

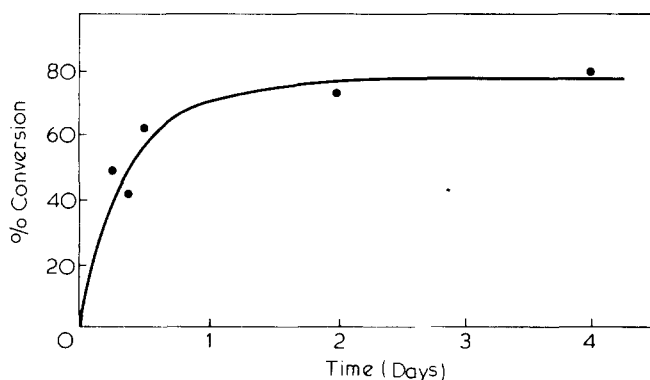
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$$\text{ArCH}_2-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$$

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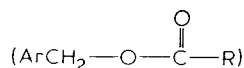
Table 1 Phase transfer catalysed polymerization of potassium 4-(*p*-bromoacetylphenyl) butanoate

Solvent	Temperature (°C)	Time (h)	Yield ^a (%)	Molecular weight of polymer × 10 ⁻³ \bar{M}_w^d	\bar{M}_n	\bar{M}_w/\bar{M}_n
Diglyme ^b	100	4	42	6.80	3.23 ^d 3.23 ^e 2.56 ^f	2.11
	60	24	35	4.63	1.30 ^d 2.38 ^e 2.56 ^f	3.56
Benzene:acetonitrile ^b (1:1 mixture)	80	24	63	5.44	1.62 ^d 2.24 ^e 2.08 ^f	3.35
	60	24	61	6.82	2.18 ^d 2.08 ^f	3.13
Chloroform ^b	60	24	57	7.73	4.12 ^d 3.84 ^f	1.88
Chloroform:H ₂ O ^c	room temperature ~20°C	100	60	4.15	1.04 ^d 2.41 ^e 1.89 ^f	4.0

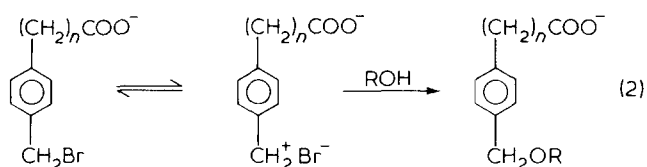
^a Based on quantitative formation of KBr^b 18-crown-6^c Aliquat 336^d From g.p.c.^e From v.p.o.^f From Br contentFigure 1 Effect of time on the yield of polymer from solid-liquid p.t.c. polymerization of potassium 4-(*p*-bromoacetylphenyl) butanoate in chloroform at 60°C

respectively. Solid-liquid p.t.c. polymerization of Ia at 100°C in nitrobenzene with Aliquat 336 produced a white polymer (IIa) insoluble in all common solvents.

In an attempt to produce a soluble polymer amenable to characterization the sodium salt of Ib was prepared and subjected to p.t.c. with 18-crown-6 in solution. This gave a white soluble polymer (IIb) with a *DP* of ~10 and showing strong i.r. absorption at 1720 cm⁻¹. However, besides peaks at 4.40 (ArCH₂Br) and 5.04 ppm

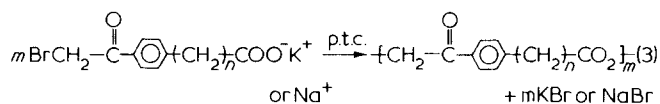


the n.m.r. spectrum contained a peak at 3.35 ppm which was attributed to ArCH₂OCH₃ groups resulting from the solvolysis of benzylic bromine (equation 2). A liquid-liquid p.t.c. polymerization



also provided evidence of solvolysis; the n.m.r. spectrum showed a peak at 4.64 ppm attributable to ArCH₂OH. Strong hydroxyl absorption in i.r. spectrum was also observed.

The occurrence of solvolysis with Ib but not Ia is understandable if displacement of bromine occurs by the S_N1 process shown in equation 2, since this is more favourable with a methylene group (Ib) rather than a carboxylate group (Ia) in the *para* position. Solvolysis or other such reactions present a serious obstacle to high polymer formation and in an effort to circumvent this problem the monomers IIIa-c (*a*, *n* = 0; *b*, *n* = 2; *c*, *n* = 3) were synthesized. These contain the phenacyl bromide group -C₆H₄COCH₂Br which should be susceptible to nucleophilic displacement of bromine by the S_N2 mechanism to yield polymer, but resistant to S_N1 attack.



IIIa, *n* = 0
b, *n* = 2
c, *n* = 3

IVa, *n* = 0
b, *n* = 2
c, *n* = 3

The monomers IIIa and IIIb underwent both solid-liquid and liquid-liquid p.t.c. polymerization but the products were insoluble in all solvents suitable for characterization.

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 ~75% after 48 h at ambient temperature. The \bar{M}_n value also reached a maximum of about 2×10^3 (*DP* ~ 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 esters¹ and the synthesis and polymerization of several 2-haloacetoxyacrylic esters². 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.)



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 Unruh³. 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