POLY(2-ETHYLACRYLIC ACID)

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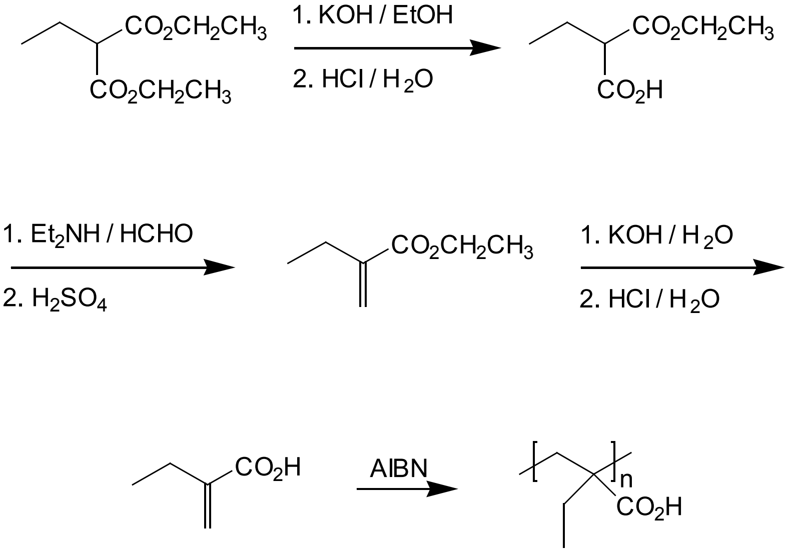

1. Procedure

a. 2-Carboethoxybutyric Acid

Diethyl ethylmalonate (100 g, 0.53 mol, Note 1) is placed in a 1 l round bottom flask along with 700 ml of 1 M KOH in 95% ethanol. The mixture is allowed to stir overnight (minimum of 12 h). At this point a large amount of white precipitate has formed and is filtered out of solution. The precipitate is placed in a 500 ml Erlenmeyer flask and the filtrate is concentrated on a rotary evaporator. The yellowish oil obtained upon concentration of the filtrate is added to the precipitate. The mixture is dissolved in a minimum amount of water and acidified with dilute aqueous HCl to a pH of 2. An oil separates from the solution. The oil is taken up into diethyl ether and the aqueous layer is extracted three times with 200 ml portions of ether. The ether extracts are combined, dried over magnesium sulfate and filtered. The ether is removed on a rotary evaporator. A quantitative yield (85 g) of crude 2-carboethoxybutyric acid is obtained as a yellowish oil. IR (neat, cm^{-1}): 3350-2600, 1740, 1710.

b. Ethyl 2-Ethylacrylate

Crude 2-carboethoxybutyric acid (84.9 g, 0.53 mol) is placed in a 1 l one-neck round bottom flask fitted with a magnetic stir bar and a reflux condenser. The reaction flask is cooled to -5°C and diethylamine is added (55 ml, 0.53 mol, Note 2). An addition funnel is placed on top of the reflux condenser and charged with a formalin solution (43.5 g, 0.54 mol, Note 3). The contents of the addition funnel are dripped slowly into the cooled reaction mixture which is then allowed to warm to room temperature. After stirring for 24 h the reaction mixture is warmed to 60°C and stirred for 8 h more. The mixture now consists of two layers. The reaction mixture is cooled to 0°C and concentrated sulfuric acid is added (Note 4). This mixture is extracted with three 200 ml portions of diethyl ether. The ether extracts are combined, dried over magnesium sulfate and filtered. The ether is removed on a rotary evaporator. Crude ethyl 2-ethylacrylate (47 g, 60%) is obtained as a yellow oil. IR (neat, cm^{-1}): 3300-2550, 1725; NMR ($CDCl_3$, *): 5.6 (s, 1H), 6.3 (s, 1H) (Note 5).

c. 2-Ethylacrylic Acid

Crude ethyl 2-ethylacrylate (10 g, 0.078 mol) is placed in a 250 ml one-neck round bottom flask. After 175 ml of 1M aqueous KOH are added, the flask is fitted with a reflux condenser and the reaction mixture is refluxed for 20 h (Note 6). The solution is allowed to cool to room temperature and acidified with dilute aqueous HCl to a pH of 2. An oil separates from the solution and the mixture is extracted four times with 200 ml portions of diethyl ether. The ether extracts are combined, dried over magnesium sulfate and filtered, and the ether is removed on a rotary evaporator. The yellow oil obtained is distilled (bp 55°C/40 mm Hg) to yield pure, colorless 2-ethylacrylic acid (4.7 g, 60% yd). IR (neat, cm^{-1}): 3300-2550, 1695; NMR ($CDCl_3$, *): 1.1 (t, 3H), 2.3 (q, 2H), 5.6 (s, 1H), 6.3 (s, 1H), 10.7 (s, 1H).

d. Polymerization

2-Ethylacrylic acid (1.00 g, 0.01 mol) is placed in an ampoule with 2,2ℕ-azobis(isobutyronitrile) (AIBN, 0.0328 g, 2 mol%, Note 7). The ampoule is subjected to three freeze-degas-thaw cycles and is sealed under vacuum. The sealed ampoule is heated at 65°C for 12 h cooled, and the resulting slurry poured into excess ethyl acetate. The powdery polymer is separated by filtration, dissolved in methanol and precipitated into diethyl ether. Drying in vacuum at 50-100°C gives poly(2-ethylacrylic acid) (0.71 g, 71% yd, Note 8). NMR (CD_3OD, *): 1.1 (m, 3H), 2.1 (m, 2H), 2.3 (m, 2H); IR (neat, cm^{-1}): 3700-2700, 1800-1600; 0_{inh} (2% in DMF, 30.0°C) = 0.29 dl/g.

2. Notes

1. Diethyl ethylmalonate (Aldrich Chemical Co., Milwaukee, WI) is used without purification.
2. Diethylamine (Aldrich) is used without purification.
3. The formalin solution (Fisher Scientific) is a 37% aqueous formaldehyde solution and is used without purification.
4. Caution! A violent reaction occurs upon addition of H_2SO_4 to the reaction mixture. The violent reaction is accompanied by the evolution of a small volume of gas. The H_2SO_4 should be added slowly until the violent reaction no longer occurs upon further addition.
5. Since the crude product is not purified for the next step, the presence of the olefinic protons in the NMR spectrum is used to confirm the intermediate structure.
6. Ethyl 2-ethylacrylate is insoluble in aqueous KOH, but the potassium salt of 2-ethylacrylic acid is soluble. Refluxing of the solution should therefore be continued until the mixture is homogeneous. This step can be shortened to 2 h by the addition of 1 ml of a 50% aqueous solution of tetrabutylammonium hydroxide (available from Aldrich).
7. 2,2ℕ-Azobis(isobutyronitrile) (AIBN, Aldrich) is recrystallized from methanol with care not to warm the solution above 45°C. The white crystals are dried in a vacuum desiccator before use.
8. Other solvent-nonsolvent systems that can be used to reprecipitate poly(2-ethylacrylic acid) are N,N-dimethylformamide (DMF)-ethyl acetate and pyridine-aqueous HCl.

3. Methods of Preparation

2-Ethylacrylic acid has been synthesized by reaction of diethyl ethylmalonate with formaldehyde followed by hydrolysis, dehydration and decarboxylation.[3]

2-Ethylacrylic acid can be solution polymerized in an aqueous solvent. Polymerization has been achieved using a 5.3% aqueous solution of the monomer initiated by 1% $K_2S_2O_8$ and 0.25% $NaHSO_3$ (w/w to the monomer).[4,5] Polymerization has also been carried out by using a 5% aqueous solution of the monomer initiated by 2,2'-azobis(isobutyramidine)-hydrochloride at about 0.5% (w/w to the monomer).[6] Both solution polymerization reports suggest the mixtures be heated for two days. The bulk polymerization of 2-ethylacrylic acid described here requires 12 h and gives pure, white polymer in good yield and in a powder form that is easily handled.

4. References

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