Only potassium 4-(*p*-bromoacetylphenyl) butanoate (IIIc) gave a chloroform-soluble buff polymer under solid–liquid and liquid–liquid p.t.c. The i.r. spectrum showed strong ester carbonyl peaks at 1635 and 1735 cm^{-1} but no terminating groups derived from solvolysis were evident in either i.r. or n.m.r. spectra. *Table 1* shows that solid–liquid p.t.c. polymerization of IIIc can be accomplished in several solvent systems at temperatures from 60° to 100°C. The g.p.c. trace of these polymers IVc showed a pronounced low molecular weight tail beside the broad peak from the polymer. As shown in *Table 1*, the (polystyrene-based) weight-average molecular weights (from g.p.c.) of the polymers IVc lie in the range $5–8 \times 10^3$ depending on solvent system used in the polymerization, and dispersities vary from 1.7 to 4.0. Number-average molecular weights from v.p.o. and elemental analysis which should be more reliable, are not generally in good agreement, possibly because of the presence of variable amounts of oligomeric material. All characterization techniques, however, point to rather low *DP*s in the range 11–16. Thus, despite the apparently much cleaner reaction of IIIc compared with Ib, the efficiency is still too low to yield high polymer.

With chloroform as solvent the polymers IVc remained in solution, while in the other solvents a proportion of the polymer usually precipitated in admixture with KBr. The higher reaction temperatures attainable with diglyme do not show any appreciable advantage, either in yield or molecular weight of the polymer. *Figure 1* shows that the reaction in chloroform reaches a limiting conversion of $\sim 75\%$ after 48 h at ambient temperature. The $\bar{M}_n$ value also reached a maximum of about 2×10^3 ($DP \sim 10$) over the same period. Under liquid–liquid p.t.c. IIIc behaved in a similar manner (*Table 1*).

We conclude that, in common with most p.t.c. polymerizations involving bifunctional nucleophiles and bifunctional electrophiles, systems of the type described in this paper are unlikely to yield high polymers.

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Some 2-propioxy- and 2-isobutyroxy-acrylic esters

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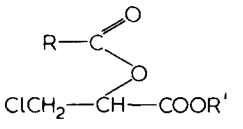
INTRODUCTION

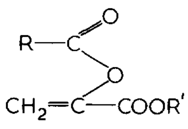
In previous papers, we reported a modified method for the preparation of 2-acetoxyacrylic esters[1] and the synthesis and polymerization of several 2-haloacetoxyacrylic esters[2]. In order to extend the scope of 2-acyloxyacrylic esters and to study the effects of the different 2-acyloxyl groups on the properties of the monomers and their polymers, there is a demand for some esters of higher 2-acyloxyacrylic acids. In this paper, we report the preparation and preliminary polymerization of several 2-propioxy- and 2-isobutyroxyacrylic esters which have not been reported in the literature.

The preparation of these monomers consists of two steps. First, acylation of 2-hydroxy-3-chloropropionic esters with propionyl or isobutryl chloride yielding the corresponding 2-acyloxy-3-chloropropionic esters (1), and second, dehydrochlorination of 1 with triethylamine in benzene solution giving the desired monomers (2) in good yields. (1a,2a: R = Et, R′ = Me; 1b,2b: R = Et, R′ = Et; 1c,2c: R = i-Pr, R′ = Me; 1d,2d: R = i-Pr, R′ = Et.)



$\mathrm{ClCH_2{-}CH(OCOR){-}COOR'}$

1



$\mathrm{CH_2{=}C(OCOR){-}COOR'}$

2

The first reaction progresses smoothly under a gentle reflux temperature and gives 1 in a promising yield. In the second reaction, we observed that triethylamine was a more effective dehydrochlorinating reagent than quinoline which has been used for the preparation of 2-acetoxyacrylic esters by Laakso and Unruh[3]. When the quinoline was used, the reaction needed heating under reflux for a number of hours and was usually incomplete. However, the dehydrochlorination with triethylamine could be carried out at room temperature or, in some cases lower; to induce rapid completion of the reaction it was only necessary to heat the reaction mixture in a water bath for a short time. It is clear that both the lower

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Table 1 Characteristics and analyses of bulk polymers of types 1 and 2

				M_R*		Analyses		
Compound	b.p. °C mm	n_D^{25}	D_4^{25}	Calculated	Found	Calculated	Found	Yield %
1a	80-2/3	1.4380	1.1939	42.70	42.79	–	–	78
1b	83-5/3	1.4355	1.1488	47.32	47.44	–	–	72
1c	81-3/3	1.4390	1.1612	47.32	47.26	–	–	68
1d	85-7/3	1.4364	1.1287	51.94	51.62	–	–	70
2a	55-6/3	1.4318	1.0972	37.37	37.37	C 53.2 H 6.4	53.0 6.4	61
2b	60-2/3	1.4292	1.0650	41.99	41.70	C 55.8 H 7.0	55.8 7.1	75
2c	61-3/3	1.4330	1.0656	41.99	41.99	C 55.8 H 7.0	55.7 6.8	68
2d	70-2/2	1.4305	1.0404	46.61	46.28	C 58.1 H 7.6	57.9 7.3	66

* Ref 5

reaction temperature and the shorter reaction time are advantageous in preventing the polymerization of the products during the preparation.

Type 2 monomers are stable for weeks on storage in a refrigerator, but in the presence of free radical initiators they readily polymerize. This fact indicates that the change of the 2-acyloxyl group seems to have little effect on the homopolymerization of the monomers. The bulk polymers of Type 2 are transparent, colourless and hard glassy solids which are closely similar to the bulk polymer of methyl methacrylate in appearance. The characteristics of bulk polymers of types 1 and 2 are listed in *Table 1*.

The method that is described above is essentially a general one for the preparation of 2-acyloxyacrylic esters[2,3].

EXPERIMENTAL

Methyl and ethyl 2-hydroxy-3-chloropropionates were prepared according to Koelsh's method[2,4]. Propionyl and isobutyryl chloride were distilled before use.

2-Acyloxy-3-chloropropionic esters (1)

The reaction mixture of 2-hydroxy-3-chloropropionic ester (0.4 mol) and the acid chloride (0.5 mol) was heated to reflux gently for 6 h. The excess acid chloride was distilled at water aspirator pressure on a water bath and the residual ester was distilled under vacuum.

2-Acyloxyacrylic esters (*2*)

2-Acyloxy-3-chloropropionic esters (compound 1) (0.1 mol), benzene (50 ml) and a little quantity of cuprous chloride as inhibitor were mixed in a flask. The flask was cooled with cold water. Triethylamine (0.15 mol) was added slowly through a dropping funnel. When the triethylamine was completely added, the reaction mixture was heated in a 70°–80°C water bath for 45 min. The precipitate of the triethylamine hydrochloride was filtered and washed with benzene. The benzene solution was washed separately with 6N hydrochloride, water, saturated sodium bisulphite and water. Then it was dried over calcium chloride and distilled under vacuum. Yields of 2 varied from 60–75%. The products contained no chloride as observed by the sodium fusion test.

Bulk polymerization of these monomers with 0.1% azobisisobutyronitrile as initiator were carried out either in sealed tubes under nitrogen or in glass plate moulds at 60°C. The polymers of 2 are transparent, hard glassy solids and soluble in chloroform and other chlorinated hydrocarbon solvents. Transparent and flexible films could be cast from the polymer solutions.

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