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On the synthesis of methacryloyloxyacetic acid

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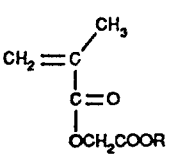
Summary

Methacryloyloxyacetic acid (I) is synthesized in 80% yield from its *tert*-butyl ester (IV) by the acid catalyzed E1 elimination of the *tert*-butyl group in dilute acetonitrile solution. The reported route to I is an improvement to previous methods in both yield and product purity. Copolymers of I with *tert*-butylstyrene (TBS) prepared by free radical methods are reported.

Introduction

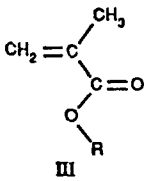
Many investigators have studied the monomer sequence distributions of poly(styrene-*co*-methyl methacrylate) (SMM)(1-6), poly(styrene-*co*-methacrylic acid) (SMA)(7-9), and poly(*tert*-butylstyrene-*co*-methyl methacrylate) (TBSMM)(10) copolymers by ^{1}H NMR. Due to the substantial shielding effects, the positions of specific methacrylate absorptions are highly dependent upon the proximity of the aromatic monomer to the methacrylate unit in the polymer chains. For example in SMM copolymers the methyl ester protons absorb at δ 3.5 ppm if both neighboring units are MM, but shift to δ 3.2 to 2.2 ppm (depending on tacticity) if the neighboring units are S (6). As part of our research we wished to study the effects of adding methylene spacer groups between the methacryloyloxy function and a terminal ester or carboxylic acid function on both the relative reactivities with aromatic monomers and on the observed NMR spectra. As a first step in these studies it was necessary to synthesize compounds I and II.



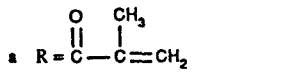
I R = H
II R = CH_3

The synthesis of II was published (11). We could find no references in the scientific literature to the isolation of I in good yield. Lucat and Devaud (12) prepared I in approximately 40% yield by the alkaline hydrolysis of II, followed by acidification. It is not clear if these workers isolated I. The preparation of I by the Schotten-Baumann reaction of methacryoyl chloride with glycolic acid in the presence of triethylamine is reported in the patent literature by Strain (13).

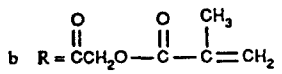
No details of the preparation are given in the patent. In our laboratory this method consistently yielded monomer which either spontaneously gelled during workup or upon free radical initiation yielded insoluble gels. Contamination of the product by the tetrafunctional anhydrides shown (IIIa, b) caused the gelation (11).



III



a



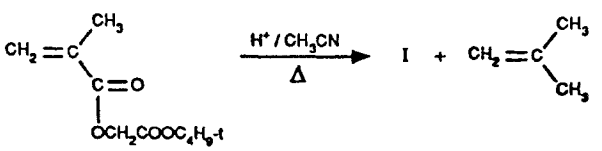
b

The anhydrides were remarkably resistant to removal by common methods (11). Though repeated recrystallizations did yield satisfactory product, the procedures were tedious and the yield (~ 25%) suffered greatly.

We now report the synthesis of I from the *tert*-butyl ester in good yield and purity. The homopolymer and copolymers with *tert*-butylstyrene have been prepared by conventional free radical methods without gelation.

Results and Discussion

The preparation of *tert*-butyl methacryoyloxyacetate (IV) from *tert*-butyl chloroacetate and methacrylate ion in the presence of Et_3N was reported earlier (11). To prepare I the *tert*-butyl group was removed by E1 elimination using a catalytic level of *p*-toluenesulfonic acid.



IV

Acetonitrile at reflux was a satisfactory medium for the elimination reaction. Other solvents were not investigated. Attempts to run the reaction neat resulted in polymerization and, even in 3/1 (V/W) acetonitrile/IV polymerization was sometimes observed. At a ratio of 10/1 (V/W) acetonitrile/IV polymerization has not been observed. The conversion of IV to I was followed by gas chromatography and found to be >98% in 48 hours.

The apparent pK_a of I was determined to be 3.1 from the half-neutralization point of a potentiometric titration curve. This is considerably lower than that of methacrylic (4.6) or acrylic (4.3) acids. This indicates a substantial, but not unexpected, inductive effect of the ester group in enhancing the acidity of I relative to the common monomers.

Data for the homopolymer and copolymers with TBS are presented in Table 1. The monomer was polymerized in the presence of azobis(isobutyronitrile).

Table 1

Data for Polymers

Sample	Time (hrs)	% Conversion	f_1[a]	F_1[a]	x 10^{-3}[b] $\overline{P}n$	x 10^{-3}[b] $\overline{P}w$
1	3	13	0.10	0.16	32.9	59.3
2	3.9	26	0.35	0.34	43.5	112.0
3	24	98	1.0	1.0	21.8	70.2

Copolymers 1 and 2 synthesized in DMA; Homopolymer 3 in toluene.

[a] f_1 = mole fraction I in feed; F_1 = mole fraction I incorporated (by nonaqueous titrimetry).

[b] $\overline{P}n$, $\overline{P}w$ = Polystyrene equivalent number and weight average molecular weights (by SEC), respectively.

Resulting polymers were completely soluble in THF. Copolymers containing more than 10 mole percent I were exceedingly difficult to isolate in nonsolvent systems typically acceptable for TBSMA copolymers. For example TBSMA is easily isolated in acetonitrile with a small amount of formic acid added to aid coagulation. This nonsolvent was unsatisfactory for TBS(I) copolymers which either dispersed or would not precipitate at all. Copolymers containing I could only be coagulated by the addition of HCl to the nonsolvent. We believe this is due to the enhanced acidity of poly(I). The methylene spacer group has placed the carboxylic acid group sufficiently far from the hydrophobic backbone to allow ionization due to increased solvation of the anion by the polar medium.

Experimental

Instrumentation

^1H NMR spectra were recorded on a Varian 300 SX spectrometer with a 300 MHz field strength. Tetramethylsilane was used as an internal standard. Fourier transform infrared spectra were obtained using a Nicolet model 60 SX FTIR. Potentiometric titration curves were recorded with a Metrohm model E636 titrator. The titrant was 0.1 N aqueous NaOH, standardized with benzoic acid. A combination glass/calomel electrode was used. Gas chromatographic analyses were carried out on a Hewlett Packard 5890A capillary GC, equipped with a 7673A autosampler. The column was a J and W, 15 N, 0.25 μ film thickness, programmed from 100-200°C at 10°C/min. Injector and f.i.d. temperatures were 200°C and 300°C, respectively. The carrier gas was He at 15 lb/in^2 and the split ratio was 100/1. Melting points were determined on an Electrothermal melting point apparatus; temperatures are not corrected. Size exclusion chromatography (SEC) was performed using three 10 μm PL gel mixed-bed-linear columns with THF as eluent. The columns were calibrated with narrow-molecular-weight-distribution polystyrene standards; thus reported results are in polystyrene equivalents.

Reagents
Tert-Butyl methacryoyloxyacetate (IV) was prepared by the published procedure (11) and distilled prior to use. Acetonitrile, and *p*-toluene-sulfonic acid were obtained from Kodak Laboratory and Research Products and used without further purification.

Synthesis of Methacryloyloxyacetic Acid (I)
20 g (0.1 M) IV, 200 mL acetonitrile and 0.1 g *p*-toluenesulfonic acid are combined and heated at a gentle reflux for 48 hours. The solvent is stripped on a rotary evaporator (bath at 40°C). A light yellow oil which may begin to crystallize results. Add 200 mL ligroine (b.p. 70-90°C), causing rapid crystallization. The mass is broken up and slurried in 40°C ligroine for 30 minutes. The product is collected by vacuum filtration, washed well with ligroine and vacuum dried for 24 hours at 40°C. Yields are 10 to 13 g (70-90%).

Analysis
M. P. 73-75°C
NMR (CDCl3): δ 1.96, s(3H), δ 4.72, s (2H), δ 5.65, s(1H), δ 6.21, s(1H). IR (KBr) ~3000 (broad), 1745 (s), 1723 (s), 1638 (br), 1620 (m), 1438 (s), 1380 (m), 1330 (m), 1310 (m), 1260 (br), 1255 (s), 1150 (s), 1050 (m), 1000 (m), 950 (s), 920 (s), 813 (s), 703 (s).
Assay by titration - 97.5 - 98.5 wt%; apparent pK_a 3.1.
Assay by GC - 98 - 99.2 area percent
Elemental Analysis-Found (Expected): C, 49.8 (50.0), 5.5 (5.6), O, 44.7 (44.4)

Polymerizations
Homopolymer: 2.0 g I is placed in a screw cap test tube with a Teflon cap liner. Add 7.2 g toluene and sparge with N_2 for 30 minutes. Add 1 mL 5.5 mg/mL AIBN in toluene. Cap tightly and seal with Teflon tape. Place in controlled temperature bath at 65°C for 24 hours. Precipitate into 100 mL ligroine (b.p. 70-90°C). Decant ligroine from gelatinous mass and add fresh 150 mL ligroine. Soak until hardened. Break up to fine powder and collect by vacuum filtration. Vacuum dry at 60°C for 24 hours. Yield 1.97 g (98%). The polymer is soluble in MeOH, THF and DMF.

Copolymers with TBS (Example)
1.82 g (0.0114M) TBS is placed in screw cap test tube with a Teflon cap liner. Add 7.1 g N,N-dimethylacetamide (DMA) into which has been dissolved 0.18 g (0.0013 M) I (mole fraction I in feed is 0.102). Sparge with N_2 for 30 minutes. Add 1 mL 5.0 mg/mL AIBN in DMA. Cap tightly and seal with Teflon tape. Place test tube in controlled temperature bath at 65°C for 3 hours. Precipitate into 100 mL 80/20 (v/v) CH_3CN/CH_3OH containing 5 mL concentrated HCl. The polymer is collected by vacuum filtration, washed with fresh CH_3CN, and vacuum dried at 60°C for 24 hours yield: 1.29 g (12.9% conversion). The polymer is soluble in THF.

Note that for monomer feeds containing more than 0.2 mole fraction I, more HCl is required in the nonsolvent.

Acknowledgement
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