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The Preparation and Properties of Poly-α-Methylene-β-Propiolactone and α-Ammoniummethacrylic Acid Salts

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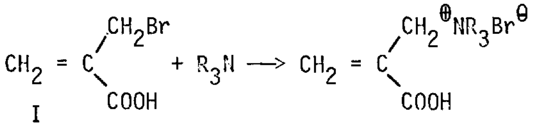
Dedicated with Fondness to Prof. Dr. Georg Manecke in Celebration of his 65th Birthday

SUMMARY

α-Bromomethacrylic acid was reacted with various amines in an attempt to prepare a new series of α-ammoniummethacrylic acid monomers. For amines of relatively low basicity such products were obtained, but they could not be polymerized with a free radical initiator at 70°C. With highly basic amines, a highly crystalline polyester was obtained instead, which presumably resulted from the formation and anionic polymerization of α-methylene-β-propiolactone.

INTRODUCTION

A convenient method for the synthesis of α-bromomethacrylic acid I, was recently reported from this laboratory[1]. Because of the ready availability of this compound, an investigation was carried out on the use of this intermediate for the preparation and polymerization of other acrylic acid monomers containing either α-ammoniummethyl or α-sulfoniummethyl groups by reactions with either amines or sulfides, respectively, as shown in the equation below for the former reactant:



$$CH_2=C(CH_2Br)(COOH) + R_3N \longrightarrow CH_2=C(CH_2{}^{\oplus}NR_3Br^{\ominus})(COOH)$$

I

RESULTS

α-Ammoniummethacrylic Acids. The reactions of either pyridine or 2- or 4-vinylpyridine with I were successfully applied to the preparation of the respective pyridinium salts, which had the properties listed in Table 1. Morpholine and dimethylaminoethylmethacrylate were also found to give the expected ammonium salts as shown in Table 1, and diethyl sulfide readily formed the desired sulfonium salt, also included in Table 1. In addition to the elemental analyses reported in this Table, the IR and ^{13}C NMR analyses were obtained and the results of each of these analyses were consistent with the structures of the expected products.

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TABLE 1

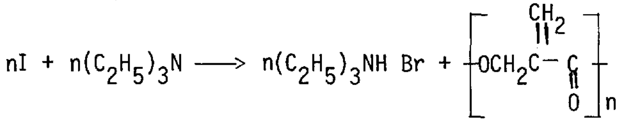
Ammonium and sulfonium derivatives obtained from I

Amine or sulfide	pK_a	M.P., °C	Product Analysis. %[a]			
			C	H	N or S	Br
Pyridine	5.26	156-157	44.30 (44.26)	4.05 (4.10)	5.79 (5.74)	32.47 (32.79)
4-Vinylpyridine	5.6	185(decomp)	48.70 (48.89)	4.66 (4.44)	5.13 (5.18)	29.56 (29.63)
2-Vinylpyridine	5.8	135.5-136.5	48.88 (48.89)	4.58 (4.44)	5.16 (5.18)	29.79 (29.63)
Dimethylaminoethyl methacrylate	7.94	96.97	44.53 (44.72	6.37 (6.21)	4.15 (4.25)	24.89 (24.84)
Morpholine	8.33	171.5-172.5	37.52 (38.10)	6.01 (5.56)	6.01 (5.56)	32.80 (31.75)
Diethyl sulfide		78-80	37.67 (37.65)	5.96 (5.88)	12.70 (12.55)	32.16 (31.37)

[a] The upper number is the analysis found; the lower number in brackets is the calculated analysis.

All the derivatives listed in Table 1 were readily soluble in water or in lower alcohols, but none of these potential monomers polymerized at the acrylic double bond function on reaction with AIBN at 70°C in water. However, as expected, the vinyl pyridine and dimethylaminoethyl methacrylate adduct monomers of I readily polymerized through their own double bonds to form polymers which were initially soluble in water or lower alcohols but which subsequently, on extended storage, became insoluble and apparently crosslinked. Attempts to copolymerize the pyridine adduct with styrene under various conditions were also unsuccessful. It is apparent, therefore, that these acrylic acid derivatives are much less reactive in free radical polymerization reactions than the analogous, neutral α-phenoxy derivatives[1].

Poly-α-Methylene-β-Propiolactone. Much different and unexpected results were obtained when I was reacted with a trialkylamine under the same conditions. For example, when I was reacted with triethylamine, TEA, a product which was insoluble in water and alcohol was obtained. Extraction of this product with chloroform yielded triethylamine hydrobromide as the soluble component and a polymer of very low solubility in chloroform but soluble in trifluoroacetic acid, which was subsequently identified by ^{13}C NMR, IR, and elemental analysis as poly-α-methylene-β-propiolactone, see Table 2. These products were formed according to the following overall equation:



$$nI + n(C_2H_5)_3N \longrightarrow n(C_2H_5)_3NH\ Br + \left[OCH_2\overset{\overset{\displaystyle CH_2}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C} \right]_n$$

The reaction of I with tri-n-butylamine, TBA, gave essentially the same product as that from TEA as shown by the data in Table 2. The polymeric product was obtained even when I was added slowly to a large excess of the amine. However, higher molecular weight polymers were obtained by addition of the amine to I.

TABLE 2.

Polymers obtained from the reaction of I with amines.

Polymer Number	Amine[a]	Yield, g(%)	[η][b]	T_m, °C[c]	Analysis, %[d] C	H	N	Br
1	TEA	2.75(90)	0.25	213	56.36 56.71	5.31 5.19	- -	- -
2	TBA	0.45(15)	0.18	202	57.00	4.96	0.1	1.64
3	TBA	1.85(60)	0.21	204	53.34	4.87	-	-
4	TEA	2.50(82)	0.13	195	55.77 54.26	5.33 4.89	0.49 0.16	0.85 0.96

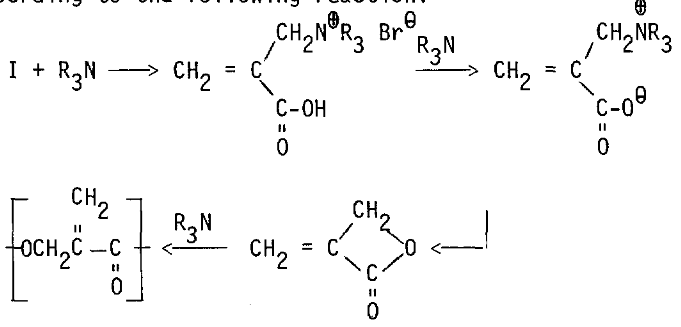
[a] TEA-triethylamine; TBA-tri-n-butylamine.

[b] Intrinsic viscosity in trifluoroacetic acid solution at 30°C.

[c] Polymer melting point taken as peak of DSC endotherm, see Figure 1.

[d] Calculated analysis for poly-α-methylene-β-propiolactone: C, 57.14; H, 4.76%.

It is believed that the polymer obtained results from the intermediate formation and polymerization of α-methylene-β-propiolactone according to the following reaction:



However, all attempts to isolate the lactone have been unsuccessful. Nevertheless, the formation of the lactone in this case instead of the adduct, as in the former case, can reasonably be attributed to the much higher pK_a values of these two trialkylamines as contrasted to the pK_a values of the other amines listed in Table 1. The latter have pK_a values ranging from 5.26 to 8.33 while triethyl and tri-n-butylamine both have pK_a values of approximately 11. Hence these two are much stronger bases, which can presumably cause the ionization and ring closure reactions as shown above.

All samples of poly-α-methylene-β-propiolactone so formed were highly crystalline according to DSC analysis with melting points ranging from 194° to 254°C depending on molecular weight (see Table 2) and thermal history. The effect of thermal annealing on their melting point is shown by the data in Table 3.

TABLE 3

Effect of annealing on the melting point of Polymer 4.

Annealing Time, min.	Annealing Temp., °C	T_m,°C[a]
30	195	239
40	195	244
60	195	246
120	195	254
60	203	265

[a] The melting point is taken as the temperature of the endothermic peak in DSC thermograms.

Long term annealing at elevated temperatures, however, resulted in insolubilization and loss of crystallinity as shown by the DSC thermograms in Figure 1 for each of the polymers after annealing. The disappearance of the melting endotherms in the thermograms numbered 3, 4 and 5 of Figure 1 can most likely be attributed to crosslinking reactions involving the pendent methylene groups. The polymers as initially formed were completely soluble in trifluoroacetic acid and showed sharp melting endotherms as seen in thermograms 1 and 2 of Figure 1.

EXPERIMENTAL

Reaction of Triethylamine with I. A solution of 6.0g of I in 35 ml of toluene was added slowly to a solution of 4.1g of triethylamine in 40 ml of toluene (the molar ration of I to the amine was 1:1.1) in a 150 ml flask equipped with a magnetic stirrer and placed in a cooling bath held at -20°C. The mixture was stirred for 40 min., during which time the temperature of the solution in the flask increased to 15°C. The flask was removed from

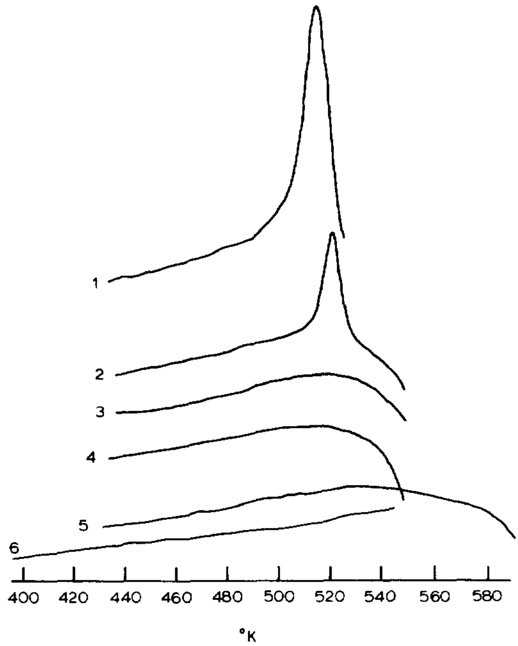


Figure 1. DSC thermograms of polymer samples after annealing for 40 minutes (unless otherwise noted) at the temperatures indicated:(1) Polymer 4 at 195°C, (2) Polymer 2 at 202°C, (3) Polymer 1 at 213°C, (4) Polymer 3 at 204°C, (5) Polymer 2 at 204°C for 60 minutes, (6) instrument baseline.

the bath and placed in a refrigerator overnight. A white precipitate formed which was filtered and washed with toluene and ether; yield:9.4g (97%). The crude product was dissolved and reprecipitated from either chloroform or trifluoroacetic acid solution into methanol. The fine, white powder which formed was filtered and dried in vacuum. Anal.: Calcd., C, 57.14; H, 4.76; for poly-α-methylene-β-propiolactone. Found, C, 56.36; H, 5.31. The remaining chloroform solution was concentrated and a solid was precipitated in ether, redissolved in ethanol and reprecipitated in ether to yield a second, crystalline product. Anal.: Calcd., C, 39.56; H, 8.79; N, 7.69; Br, 43.95 for triethylammonium bromide; Found, C, 39.77; H, 9.20; N, 7.60; Br, 44.14.

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1. R.W. LENZ, K. SAUNDERS, T. BALAKERISHMAN and K. HATADA, Macromolecules, 12, 392 (1979).

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