polymer communications

The preparation of poly(methylene esters)

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Conditions are described which allow the synthesis of poly(methylene terephthalate) from the reaction of methylene bromide with caesium terephthalate and though application of the procedure to prepare polymers from aliphatic dicarboxylic acids was unsuccessful, such polymers were synthesized from the analogous reaction with bromochloromethane.

Keywords Anionic; condensation; dicarboxylates; alkyl dibromides; fibre-forming; poly(methylene esters)

Introduction

We have recently described the reaction conditions which allow the preparation of high molecular weight polyesters from the reaction between α, ω dibromoalkanes and the alkali metal salts of dicarboxylic acids[1]. The best conditions so far found are those using the caesium salt of the acid, *N*-methyl pyrrolidone (NMP) as solvent and temperatures in the range 80°–110°C. Whilst such a procedure was used initially to prepare conventional polyesters, it was pointed out to us[2] that the procedure ought to be applicable to methylene bromide and should, in that event, give rise to poly(methylene esters). Such polyesters cannot, of course, be prepared by conventional processes because the equivalent diol does not exist. When such polymerizations were attempted, polymer was formed only when the salts of terephthalic acid were used; the salts of typical aliphatic dicarboxylic acids, such as sebacic acid, failed to give high molecular weight products, despite many variations in the polymerization procedure. However, the poly(methylene esters) of the aliphatic dicarboxylic acids were formed when bromo-chloromethane was used in place of methylene bromide and a tentative explanation of this behaviour is proposed.

Experimental

Methylene bromide and bromo-chloromethane (Aldrich) were purified by re-distillation. The preparation of the salts of the dicarboxylic acids and the purification of NMP were carried out as described earlier[1]. Reactions were generally carried out using 5–10 mmol of reagents in 3–8 ml NMP, the reaction mixture being stirred constantly. In most reactions, a 5% excess of the dicarboxylate salt was used. Reaction products were recovered by precipitation into water and, after further washing with water, were dried *in vacuo*. Yields quoted are usually for the water insoluble products. Solution viscosities were measured in chloroform at 20°C and the molecular weights of low molecular weight products were determined by vapour pressure osmometry.

Results and Discussion

Initial studies were performed by reacting the caesium salts of various dicarboxylic acids with methylene bromide in NMP, choosing conditions found to be successful in the earlier studies[1], and some of the data obtained are summarized in *Table 1*. It was immediately apparent that polymerization was very inefficient under these conditions, except in the case of the reaction involving caesium terephthalate. Only the product from this reaction, when melted, could be drawn into fibres; elemental analysis was compatible with the formation of relatively high molecular weight poly(methylene terephthalate) though further characterization was limited by the insolubility of the polymer in solvents so far examined. With the other carboxylate salts examined (*Table 1*), the yields were frequently far from quantitative, no increase in solution viscosity was observable during reaction, and the products dissolved readily in chloroform to give solutions with very low viscosities. Changes in reaction conditions such as the use of potassium salts, dimethyl acetamide as solvent or methylene chloride as reactant all failed to improve matters.

The failure to obtain high polymer from salts other than the terephthalate was initially puzzling; i.r. spectra of the crude products indicated that ester groups had formed and the elemental analyses obtained were in good agreement (*Table 1*) with those expected for high polymer. Whilst the characterization of these products is incomplete, it is believed that they are mainly the cyclic methylene esters of the respective acids, possibly, depending on the particular acid, mixtures containing cyclic monomer, dimer, etc. For example, in the case of the sebacate, the major product is believed to be the cyclic monomer since this has been tentatively identified as the solid (m.p. 59°C) obtained on cooling the ether extract of the product (found, C 61.7, H 8.50, *MW* 218; $C_{11}H_{18}O_4$ required C 61.7, H 8.41, *MW* 214). By contrast, the acetone soluble portion of the product from the isophthalate salt ($\sim$80% of the total product) had a molecular weight of 644, suggesting a mixture of the

Table 1 Reaction conditions and products from reaction of caesium dicarboxylates with methylene bromide in NMP

Acid	*T* (°C)	Time (h)	Solvent (ml)	Yield (%)	*MW*	%C	%H	%Br	%Cs	%C	%H
						(Found)				(Calculated)*	
Sebacic	100	4	4	60.3	318	61.9	8.20	1.05	1.55	61.7	8.41
	80	20	4	56.4	340	60.8	8.25	0	0		
	70	24	4	36.1	280	61.6	8.50	0	1.25		
Suberic	100	3	3	45.3	710	57.1	7.45	0	0.95	58.1	7.53
Isophthalic	110	2	4	81.3	–	60.3	3.75	0	1.45	60.7	3.37
	110	3	2.5	88.6	–	59.2	3.65	1.9	2.40		
	80	24	6.0	92.6	–	59.7	3.45	0	1.05		
Terephthalic	110	2	2.5	27.5	–	60.3	3.65	0.7	2.0	60.7	3.37
	100	16	5	79.8	–	60.2	3.50	1.85	0		
	100	20	5	90.6	–	60.2	3.95	1.95	0		

Reaction conditions: 5 mmol methylene bromide, 5.25 mmol caesium salt
* Elemental analyses calculated for infinitely high molecular weight polymer

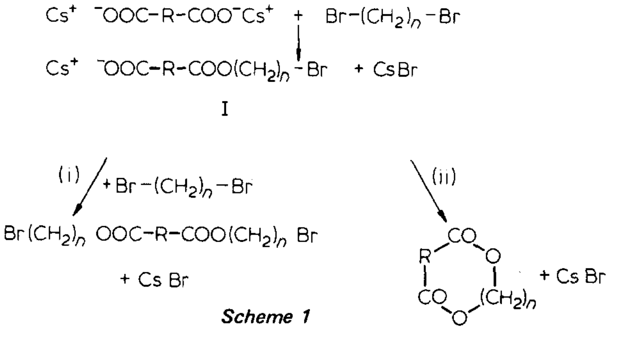
Table 2 Products from reaction of caesium dicarboxylates with bromo-chloromethane

Acid	*T* (°C)	Time (h)	Yield (%)	[η] (dl g^{-1})	T_m (°C)	%C	%H	%Br/Cl	%Cs	%C	%H
						(Found)				(Calculated)*	
Sebacic	100	2	70.5	1.21	60	61.3	8.55	0	0	61.7	8.41
Suberic	100	2	58.6	0.39	–	57.1	7.45	0	1.5	58.0	7.56
Suberic	90	3	63.4	0.61	43	57.8	7.75	0	1.1	58.0	7.56
Adipic	100	2	37.5	0.34	20	53.1	6.10	0	1.4	53.2	6.37
Isophthalic	100	4	74.7	–	–	57.9	3.70	0	1.3	60.7	3.37

Reaction conditions: 5 mmol bromo-chloromethane, 5.25 mmol caesium salt, 3 ml NMP
* Calculated for infinitely high molecular weight polymer

higher cyclic species. Examination of molecular models confirms that with isophthalic acid, the smallest cyclic methylene ester possible is the dimer. It would thus appear that the success in obtaining polymer using the terephthalate salt is associated with the reduced likelihood of cyclization of the lower linear species of this acid.

If it is accepted that, where polymerization fails to occur, it is due to very efficient cyclization reactions, then it becomes necessary to understand why cyclization is so much more efficient in the case of methylene bromide than in the case of the higher α, ω dibromoalkanes. *Scheme 1* shows the competitive routes (i) and (ii) at the first stage of the reaction involving the half carboxylate-half alkyl bromide product I. (We presume that of the various intermolecular reactions involving species I, (i) is the fastest owing to the low solubility of the dicarboxylate salts. Indeed, the analysis of the linear oligomers in the polymerization producing poly(decamethylene terephthalate) indicates that, in the early stages of the reaction, there are two alkyl bromide chain ends per molecule[3].) Clearly for the higher dibromoalkanes ($n > 1$ in *Scheme 1*), reaction (i) is the faster step for species I under the prevailing conditions and cyclization (reaction (ii)) presumably becomes even less likely for higher homologues of species I. For methylene bromide, on the other hand, ($n = 1$ in *Scheme 1*), reaction (ii) must be the faster step either for species I or for the slightly higher homologues of I, except in the case of the terephthalate salt. In other words, despite the high concentration of methylene bromide present in the early stages of the reaction, the intramolecular reaction is the faster. One explanation for this behaviour could be the activation of the C–Br bond in species I due to the adjacent oxygen of the ester group, an effect absent where $n > 1$. Such an argument leads to the proposition that polymerization will only be possible if some way can be found of reducing the rate of the intramolecular reaction in species I. One possible method would be to use bromo-chloromethane instead of methylene bromide since, presuming the C–Br bond reacted first, species I would be formed containing the less reactive C–Cl bond.



Scheme 1

The essential validity of these arguments was confirmed by the production of polymer from the reaction between bromo-chloromethane and caesium carboxylates. *Table 2* summarizes the conditions used and the polymers so far obtained and whilst further work is required, the data leave no doubt that a whole range of poly(methylene esters) can now be synthesized. What is remarkable is that high molecular weight polymer can be produced without apparently quantitative conversion of the monomers, as illustrated in the case of poly(methylene sebacate), (*Table 2*). This appears to be a characteristic of these polymerizations since we have noticed that samples of poly(methylene terephthalate) are fibre forming and have similar elemental analyses irrespective of the yield in the range 27–90% (*Table 1*). The reaction of caesium isophthalate with bromo-chloromethane failed to give polymer with a molecular weight above 2000, and it is suspected that here cyclization is still an important reaction; nevertheless it may be possible to obtain high polymer under other conditions. Indeed we have evidence which suggests that cyclization is less prevalent when the potassium salts are used, though so far we have been unable to produce more than low molecular weight polymer with such salts. The work reported here has very striking similarities with the study of the cyclization of ω-halo-carboxylate salts reported by Kruizinga and Kellogg[4] who noted remarkable efficiencies in cyclization when using the caesium salts. These workers drew attention, amongst other factors, to the tendency to intramolecular triple ion formation observed with the caesium salts of dicarbanionic species[5,6]; if such behaviour occurred in the case of the caesium dicarboxylates, it might well be a contributory factor to the efficient cyclization indicated in the present study.

The characterization of the poly(methylene esters) is in hand and will be reported elsewhere.

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Studies on phase separation in polyblends of block copolymers

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The morphologies of polyblends of block copolymers of styrene and butadiene with similar composition but different molecular weights have been examined with an electron microscope. The micrographs show that some supramolecular features, with different morphologies to those in the matrix, are randomly dispersed. These results, we believe, provide evidence of the incompatibility of the block copolymers in spite of their chemical identity.

Keywords Block copolymers; compatibility; electron microscopy; morphology; phase separation; polyblends

Introduction

In the field of multicomponent polymers, phase separation is one of the major subjects which has been extensively studied. It is well known that most homopolymer blends are incompatible because of the positive mixing enthalpy and the small mixing entropy. As to block copolymers with well-defined structures, a large number of investigations have demonstrated that the mutual incompatibility of different blocks linked by chemical bonds results in microphase separation forming characteristic domain structures. This experimental result is further substantiated by statistical and thermodynamic calculations. However, in the case of blends of block polymers and homopolymers, a complicated situation arises. Many studies[1,2] published mainly in the early seventies, suggest that homopolymer chains can be considerably solubilized in the domains of the like blocks of the copolymer provided the molecular weight of the former is not larger than that of the latter. Nevertheless, there were some reports[3,4] concerning the presence of some large supramolecular features with different interior structures from the bulk sample in certain copolymer–homopolymer blends. These features were just regarded as 'unusual structures' and no reasonable explanation of their formation was given.

In recent years, Eastmond *et al.* have presented a series of morphology studies on blends of so-called non-linear block copolymers or AB crosslinked copolymers (ABCPs) with their corresponding homopolymers[5]. In order to explain the formation of the 'unusual structures', which were inevitably found to appear in these blends under suitable combinations of molecular species and processing conditions, they suggested that the homopolymer chains are incompatible with the like blocks of copolymers at equilibrium, and the discrete regions found in the blends are virtually the copolymer-rich phase. The unusual morphologies are formed by a combination of macrophase separation between the homopolymer and the block copolymer and microphase separation in the block copolymer itself. This opinion found support from Meier's theoretical calculation[6] on the possibility of the solubilization of homopolymers in their corresponding block domains, which in fact is an extension of his theory