Polymer Vol. 37 No. 7, pp. 1267–1271, 1996
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0032-3861/96/$15.00+0.00

Synthesis of polyesters by reaction of carboxylic acid quaternary ammonium salts with alkyl halides or alkyl tosylates*

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(Received 19 December 1994; revised April 1995)

The synthesis of polyesters by the reaction of dicarboxylic acid salts with bis halides or bis tosylates or by the self-condensation of salts of ω-bromocarboxylic acids, has been investigated under two different types of conditions. When benzyltrimethylammonium salts and halides were reacted together in acetonitrile at ca. 82°C the results obtained were similar to those reported in the literature for experiments using sodium or potassium salts. Thus, the yields of polyesters were generally modest, with degrees of polymerization (*DP*s) being in the range from 17 to 47. Using liquid–liquid phase-transfer catalysis procedures the yields were high and the *DP*s were usually in the range from 22 to 161. This is the first time that the liquid–liquid phase-transfer catalysed synthesis of polyesters has produced such high *DP* values.

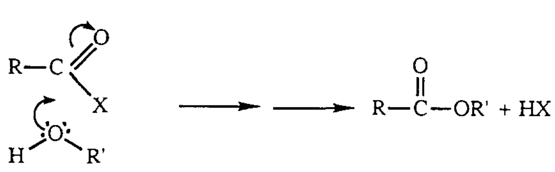
(Keywords: polyesters; phase-transfer catalysis; degree of polymerization)

INTRODUCTION

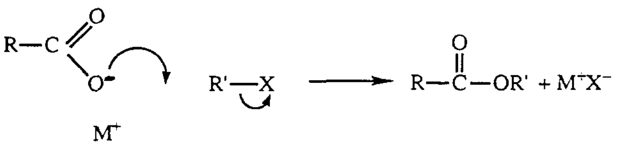
Ester linkages are most often formed by reactions of carboxylic acids or their derivatives, such as acid chlorides and anhydrides, with alcohols. The key step in these reactions is the nucleophilic attack of the oxygen atom of the alcohol on the carbonyl group (Reaction 1). Since water has a nucleophilicity similar to that of alcohols the reactions need to be carried out under anhydrous conditions. An alternative approach to the synthesis of esters involves the nucleophilic attack of carboxylic acid salts on alkyl halides or similar electrophilic species, such as mesylates and tosylates (Reaction 2). These reactions have the attractive features that they can be carried out successfully in the presence of water and that they can be carried out with substrates containing alcohol groups. Often the reactions are performed by using phase-transfer catalysis (PTC) techniques[1,2]. Such attractive features have led to considerable interest in the use of these reactions to synthesize polyesters[3–20].

Cameron and coworkers were some of the first researchers to report such studies in detail[8,9]. They studied the reactions of the dipotassium salt of sebacic acid with *m*-xylylidene dibromide[8] and the alkali metal salts of various ω-bromo carboxylic acids[9] under both solid–liquid (SL) and liquid–liquid (LL) PTC conditions. In most cases the yields were modest. The SL-PTC syntheses were generally the more successful, but even here the degrees of polymerization (*DP*) obtained were only about 20. Kielkiewicz *et al.* investigated the SL-PTC reactions of the dipotassium salts of maleic and fumaric acids with *p*-xylylidene dibromide and obtained similar results[10]. East and Morshed studied the reactions of alkali metal salts of dicarboxylic acids with dihalides in various aprotic solvents. The best results were obtained when using caesium salts in hot *N*-methylpyrrolidone (NMP) and under these conditions various terephthalates were prepared with $\overline{M}_n$s of 11 000–36 000[11]. Similar

Reaction 1



Reaction 2



X = $-Cl$, $-Br$, $-I$, $-OSO_2CH_3$, or $-OSO_2C_6H_4CH_3$

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syntheses were successfully carried out by using dihalomethanes[12–16] and pyridine-2,5-dicarboxylic acid[17]. Boileau[7] and Slieman[18] investigated analogous reactions using salts of naphthalene-2,6-dicarboxylic acid. Sepulchre and coworkers have carried out some reactions of this same general type[19] but have concentrated on the synthesis of polyesters starting from salts of malic and tartaric acids, i.e. polyesters with pendent hydroxyl groups[20]. The M_ns obtained in their study were, however, less than 4000.

In connection with our interest in functional polymers, and in particular the synthesis of cyclic polyesters using polymer-supported reactions[21–24] we have investigated further the synthesis of polyesters by using Reaction 2 (see above). It will be noted that the studies considered above used either sodium or potassium salts in PTC reactions, or caesium salts in NMP. Of the former type most of the reactions involved SL-PTC: only modest success was obtained by using LL-PTC reactions. We have now investigated the use of quarternary ammonium carboxylates instead of alkali metal salts, and have also made some further studies of LL-PTC systems[25]. In several cases, the M_ns obtained were in the range 17 000–26 000. These values are higher than those obtained in many of the earlier studies.

EXPERIMENTAL

Unless indicated otherwise all of the chemicals used in this work were commercial materials and they were used as received. All of the acids were recrystallized before use, as were the solid dihalides. The liquid dihalides were distilled prior to use. The bistosylate of triethylene glycol and the corresponding dibromide were prepared by standard methods[26,27].

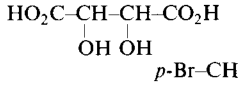
Infra-red spectra (KBr discs) were measured by using a Perkin–Elmer 1710 Fourier transform infra-red spectrometer. ^{1}H n.m.r. spectra were obtained on a Gemini 200 (200 MHz) instrument for solutions in deuterochloroform. Gel permeation chromatography (g.p.c.) was carried out using a Waters μ-Styragel 4-column set with THF as the eluent. The g.p.c. columns were calibrated by using a set of polystyrene standards ($\overline{M}_n$ = 600, 1010, 2100, 4800, 10 000, 19 800, 51 000, 110 000 and 200 000), each with a narrow molecular-weight range.

Polymer synthesis using quaternary ammonium salts

The following procedures are typical. The results are summarized in *Table 1*.

Preparation of carboxylic acid salts. A stirred solution of decane-1,10-dicarboxylic acid (50 g) in methanol (300 ml) containing a few drops of phenolphthalein solution was treated carefully at room temperature with a 40% solution of benzyltrimethylammonium hydroxide in methanol until the solution just turned pink. The colour was then discharged by the addition of a small

Table 1 Synthesis of various polymers by the reaction of benzyltrimethylammonium carboxylates with alkyl halides[a]

Entry number	Carboxylic acid used to prepare salt	Halide	Yield[b] (%)	$\overline{M}_n^c$	$\overline{M}_w^c$	*DP*	Average number of halide end-groups per chain[d]
1	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	p-$BrCH_2{-}C_6H_4{-}CH_2Br$	45	4100 2000^e	6500	25	2.0
2	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	p-$ClCH_2{-}C_6H_4{-}CH_2Cl$	34	16 050 $11\,600^e$	36 050	97	1.4
3	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$I{-}(CH_2)_8{-}I$	37	3500	5000	21	2.2
4	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$ClCH_2CH_2OCH_2CH_2Cl$	40	3150 1050^e	4750	21	3.0
5	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$Br{-}(CH_2)_4{-}Br$	39	3850 3550^e 2150^f	7500	27	1.1
6	$HO_2C{-}(CH_2)_4{-}CO_2H$	p-$BrCH_2{-}C_6H_4{-}CH_2Br$	87	3900 1800^e	6450	31	2.2
7	$HO_2C{-}(CH_2)_4{-}CO_2H$	$I{-}(CH_2)_4{-}I$	67	3600 2800^e	4800	36	1.3
8	$HO_2C{-}CH\overset{E}{=}CH{-}CO_2H$	$I{-}(CH_2)_8{-}I$	29	3900 3300^e 2050^f	18 500	35	1.2
9	$HO_2C{-}CH\overset{E}{=}CH{-}CO_2H$	$ClCH_2{-}CH\overset{E/Z}{=\!=}CH{-}CH_2Cl$	30	3950	6600	47	–
10	 $HO_2C{-}\underset{OH}{\overset{R}{CH}}{-}\underset{OH}{\overset{R}{CH}}{-}CO_2H$	p-$BrCH_2{-}C_6H_4{-}CH_2Br$	72	2100^e	–	17	–
11	p-$Br{-}CH_2{-}C_6H_4{-}CO_2H$		95	2300^e	–	17	–
12	$Br{-}(CH_2)_{10}{-}CO_2H$		61	7650 7850^e	24550	42	1.0

[a] A vigorously stirred suspension of the benzyltrimethylammonium salt of the acid in acetonitrile was treated with an equimolar amount of the halide for 18 h at reflux

[b] Weight of dried product as a percentage of the theoretical maximum weight of product

[c] Unless indicated otherwise, by g.p.c. relative to polystyrene standards

[d] $\overline{M}_n$ determined by g.p.c. divided by $\overline{M}_n$ determined by elemental analysis for halogen; the latter calculation assumes one halogen atom per chain

[e] By halogen analysis assuming one halogen end-group per chain

[f] By ^{1}H n.m.r. spectroscopy assuming one halogen end-group per chain

amount of the diacid. The solution was evaporated to dryness and the residue dried further over phosphorous pentoxide in a vacuum oven (50°C 5 mm Hg) for 2 days. The final product was a white powder. It had a ν_{max} of $1550\,cm^{-1}$ (carboxylate salt).

Polymerization. The bis(benzyltrimethylammonium) salt of decane-1,10-dicarboxylic acid (10.00 g, 26.5 mmol) was placed in the polymerization vessel and *p*-xylylidene dibromide (6.98 g, 26.5 mmol) in dry acetonitrile (35 ml) was added. The mixture was then stirred vigorously and heated at reflux under dry nitrogen for 18 h. The cooled solution was added to methanol (600 ml) to precipitate the polymeric product. The product was filtered off, washed with methanol and dried; yield (3.95 g) (45%). It had a ν_{max} of $1737\,cm^{-1}$; no band was apparent at $1550\,cm^{-1}$. The ^1H n.m.r. spectrum had bands at $\delta = 1.0$–2.0 (broad, 16H, $8CH_2$), 2.32 (triplet, 4H, $J = 13.0\,Hz$, $2\,CH_2CO_2$), 5.05 (singlet, 4H, $2ArCH_2O$) and 7.28 ppm (singlet, 4H, 4 ArH): no signals which could be attributed to $C_6H_5CH_2N^+(CH_3)_3$ groups were apparent. From elemental analysis Br = 4.0%; assuming one bromo group per chain this corresponds to an $\overline{M}_n$ of 2000. From g.p.c. $\overline{M}_n = 4100$ and $\overline{M}_w = 6500$.

Liquid–liquid phase transfer catalysed polymerizations

The following procedures are typical. The results are summarized in *Table 2*.

Procedure I. A mixture of decane-1,10-dicarboxylic acid (10.00 g, 43.5 mmol) and sufficient sodium hydroxide to dissolve it were dissolved in distilled water (55 ml). Tetra-n-butylammonium bromide (700 mg, 2.2 mmol) and 1,6-dibromohexane (10.61 g, 43.5 mmol) in chloroform (55 ml) were added. The two-phase system was stirred vigorously for 18 h while heating (ca. 62°C) under reflux. The polymeric product was isolated and characterized as described above.

Procedure II. This was identical to Procedure I, except that a 40% aqueous solution of tetra-n-butylammonium hydroxide was used to neutralize the acid and no tetra-n-butylammonium bromide was added.

Procedure III. This was identical to Procedure II, except that chloroform was replaced by chlorobenzene; accordingly the reaction temperature was ca. 100°C.

Procedure IV. This was identical to Procedure I, except that chloroform was replaced by *o*-dichlorobenzene; accordingly the reaction temperature was ca. 100°C.

Table 2 Synthesis of various polymers using liquid–liquid phase-transfer catalysis

Entry number	Carboxylic acid – used to prepare salt	Halide	Procedure[a]	Yield[b] (%)	$\overline{M}_n^c$	$\overline{M}_w^c$	DP	Average number of halide end groups per chain[d]
1	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$Br{-}(CH_2)_6{-}Br$	I	89	18 280 10 949[e]	30 850	117	1.7
2	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	*p*-$BrCH_2{-}C_6H_4{-}CH_2Br$ $+ I{-}(CH_2)_8F{-}I$	I	91	17 400 13 450[e]	36 100	105	1.3
3	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	*p*-$BrCH_2{-}C_6H_4{-}CH_2Br$	I	63	8150	12 950	–	–
4	$HO_2C{-}(CH_2)_8{-}CO_2H$	*p*-$ClCH_2{-}C_6H_4{-}CH_2Cl$	I	–	3400	6000	22	–
5	$HO_2C{-}(CH_2)_8{-}CO_2H$	*p*-$ClCH_2{-}C_6H_4{-}CH_2Cl$	I[f]	98	17 500	32 100	115	–
6	$HO_2C{-}CH\overset{E}{=}CH{-}CO_2H$	$ClCH_2{-}CH\overset{E/Z}{=}CH{-}CH_2Cl$	I	81	4620	7900	55	–
7	$Br{-}(CH_2)_{10}{-}CO_2H$		I	78	5450	11 200	30	–
8	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$Br{-}(CH_2)_6{-}Br$	II	84	7195	12 716	46	–
9	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	*p*-$BrCH_2{-}C_6H_4{-}CH_2Br$	II	82	21 345	44 663	129	–
10	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	*p*-$ClCH_2{-}C_6H_4{-}CH_2Cl$	II	96	26 896	42 441	161	–
11	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$I - (CH_2)_4{-}I$	II	89	12 721	20 390	90	–
12	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$Br{-}CH_2{-}Br$	II	45	1693	1860	14	–
13	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$Ts{-}(OCH_2CH_2)_3{-}OTs$	II	58	3454	6037	19	–
14	$HO_2C{-}(CH_2)_{10}{-}CO_2H$	$Br{-}(CH_2CH_2O)_2CH_2CH_2{-}Br$	II	60	2967	4510	16	–
15	$HO_2C{-}CH\overset{E}{=}CH{-}CO_2H$	$Br{-}(CH_2)_6{-}Br$	II	82	4555	8451	55	–
16	$HO_2C{-}CH\overset{E}{=}CH{-}CO_2H$	$ClCH_2{-}CH\overset{E/Z}{=}CH_2{-}CH_2Cl$	II	88	6850	10 430	82	–
17	*p*-$ClCH_2{-}C_6H_4{-}CO_2H$		II	78	796[g]	995[g]	6	–
18	$Br{-}(CH_2)_7{-}CO_2H$[h]		II	84	5263	8722	37	–
19	$Br{-}(CH_2)_{10}{-}CO_2H$		II[i]	87	8000	14 500	43	–
20	$Br{-}(CH_2)_{10}{-}CO_2H$		II	89	22 656	33 560	123	–

[a] See Experimental and Discussion sections for full details of procedures used

[b] Weight of dried product as a percentage of the theoretical maximum weight of product

[c] Unless indicated otherwise, by g.p.c. relative to polystyrene standards

[d] $\overline{M}_n$ determined by g.p.c. divided by $\overline{M}_n$ determined by elemental analysis for halogen; the latter calculation assumes one halogen atom per chain

[e] By halogen analysis assuming one halogen end-group per chain

[f] Reaction carried out as entry 4 but for 96 h; up to at least 96 h the molecular weights increased almost linearly with time

[g] Most of the product was insoluble in THF; molecular-weight values are for soluble material

[h] This monomer was only 98% pure; the nature of the minor impurities is not known

[i] Reaction time of only 2.5 h

Procedure V. This was identical to Procedure II, except that the tetra-n-butylammonium hydroxide was added in two equal portions, with the second portion being added 2 h after the start of the reaction.

RESULTS AND DISCUSSION

Polymer synthesis by the reaction of the benzyltrimethylammonium salts of carboxylic acids with alkyl halides

One of the factors limiting the success of the polymerizations when using alkali metal salts of carboxylic acids appears to be the poor solubilities of the salts in the reaction solvents. We considered that lipophilic quaternary ammonium carboxylate salts might be more soluble, and hence more effective in the polymerizations, and we have now investigated this approach.

Benzyltrimethylammonium salts were selected for our study. This is partly because benzyltrimethylammonium hydroxide is the cheapest quaternary ammonium hydroxide that is available and partly because the presence of any of this cation as end groups in the polymeric products would be detected relatively easily by inspection of the aromatic regions of the ^1H n.m.r. spectra of the products. Each carboxylate salt was prepared by neutralizing a solution of the acid in methanol with a solution of benzyltrimethylammonium hydroxide in methanol, followed by evaporation of the solvent and drying of the product in a vacuum oven. The salts were obtained as white powders, which in many cases were hygroscopic. Acetonitrile was selected as the reaction solvent since it was shown to be one of the most effective in the PTC studies of Durst[2] and Cameron and Law[8]. The polymerizations were carried out by treating suspensions of the acid salts in acetonitrile with equimolar amounts of the halides at reflux temperature (ca. 82°C) for 18 h. The polymeric products, isolated by precipitation into methanol, were characterized by i.r. and ^1H n.m.r. spectroscopy, g.p.c. and elemental analysis. The results obtained are summarized in *Table 1*. The range of monomers used is significantly wider than in earlier studies.

The main conclusion to be drawn from these results is that in general they are very similar to those referred to in the Introduction which used sodium or potassium salts together with small amounts of phase-transfer catalysts. It again appears that dissolution of the bis salts is very slow, that dissolution is the rate-limiting step, and that when the salts do dissolve they react relatively rapidly with the bis halides. Several aspects of the results are consistent with this. First, the yields of the polymers were usually low. Secondly, in most cases the polymers had on average more than one halogen end-group per chain and, in the few cases investigated (entries 1 to 3), there was neither ^1H n.m.r. nor *FT*i.r. spectroscopic evidence for the presence of $-CO_2^-N^+(CH_3)_3CH_2C_6H_5$ end-groups. Thirdly, the syntheses carried out using, for example, the bis salt of decane-1,10-dicarboxylic acid produced very similar results even though the bis halides used have very different reactivities. Except for one case (entry 2) when the *DP* was 97, the *DP*s obtained were usually in the range 17 to 47. As expected, the mono salts dissolved more rapidly than the bis salts and this resulted in higher yields. The *DP* obtained when using 4-bromomethylbenzoic acid was limited by the poor solubility of the product in the reaction solvent. When using the salt of 11-bromoundecanoic acid a polymer with a *DP* of 42 was obtained.

With both the bis and mono salts both higher yields and *DP*s could almost certainly be obtained by using more vigorous reaction conditions. However, the results indicate that the use of benzyltrimethylammonium salts, rather than sodium or potassium salts, confers no major advantage. This prompted us to investigate a different approach, i.e. the LL-PTC reactions discussed below, and this proved to be more successful.

Liquid–liquid phase transfer catalyzed polymerizations

A range of LL-PTC polymerizations were carried out using various reaction procedures. To facilitate comparisons many of the carboxylic acids and halides used were the same as those employed in the above study.

In Procedure I the reactions were carried out by treating an aqueous solution of the sodium salt of the acid with an equimolar amount of the halide in chloroform. Tetra-n-butylammonium bromide (5 mol%) was added as the catalyst and the mixture was vigorously stirred at reflux (ca. 62°C) for 18 h. The polymeric products were isolated by precipitation into methanol and were characterized as in the preceding study. The results are summarized in *Table 2*, entries 1 to 7. It is evident that the yields of the polyesters, which are in the range 63–98%, were considerably higher than those obtained in the similar polymer syntheses using the benzyltrimethylammonium carboxylates, whilst the *DP*s were usually similar or somewhat larger. The rate of transfer of the quaternary ammonium salt into the organic phase still appears to be rate-limiting however, as each of the products from the reactions summarized in entries 1 and 2 had on average more than one bromo end-group per chain and the molecular weight of the polymer formed from decane-1,10-dicarboxylic acid and *p*-xylylidene dichloride increased almost linearly with time up to at least 96 h (compare entries 4 and 5).

In an attempt to try to increase the rate of transfer of the quaternary ammonium salt into the organic phase, Procedure II was used. This procedure was similar to Procedure I except that the tetra-n-butylammonium carboxylates were used in place of the sodium carboxylates, i.e. a much higher concentration of quaternary ammonium ions was present in the reaction. It is evident by comparing the corresponding results in *Table 2*, i.e. entries 1, 4, 6 and 7 with entries 8, 9, 16 and 20, respectively, that Procedure II results in higher *DP*s. In three syntheses (entries 9, 10 and 20) *DP*s of 123–161 were obtained.

Other attempts (not summarized in *Table 2*) were made to improve the *DP*s that were obtained but without any success. Reactions analogous to those summarized in entries 8 and 10 were carried out, using, respectively, chlorobenzene (Procedure III) and *o*-dichlorobenzene (Procedure IV) as the reaction solvent at a temperature of ca. 100°C, but these gave polymers with *DP*s of only 12 and 109, respectively. Procedure V was similar to Procedure II, except that the equimolar amount of tetra-n-butylammonium hydroxide was added in two equal portions, with an interval of 2 h. It was expected that after half of the base had been added a substantial amount of the half-acid salt would be present and that this would be more soluble in the organic phase than the bis salt. It was hoped that by the time the second portion of base was added most of the diacid monomer would already have reacted at least once with the dihalide. The reaction carried out was the analogue of that summarized in entry 8. In the event, Procedure V gave a polymer with a *DP* of only 14.

Other reactions were carried out using Procedure II. These include those summarized in entries 12, 13, 14, 17 and 18. In the first three cases only the modest yields and *DP*s were obtained, possibly in the first example owing to the modest reactivity of the dihalide. The *DP* from the reaction with 4-chloromethylbenzoic acid was limited by the poor solubility of the polymeric product, while that from the reaction with 8-bromooctanoic acid was probably reduced because the starting material was only 98% pure. Attempts to prepare polyesters with malonic or glutaric acids by Procedure II were unsuccessful.

CONCLUSIONS

The synthesis of polyesters by the reaction of dicarboxylic acid salts with bis halides or tosylates, or by the self condensation of ω-halogenocarboxylic acid salts has been investigated under two different types of conditions.

When benzyltrimethylammonium salts were treated with the halides in dry acetonitrile at ca. 82°C, the results were similar to those reported in the literature for experiments using sodium or potassium salts. Thus, yields were poor and *DP*s were usually only 17–47. The rate of dissolution of the salts in the organic solvent appears to be very slow and rate-limiting.

LL-PTC reactions were also investigated. Using aqueous solutions of the sodium salts of the carboxylic acids, the halides in chloroform at ca. 65°C, and 5 mol% of tetra-n-butylammonium bromide as the catalyst (Procedure I), polyesters were generally obtained in high yield with *DP*s in the range 22 to 117. Procedure II was similar except that initially the acids were neutralized with tetra-n-butylammonium hydroxide. This procedure gave high yields of polyesters and, using similar monomers to those used with Procedure I, *DP*s in the range 31 to 161 were obtained. The LL-PTC synthesis of polyesters has been reported previously to give very low *DP*s and this present work appears to be the first where substantial *DP*s have been obtained.

ACKNOWLEDGEMENT

We thank the SERC/EPSRC for financial support for RO'D and MSKL.

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