precipitated by addition to diethyl ether. This procedure is repeated twice giving poly(EHMA) as a white powder which is then dried at 50-80°C under vacuum; higher temperatures may cause transesterification and crosslinking.

4. Procedure 2 (Solution Polymerization)

Ethyl "-(hydroxymethyl)acrylate (1.027 g, 7.9 mmol), AIBN (21.1 mg, 2% w/w) and ethyl acetate (10 ml) are sealed in a 20-ml vial equipped with a rubber septum, degassed three times using a freeze-thaw method and then heated to 60°C for 12 h. During this time the viscosity of the solution does not increase to any significant extent. The reaction mixture is cooled to room temperature, precipitated by addition to diethyl ether and filtered. The product is redissolved and reprecipitated by addition to diethyl ether. This procedure is repeated twice to give low molecular weight poly(EHMA) as a white powder which is dried at 110°C under vacuum. Yields are 195-240 mg (19-23%).

5. Polymer Characterization

Poly(MHMA) is only soluble in HFIP while poly(EHMA) is soluble in HFIP, dimethylsulfoxide, N,N-dimethylacetamide, tetrahydrofuran, dimethylformamide, N-methylpyrrolidone, ethyl acetate, chloroform and acetone. Poly(EHMA) is slightly soluble in ethanol and methanol, and insoluble in carbon tetrachloride, water, benzene and diethyl ether. The presence of even small amounts of the ether dimer gives crosslinked and insoluble products. The poly(EHMA) obtained by bulk polymerization has an intrinsic viscosity (Note 4) of 0.18 dl/g in acetone at 25°C and 0.32 dl/g in DMSO at 25°C. (The checkers obtained values of 0.18 and 0.28 dl/g, respectively.)

The IR spectrum (Note 5) shows the following absorption bands for poly(MHMA): 3452 (OH stretch), 2959 (CH stretch), 1737 (C=O stretch), 1442, 1401, 1245, 1163 and 1040 cm^{-1}. The 200 MHz ^{1}H NMR spectrum (Note 6) in DMSO-d_6 at room temperature for poly(MHMA) gives broad peaks at 4.8 (OH), 3.3 (methoxy absorption), and 2.1 (methylene absorption) ppm from TMS. The 50 MHz ^{13}C NMR spectrum in DMSO-d_6 for poly(EHMA) at room temperature has peaks at the following positions: 173.7-174.2 (carbonyl); 60.1-60.9 ("-CH_2OH and ester "-methylene); 13.5 (methyl of ester group); and 42 and 50 ppm (broad backbone peaks centered at these values).

A glass transition of 145°C is found for poly(MHMA), and 96°C for poly(EHMA) solution and bulk polymer as determined by differential scanning calorimetry (Note 7). Repeated DSC scans and drying at too high a temperature cause thermal lactonization and transesterification which lead to higher T_g and crosslinked polymers.

6. Notes

1. Gas chromatography is run on an HP 5880 level 4 system equipped with FID detectors and a 5% phenyl methyl polysiloxane fused silica open tubular capillary column.
2. AIBN is recrystallized from methanol, dried under vacuum and stored in a desiccator until used.
3. HFIP is corrosive and irritating, and requires extreme care.
4. A Cannon-Ubbelohde #50 semi-micro viscometer is used.
5. A Nicolet 5DX FTIR is used to obtain the infrared spectra.
6. A Bruker MSL-200 is used to obtain the NMR spectra.
7. A DuPont 9900 computer equipped with a DuPont 910 DSC unit is used for thermal analysis.

7. Methods of Preparation

MHMA is prepared by the action of paraformaldehyde and methyl acrylate in the presence of DABCO.[6] MHMA and EHMA are also prepared by carboxylation of propargyl alcohol followed by esterification,[7,8] and by the reaction of alkyl acrylate and formalin in the presence of DABCO.[9] Additionally, EHMA is prepared by the action of mineral acid on bis(hydroxymethyl)malonate followed by esterification,[10] and by Wittig-Horner reaction of triethylphosphonoacetate with formaldehyde.[11,12,13,14]

Most of the above procedures suffer from a variety of drawbacks such as drastic reaction conditions, toxicity of reagents, poor yields, difficulties in obtaining reagents, and/or formation of by-products and impurities leading to poor polymerizability. While yields with our procedure are not high, materials obtained are easily purified, and recovered starting materials may be recycled. Generality is demonstrated by the fact that other ester derivatives have been prepared including the n-butyl (BHMA) and t-butyl (TBHMA) monomers. The latter and its polymer are readily converted to the free acid derivatives by treatment with trifluoroacetic acid.[15]

EHMA has been the subject of a number of polymerization and copolymerization studies,[16,17,18,19] although MHMA has apparently not been deliberately polymerized previously. The multifunctionality of these monomers makes available a variety of additional monomer derivatives and functionalized polymers. Radical polymerization gives the homopolymers (as reported here) with pendent alkoxycarbonyl and methylol groups which can be lactonized, crosslinked or chemically modified in a variety of ways. Copolymerization is facile with MHMA and EHMA showing reactivity ratios comparable to those of methyl methacrylate with styrene.[20,21]

8. References

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