that graft chains bound to the surface of one bead are miscible with similar bound chains on another bead but not with free homopolymer chains. This conclusion is not really surprising in view of our previous report that block/graft copolymers are, to a first approximation immiscible with homopolymer[5], i.e. chains of homopolymer and the corresponding blocks in copolymers do not mix at equilibrium. It should make no real difference in determining the miscibility of free homopolymer and bound chains whether the bound chains are grafts attached to glass beads or blocks attached to a domain or microphase of different polymer in a block or graft copolymer. This study therefore extends the range of systems which demonstrate immiscibility of free and bound polymer chains which must arise from an unfavourable entropy of mixing because mixing chemically identical grafts and homopolymer chains should be athermal. The only factors which should be important in determining the miscibility of bound and free chains should be the number of chains per unit area of impenetrable interface, the molecular weights of the chains and whether or not equilibrium is achieved. To obtain a detailed understanding of this situation we need to be able to determine and vary the density and lengths of bound chains. We have recently developed a technique for detachinggrafts from glass beads and isolating them for characterization[6]; we hope to describe the procedure in a separate publication. Present indications are that the molecular weights of the grafts on the surfaces of the beads have a hibher molecular weight than the homopolymer used in forming the composites; a situation which should favour miscibility[7].

The conclusion that free and bound polymer chains are generally immiscible has important implications with respect to the nature and properties of many composite materials. Physical separation of bound and free chains to form weak polymer–polymer interfaces could result in composites with inferior properties to those in which the surface of the dispersed phase was treated in some way to produce a favourable interaction between the matrix and the dispersed phase. Alternatively, composites with potentially good properties could be prepared by choosing situations which avoid the equilibrium separation of bound and free chains, as illustrated in this study, or by chemically attaching the bound and matrix chains, e.g. by crosslinking.

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High molecular weight polyesters from alkali metal dicarboxylates and α,ω-dibromo compounds

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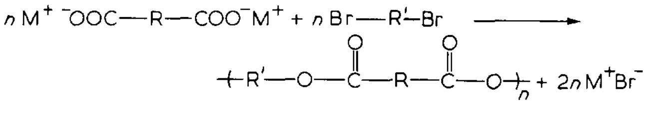
The reaction of alkali metal salts of dicarboxylic acids with α,ω dibromo compounds to form high molecular weight polyesters is best performed using the caesium salts of the acids in *N*-methyl pyrrolidone.

Key words Polyesters; condensation; dicarboxylates; alkyl dibromides; fibre-forming

Introduction

There are several references[1–4] in the literature to the synthesis of polyesters *via* the reaction:



$$n\,M^+\,{}^-OOC{-}R{-}COO^-M^+ + n\,Br{-}R'{-}Br \longrightarrow {+}R'{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{+}_n + 2n\,M^+Br^-$$

However, as far as we are aware, the procedures described give rise only to relatively low molecular weight products. Recently, there have been attempts to apply phase transfer catalysis to this reaction[5–7]; here again, yields were far from quantitative and molecular weights were relatively low. We wish to report results which define the conditions under which the above reaction leads to a high molecular weight polymer. Whilst most of the study has been devoted to the preparation of poly(decamethylene terephthalate) (10 GT), preliminary observations suggest that the procedure is of general application. With the appropriate choice of solvent, counterion and temperature, the reaction to form polyesters can be rapid, virtually quantitative and gives rise to fibre forming polymers with number average molecular weights in excess of 10000.

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Experimental

1.10 Dibromodecane (Aldrich) and α,α′ dibromo-*p*-xylene (Koch–Light) were re-crystallized from methanol and benzene respectively. 1.2 Dibromoethane (BDH), 1.4 dibromobutane and 1.6 dibromohexane (Aldrich) were re-distilled under reduced pressure before use. Alkali metal salts of the dicarboxylic acids studied were prepared by adding a slight excess of the acid to the appropriate aqueous alkali metal hydroxide solution, followed by precipitation into acetone. The precipitated salt was washed with acetone, dried *in vacuo* (50°–60°C) and stored in a desiccator prior to use. Dimethyl formamide (DMF), dimethyl acetamide (DMA) and dimethyl sulphoxide (DMSO) were dried over calcium hydride, re-distilled under reduced pressure and stored over molecular sieves before use. *N*-methyl pyrrolidone (NMP) was treated identically, apart from omitting the drying over calcium hydride.

Polymerizations were generally carried out using 5–10 m mol of each reagent in 4–8 ml solvent, the reaction mixture being stirred magnetically in a flask fitted with a condenser. Polymers were recovered by precipitation into water followed by extensive water washing in a blender. After filtration, the polymers were washed with ethanol and acetone and dried in a vacuum oven at 50°C. Solution viscosity measurements were carried out, generally using 1:1 phenol: tetrachlorethane as solvent at 20°C; in appropriate cases, other solvents (*o*-chlorophenol for poly(ethylene terephthalate), chloroform for poly-(decamethylene sebacate)) were used. Where possible, number average molecular weights were calculated from published relationships.

Results and Discussion

Initial studies using sodium terephthalate and dibromodecane in DMF at temperatures around 100°C gave only low molecular weight polymer ($\bar{M}_n \sim 1000$). Using the potassium salt in DMA at similar temperatures gave more encouraging results, but the most successful polymerizations were those in which caesium terephthalate was used with NMP as solvent. One characteristic of all the systems studied was that the dicarboxylate salts appeared to be essentially insoluble in the reaction medium. This heterogeneity was maintained throughout the reaction since, as reaction proceeded, the alkali metal bromide salt precipitated. Indeed, if temperatures less than 75°C were used, the 10 GT polymer itself precipitated. The poor solubility of the carboxylate salts suggested that it might be possible to use excess of the salt without a consequent lowering of molecular weight, and as the data in *Table 1* show, this proved to be the case. Whilst 10% excess of the carboxylate salt caused no lowering in molecular weight (indeed a small increase is noted), a 10% excess of the dibromodecane gave the expected lowering in molecular weight. Accordingly all subsequent experiments were carried out using ca. 5% excess of the carboxylate salt.

Table 1 Effect of variation in stoichiometric ratio in preparation of 10 GT

Carboxylate salt/ dibromodecane	[η] (dl g^{-1})	$\bar{M}_n$
1.0	0.490	6360
1.10	0.520	6880
0.91	0.288	3130

Reaction conditions: 5 m mol reactants, 5 ml NMP, 20 h, 100°C, potassium salt

Table 2 illustrates the profound effect of solvent on the reaction. NMP alone of the solvents used gave rise to high molecular weight polymer in essentially quantitative yields. (Some loss in yield is probably due to the loss of low molecular weight cyclic species during work up). The poor performance of the other solvents studied is certainly not attributable to polymer insolubility, but more probably reflects higher rates of side reactions. It is suspected, particularly in view of the poor results obtained in DMSO, that decomposition of the alkyl bromide end groups is the most important side reaction since such a decomposition is known to be significant in DMSO at quite moderate temperatures[8]. It is, of course, possible that the carboxylate salts are more soluble in NMP, but as we have no measurements of such solubilities at present, such a suggestion remains speculative.

Table 3 summarizes the conditions under which high molecular weight polymer has been prepared. Whilst high polymer can be prepared using the potassium salt, the caesium salt reacts much more rapidly. Such a results is perhaps not surprising since the advantages of using caesium salts in the analogous reaction for simple esters have already been noted[9,10]. Although the precise reasons for the faster rate of reaction of the caesium salt are not clear, the practical effect is quite spectacular. Under typical polymerization conditions at 110°C, the reaction mixture becomes noticeably viscous after 2 h and stirring becomes quite difficult after 3 h. A preliminary examination of the effect of time on the build up of molecular weight has been made. With both salts, the increase in molecular weight appears to be almost exponential with time, so that it is easy to obtain only low molecular weight polymer if the reaction is stopped prematurely. However, with the potassium salt at 100°C,

Table 2 Effect of solvent on yield and molecular weight in preparation of 10 GT

Solvent	Time (h)	Yield (%)	[η] (dl g^{-1})	$\bar{M}_n$
DMSO	5	40	0.082	587
DMF	5	78	0.283	3060
DMA	4	91	0.490	6360
NMP	3	93	1.18	20500

Reaction conditions: 5 m mol dibromodecane, 5.25 m mol caesium terephthalate, 4 ml solvent, 110°C

Table 3 Effects of temperature and counterion in preparation of 10 GT

Counterion	Temperature (°C)	Time (h)	[η] (dl g^{-1})	$\bar{M}_n$
K^{+}	80 (a)	37	1.210	21230
	90 (a)	23	1.352	24620
	100 (a)	10	0.882	13930
Cs^{+}	80 (a)	14	1.835	36990
	90 (b)	8	1.061	17800
	100 (b)	5	0.982	16070
	110 (b)	3	1.180	20500
	120 (b)	2	0.895	14200

Reaction conditions: (a) 50 m mol dibromodecane, 50 ml NMP; (b) 5 m mol dibromodecane, 4 ml NMP, terephthalate salt, 5% excess

Table 4 Other polyester preparations

Polymer	Temperature (°C)	Time (h)	[η] (dl g^{-1})	$\bar{M}_n$
Poly(ethylene terephthalate)	110	3	0.145	3400
Poly(1,4 butylene terephthalate)	110	2	0.392	11 130
Poly(hexamethylene terephthalate)	120	2	0.660	10650
Poly(*p*-xylylene sebacate)	100	½	0.980	–
Poly(decamethylene sebacate)	110	2	1.100	–

Reaction conditions: 5 m mol dibromo compound, 5.25 m mol caesium dicarboxylate, 4 ml NMP

prolonging the reaction time beyond 10 h leads to a fall in molecular weight.

The general applicability of this polymerization procedure has been examined for the polyesters listed in *Table 4*. Apart from poly(ethylene terephthalate), (2GT), quite satisfactory polymers were obtained which appeared to have high molecular weights as judged by solution viscosity measurements and by the ease with which fibres could be drawn from molten samples. In the case of 2 GT, discolouration was very apparent during synthesis, possibly due to the greater ease of the elimination reaction. No doubt the conditions could be modified to improve this particular polymerization.

Some structural characterization of the polymers has been made. Infra-red and n.m.r. spectra of samples of 10 GT prepared by this procedure are identical with those of a conventionally prepared sample. The d.s.c. behaviour is also very similar though the melting point of the 10 GT prepared *via* this procedure appears to be 4°–5°C lower than the conventionally prepared sample. Elemental analyses gave satisfactorily high carbon contents, but rather erratic (though low) bromine contents.

In conclusion, it is clear that the procedure outlined offers a very convenient and rapid method for preparing a variety of polyesters of reasonably high molecular weight. Stoichiometric equivalence of reagents is not necessary provided the reagent present in excess is the carboxylate salt. It seems likely that the overall rate of reaction is governed by the rate of dissolution of the carboxylate salt, so that the predominant end groups in the growing polymer are the alkyl bromide species. Whilst further studies of this reaction are in progress, it has not escaped our attention that this procedure offers a route to the hitherto unprepared poly(methylene esters) and we are at present engaged in their synthesis.

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The concentration dependence of the angular dissymmetry of light scattered by micellar solutions

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A light scattering investigation was made of micelles formed from a polystyrene-poly(ethylene/propylene) two-block copolymer in n-nexane. n-Hexane is a selectively bad solvent for polystyrene and so polystyrene blocks formed the cores of the micelles. The light scattering measurements were made at 25°C for concentrations up to 0.015 g cm^{-3}. The dissymetry ratio ($I_{45°}/I_{135°}$) was found to decrease with increase in concentration and it was below unity for measurements at $c > 4.8 \times 10^{-3}$ g cm^{-3}. The effect of concentration on the dissymmetry ratio was predicted quite well by assuming the micelle packing could be described by radial distribution functions for hard spheres.

Keywords Polystyrene; scattering; light scattering; copolymer micelles; concentration dependence; dissymmetry ratio

Introduction

When a block or graft copolymer is dissolved in a hydrocarbon solvent that is selectively bad for one of the polymer components, the copolymer molecules can associate reversibly to form micelles[1–6]. The micelles generally consist of a compact swollen core of insoluble polymer blocks surrounded by a protective fringe of soluble blocks. Gel permeation chromatography and electron microscopy studies have shown that in many cases the micelles have a very narrow size distribution[2].

In some copolymer/selective–solvent systems[2,5] the association equilibrium

$$NP_1 \rightleftarrows P_N$$

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