Polyester synthesis from phase transfer catalysed polymerizations involving *m*-xylylene dibromide

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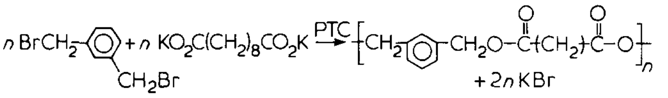
There is currently some interest in the application of phase transfer catalysis (*PTC*) to induce polymerization between bifunctional nucleophiles and bifunctional electrophiles. Among the latter the xylylene dihalides have featured prominently, for example in the syntheses of polyethers[1] and polycarbonates[2]. In our investigations of polyester synthesis promoted by *PTC*[3] we have also employed these bifunctional electrophiles and have found that dipotassium carboxylates, for example dipotassium sebacate, form polymers only with the *m*-isomers, particularly *m*-xylylene dibromide.



The above polymer was obtained as a powder with a very low softening point (35°–40°C).

Although this reaction is induced by several different phase transfer catalysts (see *Table 1*) the solvent employed is critical. Acetonitrile and acetonitrile–benzene (1:1 by vol) were the only solvents which yielded polymers in these solid–liquid systems. With benzene, dimethylformamide, dimethylsulphoxide, diglyme and chloroform little or no polymer was obtained. Presumably acetonitrile permits more rapid dissolution of the dicarboxylate[4]. Attempts to carry out the reaction in a liquid–liquid system also failed, possibly because of a highly unfavourable partition of the dicarboxylate between the organic and aqueous phases. It is likely that in the presence of water solvolysis of benzylic bromide also occurred to some extent[3].

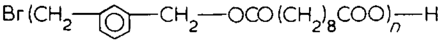
For the crown ether, *Table 1* shows that the yield of product is not at all sensitive to the amount of catalyst used and that there is no advantage in running the reaction beyond ~4 days at 80°C. Temperature is, however, important. At 60°C the yield of polymer is greatly diminished and the product contains more oligomeric material as evidenced by discrete low molecular weight peaks in the gel permeation chromatogram (*Figure 1*).

The i.r. and n.m.r. (100 MHz, $CDCl_3$ solution) spectra of the polymer are consistent with the above structure. The latter shows absorptions at δ5.10 and 4.48 ppm, characteristic of $-OCH_2Ar-$ and $BrCH_2Ar-$ respectively, in the ratio ~33:1 which indicates a degree of polymerization in the region 30–35, corresponding to a molecular weight in the range 4500 to 5500. This is slightly higher than the molecular weight data listed in *Table 1*, though we note, as before[3], that agreement among the values obtained by different methods is not wholly satisfactory.

Since *m*-xylylene dibromide appears more reactive than the *p*-isomer in these reactions we compared their reactivities in the polycarbonate synthesis[2] with K_2CO_3. In

Table 1 Solid–liquid phase transfer catalysed polymerization of *m*-xylylene dibromide and dipotassium sebacate

Catalyst	Concentration mol dm^{-3}	Temperature °C	Time days	Yield %	Elemental analysis % C	H	Br	Molecular weight x 10^{-3} $\bar{M}_n$	$\bar{M}_w$[a]
Hexadecyltriphenyl phosphonium bromide	3.81 x 10^{-2}	80	4	75	69.7	8.1	2.34	2.94[a] 3.41[b]	8.90
Aliquat 336	4 drops in 20 ml	80	4	85	69.8	8.1	2.35	4.57[a] 3.40[b]	12.50
Cryptand [2.2.2]	1.91 x 10^{-2}	80	4	67	67.9	8.2	2.35	4.37[a] 3.40[b]	10.17
18–Crown–6	9.46 x 10^{-3}	80	4	64	68.3	7.5	2.90	3.67[a] 3.76[b]	8.04
	9.46 x 10^{-3}	80	5	70	–	–	–	–	–
	9.46 x 10^{-3}	80	8	66	–	–	–	–	–
	9.46 x 10^{-3}	60	4	10	–	–	–	–	–
	1.90	80	4	66	–	–	–	4.66[a]	10.02

[*m*-Xylylene dibromide] = [Dipotassium sebacate] = 0.19 mol dm^{-3}; solvent–acetonitrile/benzene 1 : 1 by vol.;
[a] from g.p.c. (polystyrene standards)
[b] from Br analysis
[c] in  $Br(CH_2-C_6H_4-CH_2-OCO(CH_2)_8COO)_n-H$ with n = 11, $\bar{M}_n$ = 3429, and C 69.34, H 7.79, Br 2.33%; experimental procedure as described in ref. 3

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each case the acetonitrile–benzene mixture (20 ml) was used, with 3.8 mmol of K_2CO_3 and the dibromide, and 0.19 mmol of 18-crown-6. After stirring at 80°C for three days the polycarbonates were recovered as before. From the *m*- and *p*-xylylene dibromides respectively the yields were 27 and 12%, and the molecular weights (by g.p.c.) were 1.8×10^3 and 1.0×10^3.

Clearly there are advantages to be gained by using the *m*-isomer in these systems, though it is not entirely clear why this should be so. If the reaction involved a simple nucleophilic substitution then one would expect the *p*-isomer to react slightly faster[5] than the *m*-compound. Our results suggest that the *p*-isomer is more prone to interfering side reactions.

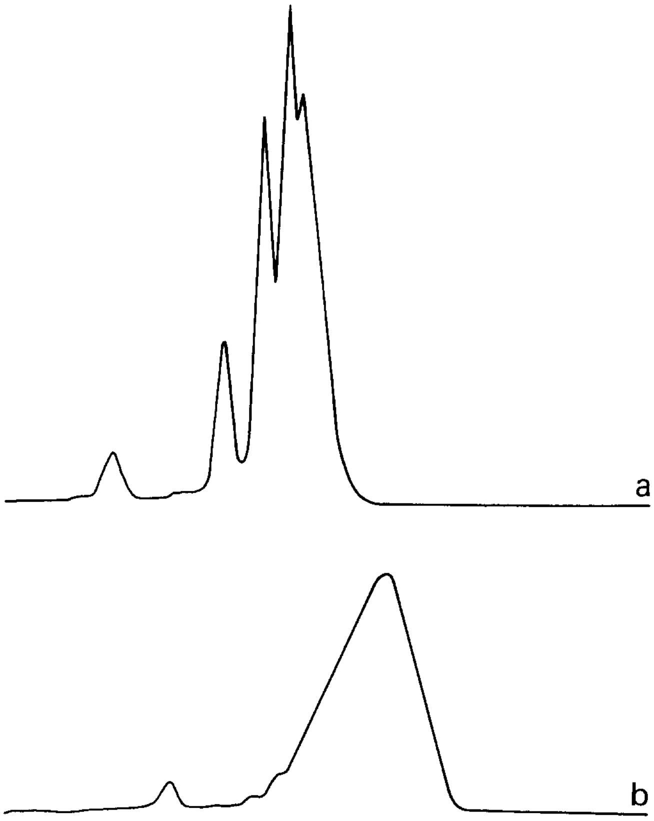

Figure 1 Gel permeation chromatographs of polymers from crown ether catalysed reaction of *m*-xylylene dibromide and dipotassium sebacate at (a) 60° (b) 80°C; reaction time 4 days; reaction conditions as in *Table 1*

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Kinetics of hydrolytic polymerization of ε-caprolactam:
3. Formation of cyclic dimer

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INTRODUCTION

The authors have investigated the mechanism and kinetics of the hydrolytic polymerization of ε-caprolactam[1] (CL) and proposed improved sets of kinetic and thermodynamic constants necessary to formulate the rate equations[2]. In these studies, the three main equilibrium reactions, i.e. ring-opening of CL, polycondensation of chains, and poly-addition of CL, are taken into account. However, cyclic oligomers, $[NH(CH_2)_5CO]_x$ with $x = 2, 3, \ldots,$ exist in polymeric equilibrates as by-products. This study deals with the formation of cyclic dimer (CD, $x = 2$), the major portion of the cyclic oligomers.

Many investigations have been concerned with separation and analytical techniques such as fractional sublimation[3], thin-layer chromatography[4], infrared spectrometry[5], gas chromatography[6], and gel permeation chromatography[6,7], the cyclization equilibria[6,8,9], and the formation of cyclic oligomers[10]. But there have been few reports of kinetic studies of the hydrolytic polymerization of ε-caprolactam for a variety of polymerization conditions because of the lack of either rapidity or accuracy in the analysis of CD. Thus, the effects of temperature and initial water concentration on the behaviour of CD formation during the reaction have not yet been clarified.

A rapid quantitative analysis to determine the concentration of CD by gas chromatography is established. The kinetic data for CD formation are obtained in various reaction conditions, and the mechanism and the kinetics of CD formation are discussed.

EXPERIMENTAL

Material

A molten ε-caprolactam of fibre grade was used as the reactant without further purification, and the concentration of water contained was determined by the Karl-Fisher method.

Cyclic dimer of ε-caprolactam, $[NH(CH_2)_5CO]_2$, was prepared from the product of the refining process of

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