Synthesis and Copolymerisation of α-Acrylic Acids and Esters

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Summary Copolymerisation of alkyl- and substituted alkyl-acrylic acids with styrene is successful provided that very pure monomers are used.

MODEL compounds for the study of the physiological mechanisms associated with calcification of tissues, have included α-substituted acrylic monomers. The substituents are alkyl, or alkyl terminated in a functional group, *e.g.* OH, NH_2. The usefulness of monomers of this type for producing biomedical materials has already been discussed.[1,2]

α-Alkyl substituted monomers were synthesised from diethyl malonate by a modification of the method of Crawford and Swift,[3] the reaction of alkyl halides with the sodiomalonate, followed by a Mannich reaction. I.r. spectra confirmed the presence of a vinylic double bond.

Polymerisation of α-alkyl substituted acrylics is notoriously difficult. Crawford was unsuccessful, and apart from a high-temperature[4] and a high-pressure method,[5] only one report has been published, describing anionic initiation.[6] I report successful copolymerisation of very pure monomers with very pure styrene as co-monomer, using azoisobutyronitrile as initiator. Monomer purity was established by g.l.c. Polymerisation was performed under high vacuum, in sealed tubes, at 70°. Monomer reactivity ratios are listed in the Table Alkyl substituents larger than hexyl have been introduced.

Homopolymerisation with free-radical initiator was not successful. γ-Irradiation produced insignificant changes in the refractive index of the monomers. The sodio-derivative of naphthalene readily produced a solid polymer not yet characterised.

TABLE

	Molar ratio acid : styrene (monomer	Molar ratio acid : styrene (polymer	r_1	r_2	r_1r_2
Ethylacrylic acid	2·24	1·03			
	1·12	0·84			
	0·56	0·53			
	0·18	0·15 benzene sol. fraction	0·31 ± 0·01	0·68 ± 0·01	0·21
		0·13 benzene isol. fraction			
n-Propylacrylic acid	0·97	0·55			
	0·48	0·62			
	0·10	0·13	0·68 ± 0·08	0·725 ± 0·005	0·48
n-Butylacrylic acid	0·85	0·78			
	0·43	0·52 benzene sol. fraction			
		0·68 benzene isol. fraction			
	0·09	0·12	0·32 ± 0·04	0·52 ± 0·01	0·16
Methacrylic acid 60°	—	—	0·7 ± 0·01	0·15 ± 0·05	0·105
Acrylic acid 60°	—	—	0·25 ± 0·02	0·15 ± 0·01	0·038

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