# Polyester synthesis by phase transfer catalysis

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### INTRODUCTION

Since its introduction around 1965, phase transfer catalysis (p.t.c.) has become a firmly established technique in organic chemistry. In polymer chemistry, however, applications of p.t.c. have been comparatively few, though recently it has been shown to have promise for the chemical modification of polymers<sup>2-4</sup>, and there have been several reports on the application of p.t.c. to induce or accelerate condensation polymerizations yielding, for example, polycarbonates<sup>5</sup> and polysulphonates<sup>6</sup>. In most of these reactions crown ethers have been the catalysts of choice in solid–liquid systems<sup>5.6</sup>, although quaternary ammonium salts have been used for many years to accelerate interfacial polycondensation reactions<sup>7</sup>.

The recent reports concerning crown ether catalysts have all involved reaction of a bifunctional nucleophile with a bifunctional electrophile, but in principle polymerization should be possible with one monomer species carrying both types of functional group. In this communication we report investigations on the polymerization of salts of 4-(p-bromoacetylphenyl) butanoic acid and related compounds by solid-liquid and liquid-liquid p.t.c.

### **EXPERIMENTAL**

#### Materials

18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) Aliquat 336 (tricaprylylmethylammonium chloride) and the acids,  $\alpha$ -bromo-p-toluic, acetylbenzoic, 4-phenylbutanoic and cinnamic, were obtained from the Aldrich Chemical Company.

4-( $\alpha$ -Bromo-p-tolyl) butanoic acid was synthesised by the method of Kubiczek<sup>8</sup>.  $\alpha$ -Bromoacetylbenzoic,  $\alpha$ -bromoacetylhydrocinnamic and  $\alpha$ -bromoacetylphenylbutanoic acids were prepared by bromination in glacial acetic acid<sup>9</sup> of p-acetylbenzoic, p-acetylhydrocinnamic and p-acetylphenylbutanoic acids<sup>10</sup> respectively. The latter two acids were prepared from cinnamic and 4-phenylbutanoic acids respectively. Sodium or potassium salts of the  $\alpha$ -bromoacids were obtained by neutralization with the appropriate hydroxide.

#### Polymerization procedures

Solid—liquid p.t.c. polymerization. A fine suspension of the potassium salt (from 1.0 g of bromoacid) was stirred with the appropriate solvent (20 ml) with the phase transfer catalyst (52.6 mg) for 24 h. After cooling, the mixture was filtered through a porosity 3 glass sinter to remove potassium bromide and any unreacted salt.

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washed with water, methanol, and finally ether. The product was dried under vacuum at 40°C for 24 h.

Liquid-liquid p.t.c. polymerization. The potassium or

Addition of methanol to the filtrate precipitated the polymer as an off-white powder which was thoroughly

Liquid-liquid p.t.c. polymerization. The potassium or sodium salt (from 1.0 g of the bromoacid) was dissolved or suspended in distilled water (10 ml) and Aliquat 336 (2 drops). The milky emulsion cleared after 2 days and reaction was continued for a further 2 days. The organic layer was then separated and added to methanol and the product treated as in the solid-liquid p.t.c. polymerization.

# Polymer characterization

I.r. spectra of the polyesters were obtained with a Perkin-Elmer Model 197 Spectrophotometer from films cast on sodium chloride discs from chloroform solution. N.m.r. spectra were recorded with a Varian 100 MHz instrument from deuterochloroform solutions with trimethylsilane as internal standard. Molecular weights were determined with a Waters M6000A gel permeation chromatograph with four  $\mu$ -Styragel Columns (10<sup>4</sup>, 10<sup>3</sup>, 500 and 100 Å) and a Model 440 u.v. detector. The solvent was chloroform pumped at 1.0 ml min  $^{-1}$ . Polystyrene fractions were used as calibration standards. Numberaverage molecular weights were also determined with a Perkin-Elmer Model 115 vapour pressure osmometer and from the elemental analyses of the polymers.

Details of the reactions, yield and nature of the products are summarized in *Table 1*.

### RESULTS AND DISCUSSION

Preliminary investigations showed that when liquid–liquid p.t.c. polymerization of the sodium salt of  $\alpha$ -bromo-p-toluic acid (Ia) was carried out with a few per cent of Aliquat 336 as catalyst, a polymer

$$m \operatorname{BrCH}_2 \longrightarrow \operatorname{+CH}_2 \xrightarrow{h_1} \operatorname{COO}^- \operatorname{Nd}^+ \xrightarrow{\operatorname{pt.c.}} + \operatorname{CH}_2 \longrightarrow \operatorname{+CH}_2 \xrightarrow{h_1} \operatorname{C-O} \xrightarrow{h_2} + m \operatorname{NaBr}$$

with a degree of polymerization  $(DP) \sim 3$  was obtained (Ia, n=0,  $\alpha$ -bromo-p-toluic acid, IIa, n=0; Ib, n=3,  $\alpha$ -bromo-p-tolylbutanoic acid, IIb, n=3). The n.m.r. spectrum of the polymer showed peaks at  $\delta 4.58$  and 5.42 ppm, characteristic of ArCH<sub>2</sub>Br and

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

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

<sup>&</sup>lt;sup>a</sup> Based on quantitative formation of KBr

<sup>&</sup>lt;sup>f</sup> From Br content

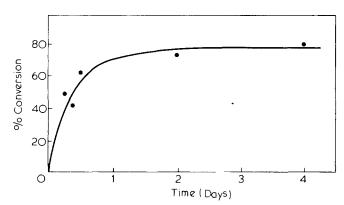


Figure 1 Effect of time on the yield of polymer from solid-liquid p.t.c. polymerization of potassium 4-(p-bromoacetylphenyl) butanoate in chloroform at 60°C

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  $\sim 10$  and showing strong i.r. absorption at 1720 cm<sup>-1</sup>. However, besides peaks at 4.40 (ArCH<sub>2</sub>Br) and 5.04 ppm

the n.m.r. spectrum contained a peak at 3.35 ppm which was attributed to ArCH<sub>2</sub>OCH<sub>3</sub> groups resulting from the solvolysis of benzylic bromine (equation 2). A liquid-liquid p.t.c. polymerization

$$(CH_2)_nCOO^{-} \qquad (CH_2)_nCOO^{-} \qquad (CH_2)_nCOO^{-}$$

$$ROH \qquad (2)$$

$$CH_2Br \qquad CH_2Br^{-} \qquad CH_2OR$$

also provided evidence of solvolysis; the n.m.r. spectrum showed a peak at 4.64 ppm attributable to ArCH<sub>2</sub>OH. 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 -C<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>Br which should be susceptible to nucleophilic displacement of bromine by the S<sub>N2</sub> mechanism to yield polymer, but resistant to  $S_{N1}$  attack.

$$\begin{picture}(2000,0) \put(0.00,0){\line(1,0){100}} \put($$

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.

b 18-crown-6

Aliquat 336

d From g.p.c.

 $<sup>^</sup>e$  From v.p.o.

### Polymer reports

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<sup>-1</sup> 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 DPs 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  $2 \times 10^3$  (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 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 Unruh<sup>3</sup>. 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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