Polyesterification of solid dicarboxylic acids by oxiran

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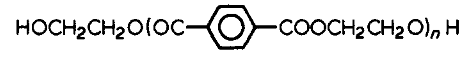
Poly(ethylene terephthalate) is synthesized by direct conversion of solid terephthalic acid into solid poly(ethylene terephthalate) without the formation of a separate liquid phase. The method, which is based upon catalysed high-temperature reaction of oxiran with the dicarboxylic acid, is also applicable to synthesis of other high-melting poly(ethylene arylenedicarboxylates). Several catalyst systems are evaluated and other reaction parameters examined.

Keywords Polyesters; terephthalic acid; oxiran; ethoxylation; polycondensation; catalysts

INTRODUCTION

During the manufacture of poly(ethylene terephthalate) from terephthalic acid or dimethyl terephthalate by reaction with ethylene glycol, the initial stage involves formation of a mixture of low-melting oligomers possessing hydroxyl end-groups, of the general formula (I)



(I)

where the predominant species have value of n up to about 5.

Processes based upon terephthalic acid and oxiran (ethylene oxide) have also been described. Here the intermediate product is bis(2-hydroxyethyl) terephthalate (I; $n=1$), which melts at 110°C. Such processes are mostly conducted in the presence of a liquid phase that contains a dissolved salt of terephthalic acid, but direct reaction of oxiran with solid terephthalic acid in the presence of diethylamine as catalyst under pressure at 120°C also leads to formation of bis(2-hydroxyethyl)terephthalate[1]. In all these cases the low-melting product from the first stage is then subjected to polymerization in the molten state, although sometimes a final polymerization in the solid state is also carried out after isolation of high-melting solid polymer. Such solid-state polymerization requires temperatures above about 200°C to proceed at a useful rate.

Bis(2-hydroxy ethyl) terephthalate has previously been shown[2] to undergo a polycondensation reaction in the solid phase, but the reaction is very slow indeed and is unlikely, even at very extended reaction times, to produce a high polymer. In general, the lower hydroxyl-ended oligomers of poly(ethylene terephthalate) are so much lower-melting than the polymer[3] (*Figure 1*) that any process for polymer production that involves their formation in a substantial proportion must inevitably form a liquid phase. The oligomers with one hydroxyl and one carboxyl end-group are also comparatively low-melting[3]. The lower carboxyl-ended oligomers, on the other hand, melt at higher temperatures than the polymer, and therefore offer the possibility of a process for converting terephthalic acid into poly(ethylene terephthalate) without formation of a separate liquid phase[3,4].

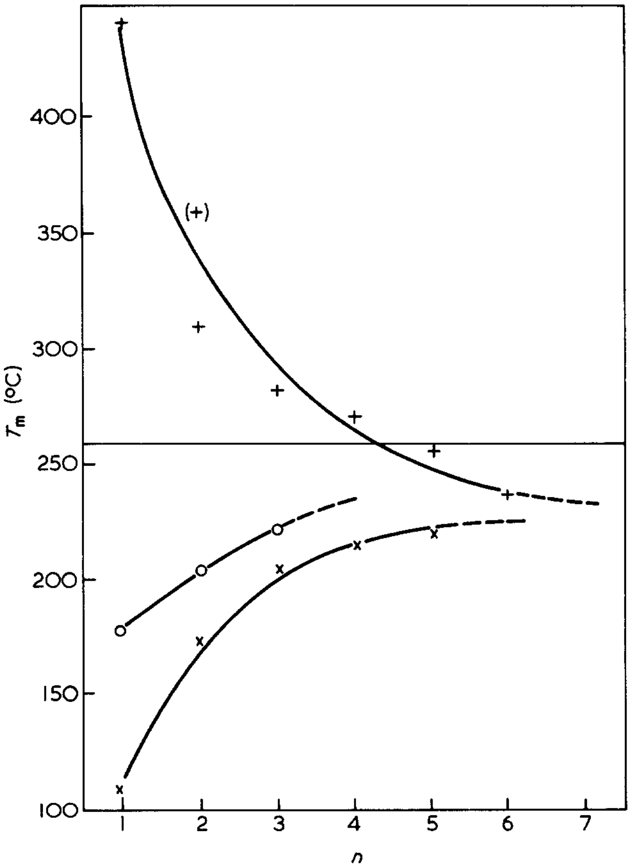


Figure 1 Melting points of compounds $ROOC\phi CO(OCH_2CH_2OOC\phi CO)_{n-1}OR'$ (ϕ=p-phenylene). +, $R=R^1=H$–; ○, $R=H$–, $R^1=HOCH_2CH_2$–; x, $R=R^1=HOCH_2CH_2$–

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EXPERIMENTAL

Reactor

A vertical glass tube, 4 cm in diameter and 45 cm in height, contained at the lower end a horizontal sintered glass plate sealed to the walls, and was fitted with a glass thermocouple pocket whose end was located 3 cm above the sintered glass plate. Terephthalic acid (or other solid reactant) was placed on the sintered glass plate. Inert gases and reactive vapours were supplied through a glass tube sealed to the foot of the reactor; they passed through the sintered plate, fluidized the solid reactant, and were removed from the top of the reactor by a tubular outlet leading to a trap vessel and then to the atmosphere. The reactor was heated by insertion in the central chamber of a Wallace seven-cell ageing oven.

Gas feed system

A vertical tubular glass vessel containing facilities for internal heat exchange by warm or cold water was used to mix nitrogen and oxiran in the required proportions. Liquid oxiran was fed into the vessel and collected at the foot, where its temperature was controlled by the heat exchange. Nitrogen was passed through the vessel by two routes: directly through the upper part of the vessel, and bubbled through the liquid oxiran. The amount of oxiran vaporized was controlled by controlling the proportion of the nitrogen taking each route. The total nitrogen flow rate into the vessel and the total gas flow rate out of the vessel were measured by rotameters. The unit was fitted with a pressure relief valve operating at a pressure of 1.6 bar.

The mixed gases were heated to the reaction temperature by passage through six glass chambers, each packed with glass wool, connected in series and inserted in the six outer chambers of the Wallace oven, and finally were fed to the foot of the reactor.

Volatile catalyst feed system

Where continuous feed of triphenyl phosphine catalyst was required, it was provided by placing glass wool coated with triphenyl phosphine in the body of a second reactor vessel in a second Wallace oven, and passing through it nitrogen preheated in six preheater vessels in the six outer chambers of the oven. The rate of feed of triphenyl phosphine could be adjusted by altering either the volatilization temperature or the nitrogen flow rate, and was measured by determining the loss of triphenyl phosphine after each run. A sufficient excess of triphenyl phosphine was present in the evaporator to ensure essentially constant rate of vaporization. The vaporized triphenyl phosphine was fed to the reactor through a heated transfer line and combined with the main gas flow just before entry into the reactor.

Reagents

Terephthalic acid was polyester grade powder of mean particle size 95 μm (range 20–400 μm). In some experiments powder of mean particle size 25 μm (range 3–200 μm) was used.

Naphthalene-2,6-dicarboxylic acid, *1,2-bis(4-carboxyphenoxy)ethane* and *biphenyl-4,4′-dicarboxylic acid* were made by pressure hydrolysis of the corresponding dimethyl esters using 3 moles of 1.5 molar aqueous sodium hydroxide per mole of ester at 160°C for 10 h. The acids were precipitated from the hot aqueous solution by pouring into aqueous hydrochloric acid, then filtered off, washed, and dried. *Diphenyl sulphone 4,4′-dicarboxylic acid* was prepared similarly from the dibutyl ester. The purities of the acids were checked before use by measuring the neutralization equivalents.

Oxiran was supplied in cylinders by Air Products Ltd, and stored in a refrigerated compartment until required.

Catalysts were standard laboratory reagents where available. Triphenyl phosphine was shown by mass spectrometry to contain less than 0.5% triphenyl phosphine oxide. The basic polyamide catalyst was synthesized by the polycondensation in the molten state of bis(2-aminopropyl)piperazine and adipic acid.

Catalysts were preblended with the solid acid reactant. In the case of antimony trioxide, sieved powder (<10 μm) was tumbler-blended with the acid for 6 h and the antimony concentration was measured on five random samples. Soluble catalysts were dissolved in a suitable solid, the acid reactant was slurried in the solution, and the solvent was evaporated with continuous agitation of the mixture.

Analytical methods

Samples of the product were analysed by the following procedure:

(1) A sample of the total product was weighed (A).

(2) Soluble components were removed by Soxhlet extraction with chloroform. After removal of the chloroform the residue was dried and weighed (B).

(3) The residual extracted solid was slurried with cold dilute sodium hydroxide solution to remove soluble acids. The acids were precipitated from the alkaline extract with dilute hydrochloric acid, isolated by filtration, dried and weighed (C).

(4) The alkali-extracted residue was washed with dilute hydrochloric acid then water, dried, and weighed (D).

The chloroform extract (B) is a mixture of compounds, mainly linear low-molecular weight oligomers, and is referred to later as 'oligomers'. The alkali extract (B) consists essentially of terephthalic acid or other reactant acid; in some cases small amounts of carboxyl-ended low-molecular-weight oligomers were also present. The final residue (D) is essentially polyester, which was further characterized as shown below.

Limiting viscosity number $[\eta]$ was obtained by measuring the viscosity ratio at 1% concentration in *o*-chlorophenol at 25°C and calculating the appropriate value of limiting viscosity number from tables established for poly(ethylene terephthalate). Because of the high crystallinity of many samples, it was necessary before solution to produce amorphous films by briefly melting the samples under dry nitrogen then quenching them to room temperature.

Diethylene glycol (DEG) content was measured by methanolysis then gas–liquid chromatographic separation of the diols isolated.

Thermal properties were determined from thermograms from a Perkin–Elmer DSC-1B. Melting points (T_m') were measured on a first scan. The samples were immediately quenched to room temperature, and the glass transition (T_g), temperature of maximum cold-crystallization rate (T_c), and melting temperature (T_m'') were measured on a second scan. Scanning rates were 10°C min^{-1}.

Phosphorus contents were measured on samples of the total product by wet oxidation.

Antimony and titanium contents were measured on samples of the total product using a Phillips X-ray fluorescence spectrometer.

Cyclic oligomer contents were measured by Soxhlet extraction of the polymer by trichloroethylene.

Hazards

Oxiran is toxic and explosive when mixed in a wide range of concentrations with oxygen-containing gases, so precautions were taken to avoid inhalation of gas and formation of such explosive mixtures. It is also explosive even in contact with inert gases if present at a sufficiently high vapour concentration at high temperatures. The range of potentially hazardous conditions has been defined by Burgoyne[5]. For this work, reaction conditions falling within the explosive limit were avoided; in practice this meant that partial pressures of oxiran above 0.5 bar were not employed. Moreover, direct vaporization of oxiran without dilution was considered unwise so vaporization was carried out by passing nitrogen through liquid oxiran in a specially constructed vaporizer.

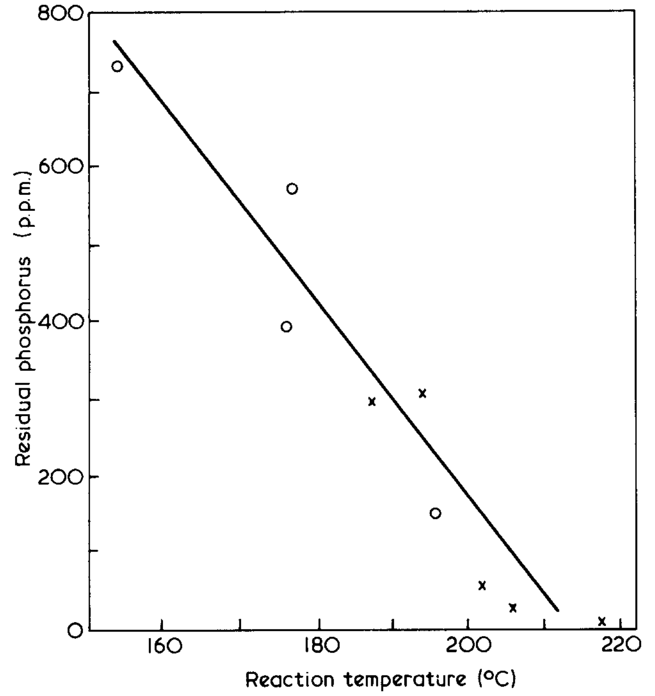


Figure 2 Loss of triphenyl phosphine as a function of reaction temperature. Initial concentration: 0.63 mol% (1183 ppm P). Time: 21 h, 5 h with passage of oxiran + nitrogen (0.5 bar each), 21 h with passage of nitrogen only. ×, Triphenyl phosphine alone; ○, triphenyl phosphine + tetra-isopropyl titanate (0.12 mol%)

RESULTS

Catalysts

Little or no reaction took place between terephthalic acid and oxiran in the absence of a catalyst at temperatures up to 230°C, and the infusible base sodium terephthalate was almost ineffective as a catalyst. This result is not surprising in view of the inability of such inorganic bases to catalyse the reaction of solid terephthalic acid with liquid oxiran under pressure to produce bis(2-hydroxyethyl) terephthalate.

Nitrogen and phosphorus bases, on the other hand, did catalyse the hydroxyethylation reaction. Triphenyl phosphine, which proved to be a powerful catalyst, was evaluated in greater detail.

Triphenyl phosphine

At temperatures in the range 110°–140°C, triphenyl phosphine catalysed formation of bis(2-hydroxyethyl) terephthalate together with small amounts of other linear oligomers. Consequently fusion occurred at a low degree of conversion. Above about 160°C, further slow conversion of the reaction product into polymer took place. Both hydroxyethylation and conversion into polymer became slightly faster at higher temperatures up to about 200°C, but above 200°C there was a rapid decline in the degree of conversion of terephthalic acid in a given time due to removal of triphenyl phosphine from the bed by volatilization. The vapour pressure, p, of triphenyl phosphine at 200°C is 4.8 mmHg based on the relationship[6]:

$$\log p = 8.539 - \frac{3717}{T}$$

where T is the absolute temperature. Removal of phosphorus from the bed was confirmed by analysis. *Figure 2* shows the residual phosphorus content as a function of temperature for a total residence time of 21 h.

Continuous feed of triphenyl phosphine into the reaction bed at 235°C, without any other catalyst, overcame this problem and permitted attainment of higher conversions. The reaction rate depended upon the feed rate (*Table 1*). The presence of a high proportion of oligomeric material in these products led to fusion of the reaction bed before complete conversion of terephthalic acid was attained.

Tetra-isopropyl titanate

Tetra-alkyl titanates are powerful catalysts for the polycondensation stage of poly(ethylene terephthalate) preparation, and also possess catalytic activity in the direct esterification of terephthalic acid by ethan-1,2-diol. Tetra-isopropyl titanate on its own, however, proved relatively ineffective as a catalyst for heterogeneous

Table 1 Dependence of conversion upon triphenyl phosphine feed rate

Reaction time (h)	TPP feed rate (g min^{-1} per g TA)	Conversion (%)	Product composition (%)		Final P in bed (ppm)
			Oligomers	Polymer	
5	31×10^{-5}	51.5	35	65	387
5	4.5×10^{-5}	6.1	84	16	20
10	4.5×10^{-5}	55.9	37	63	296

Oxiran partial pressure 0.25 bar
Reaction temperature 235°C

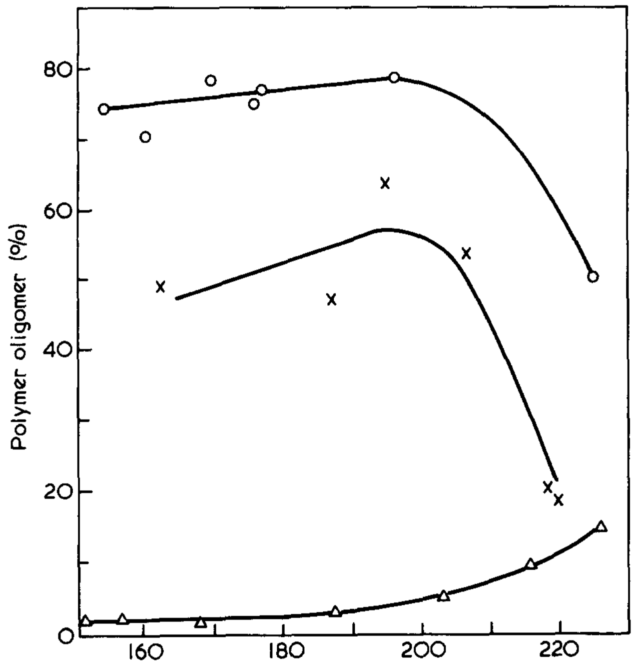


Figure 3 Conversion of terephthalic acid into oligomeric and polymeric products. Reaction conditions as *Figure 2*. ×, Triphenyl phosphine (0.63 mol%); ○, triphenyl phosphine (0.63 mol%) + tetra-isopropyl titanate (0.12 mol%); △, tetra-isopropyl titanate (0.12 mol%)

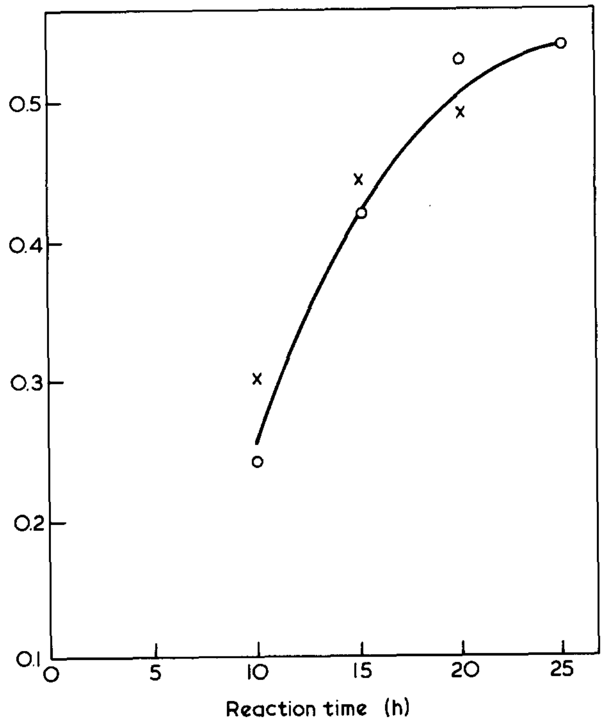


Figure 4 Increase of limiting viscosity number with reaction time at 200°C. Catalysts: triphenyl phosphine (0.63 mol%) + tetra-isopropyl titanate (0.12 mol%). Oxiran partial pressure: 0.25 bar. ○, Further addition of triphenyl phosphine (0.63 mol%) at 5 h intervals; ×, no further addition of triphenyl phosphine

reaction of terephthalic acid with oxiran. At 0.12 mol% concentration in the terephthalic acid, with a partial pressure of oxiran of 0.5 bar, it produced only 15% conversion into reaction products after 5 h exposure at 220°C and less at lower temperatures (*Figure 3*). Since it is not volatilized out of the bed, complete conversion into polymer can no doubt be reached at very extended reaction times.

Tetra-isopropyl titanate plus triphenyl phosphine

A combination of tetra-isopropyl titanate (0.12 mol%) with triphenyl phosphine (0.63 mol%) proved more effective than either catalyst alone. Comparison of the results of reaction with oxiran for 5 h using the catalysts separately and in combination (*Figure 3*) suggests that the combination is synergistic, a result that might be expected if the triphenyl phosphine acts mainly on the ethoxylation stage and the titanate on the subsequent polycondensation stage.

With this combination it proved possible to obtain complete conversion of terephthalic acid into polyester. After 10 h at 200°C with a partial pressure of oxiran of 0.25 bar, the polymer produced had a limiting viscosity number in the range 0.2–0.3 dl g^{-1}, and this rose with further reaction time to values above 0.5 dl g^{-1} (*Figure 4*). Further solid-phase polycondensation at 230°C for 20 h in the absence of oxiran raised the limiting viscosity number to 0.70 dl g^{-1}.

Antimony trioxide and triphenyl phosphine

Antimony trioxide proved a poor ethoxylation catalyst with negligible activity at 200°C, so it was essential to have a continuous feed of triphenyl phosphine into the reaction bed when these two catalysts were used in combination. Typically, with the triphenyl phosphine all charged initially it was not possible to reach complete conversion into polymer at 235°C, whereas complete conversion was possible even at quite low continuous feed rates (*Figure 5*). In the former case, although the conversion of tereph-

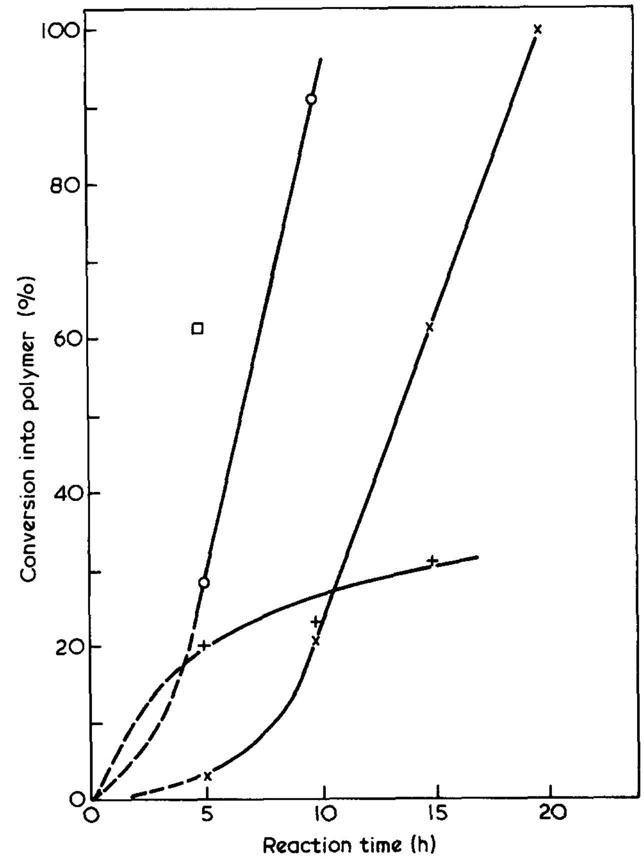


Figure 5 Rate of conversion of terephthalic acid into polymer as a function of triphenyl phosphine feed rate at 235°C. Oxiran partial pressure: 0.25 bar. Antimony trioxide concentration: 0.024 mol%. Triphenyl phosphine supply: +, 0.63 mol% initially; ×, 6.9×10^{-3} g min^{-1} continuous feed; ○, 4.8×10^{-3} g min^{-1} continuous feed; □, 7.9×10^{-3} g min^{-1} continuous feed

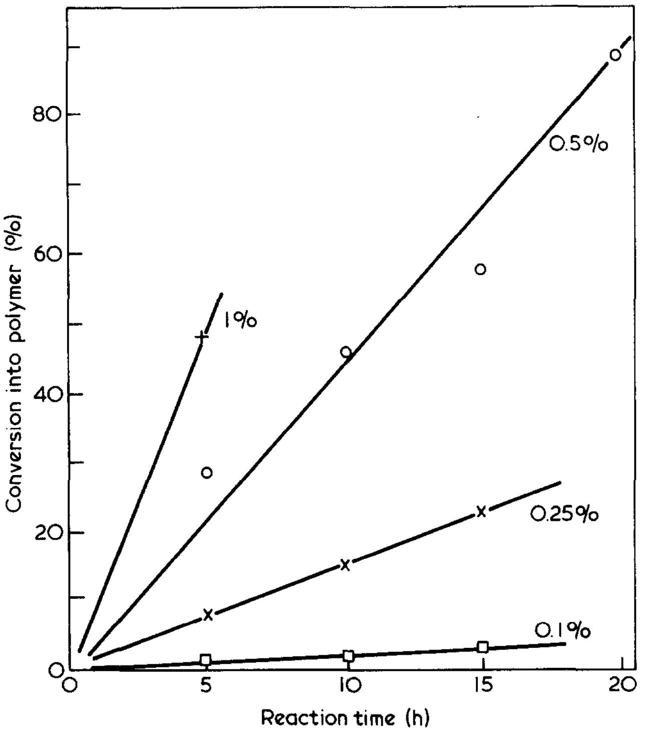


Figure 6 Rate of polymer formation at 230°C at different initial concentrations of phosphorous acid. Antimony trioxide concentration: 0.028 mol%. Oxiran partial pressure: 0.25 bar

thalic acid did not exceed 30%, the polymer isolated from the product had a limiting viscosity number above 0.3. With continuous feed the conversion–time relationship showed an acceleration in rate, as expected since the triphenyl phosphine content of the bed will increase from zero to some equilibrium value as it is absorbed from the gas stream, and the ethoxylation rate should consequently increase. The acceleration in rate is greater, again as expected, the higher the feed rate (*Figure 5*).

Using this catalyst system, limiting viscosity numbers in the range 0.53–0.68 were reached after 15 h reaction. Carboxyl end-group contents were then 10–15 μEq g^{-1} and cyclic oligomer contents 0.35–0.41% by weight, values characteristic of polyester made by a solid-phase process and much lower than those found for melt-polymerized products. Extension of the reaction time to 30 h raised the limiting viscosity number to 0.82.

Phosphorous acid

Reactions at 230°C catalysed by phosphorous acid in 0.1–1.0% concentration, with antimony trioxide present in addition, exhibited linear rates of conversion of terephthalic acid with polymer (*Figure 6*). A curious feature is that although the reaction is apparently first order with respect to phosphorous acid concentration (*Figure 7*), the rates of conversion are proportional not to the initial phosphorous acid concentration, C_p, but to a slightly lower value, $C_p - C_0$, where C_0 represents a small but clearly defined intercept on the y axis of *Figure 7* that implies zero rate of conversion at about 0.07% phosphorous acid. This behaviour implies that the antimony trioxide not only has no catalytic activity at all in the presence of phosphorous acid at 230°C, which in view of its high polycondensation activity in conjunction with triphenyl phosphine is surprising, but also inactivates a small amount of the phosphorous acid. In fact antimony trioxide at this temperature oxidizes phosphorous acid to phosphoric acid, and is itself reduced to antimony metal. Phosphoric acid was found to possess only about 10% of the catalytic activity of phosphorous acid, and antimony metal is inactive as a catalyst. The quantity of antimony trioxide present, 0.049%, was sufficient to oxidize 0.041% of phosphorous acid to phosphoric acid, somewhat less than the intercept value of about 0.07%.

It follows that the antimony trioxide contributes nothing positive to reaction rate in this catalyst system, and in fact phosphorous acid alone was found to be as effective as the mixture at high phosphorous acid concentration and more effective at low phosphorous acid concentration.

Melting points

The melting points of all polymers were substantially higher, by up to 28°C, on the first determination than after quenching from the melt and redetermining the melting point. For polymers of limiting viscosity number 0.35 or above containing up to 2.6 mol% of diethylene glycol units, the melting point of the isolated polymer was in the range 267°–276°C, and of the fused, quenched and recrystallized polymer 248°–257°C. Elevation of the melting point in this way is typical of polymer annealed at solid-phase polymerization temperatures.

Ether-forming side-reactions

Formation of repeating units formally derived from 3-oxapentan-1,5-diol (diethylene glycol) instead of from ethan-1,2-diol (ethylene glycol) occurred with all catalysts, but was much affected by catalyst type and by temperature. The basic catalyst triphenyl phosphine (1%)

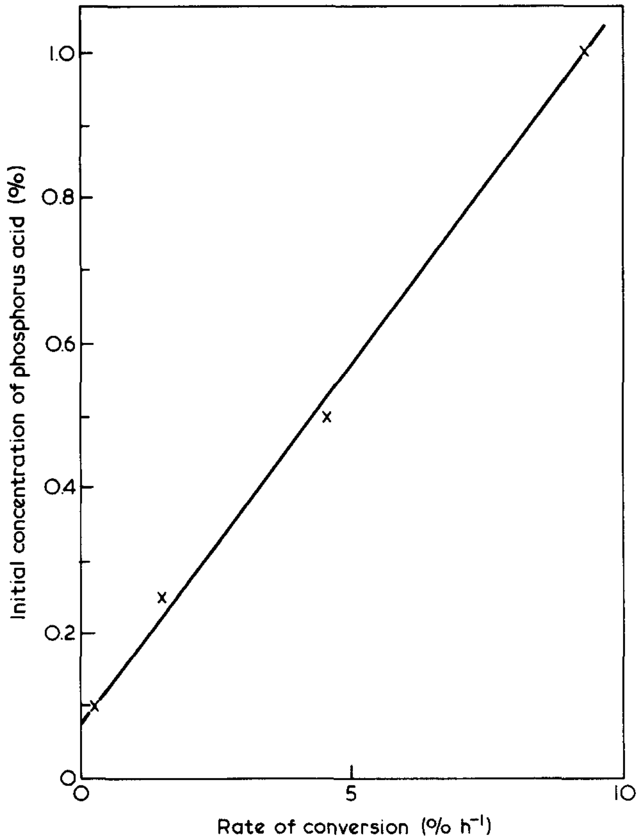


Figure 7 Effect of initial concentration of phosphorus acid upon rate of conversion of terephthalic acid into polymer. Conditions as *Figure 6*

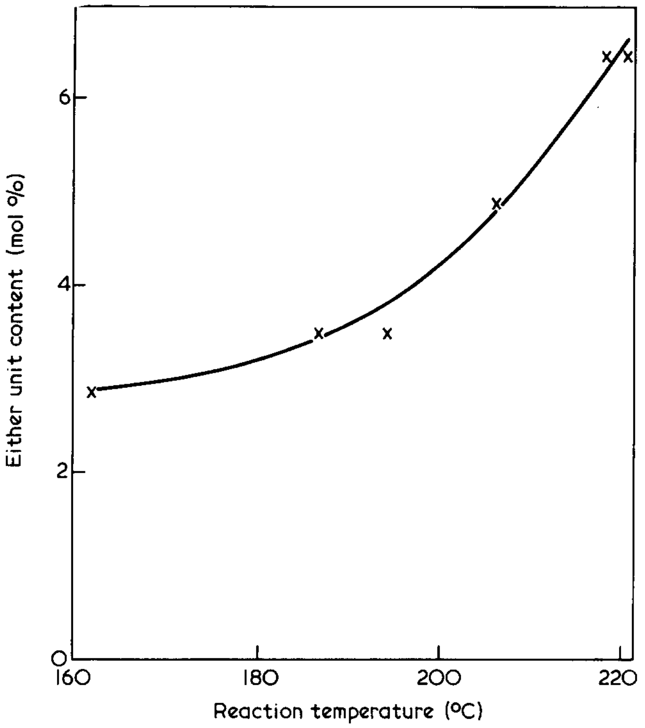


Figure 8 Effect of reaction temperature on ether link content of polymer. Catalyst: triphenyl phosphine (0.63 mol%). Oxiran partial pressure: 0.5 bar

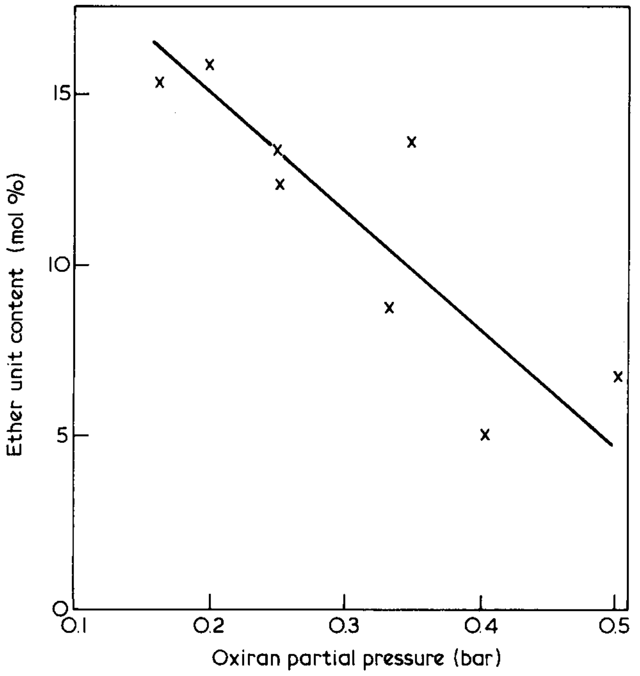


Figure 9 Effect of oxiran partial pressure on ether link content of polymer. Catalysts: triphenyl phosphine (0.63 mol%); tetra-isopropyl titanate (0.12 mol%). Reaction temperature and time: 200°C/5 h

alone gave more such units in the polymer the higher the temperature (*Figure 8*), although since the rate of polymer formation was lower at the higher temperature, due to volatilization of the catalyst from the bed, this result approximates to a constant absolute rate of ether unit formation from one temperature to another. The additional presence of a tetra-isopropyl titanate catalyst (0.2%) increased the proportion of ether units formed. The effect of oxiran partial pressure was examined for this combination of catalysts at 200°C, and it was found (*Figure 9*) that higher oxiran concentration reduced ether unit content, but even the lowest value was over 5 mol%. Here, too, the higher the rate of conversion, the lower the ether unit content in the polymer (*Figure 10*).

A combination of triphenyl phosphine with antimony trioxide (0.043%) gave quite a different pattern. Here the ether unit content fell markedly with increase in reaction temperature; above about 230°C the ether unit content fell to the low value of 2 mol% or below. The simplest, though not necessarily the correct, explanation is that there are competitive reactions in which hydroxyethyl end-groups react with carboxyl groups to form ethylene diester groups, or with oxiran to form ether links, and that the former reaction has a higher activation energy than the latter. If so, there should be a linear relationship between log(ether unit content) and the reciprocal of the absolute reaction temperature, and the data do fit such a relationship very well (*Figure 11*). The difference in activation energies calculated from the slope is approximately $40\,\text{kJ mol}^{-1}$. Within the range of reaction conditions studied, there was no significant deviation from this relationship due to changes in the initial antimony trioxide concentration (172–696 ppm), partial pressure of oxiran (0.2–0.33 bar), or triphenyl phosphine feed rate ($0.07\text{–}1.3 \times 10^{-3}\,\text{g l}^{-1}$ at $6\,\text{l min}^{-1}$).

Ether unit contents below 2 mol% were also obtained with a basic polyamide/antimony oxide catalyst combination at reaction temperatures above 230°C, but the phosphorous acid and phosphorous acid/antimony trioxide catalysts at similar temperatures gave higher ether unit contents, in the range 3–7 mol%.

Oxiran concentration

The effect of partial pressure of oxiran upon rate of conversion of terephthalic acid into reaction products was examined for four catalyst systems:

(i) tetra-isopropyl titanate + triphenyl phosphine at 200°C;

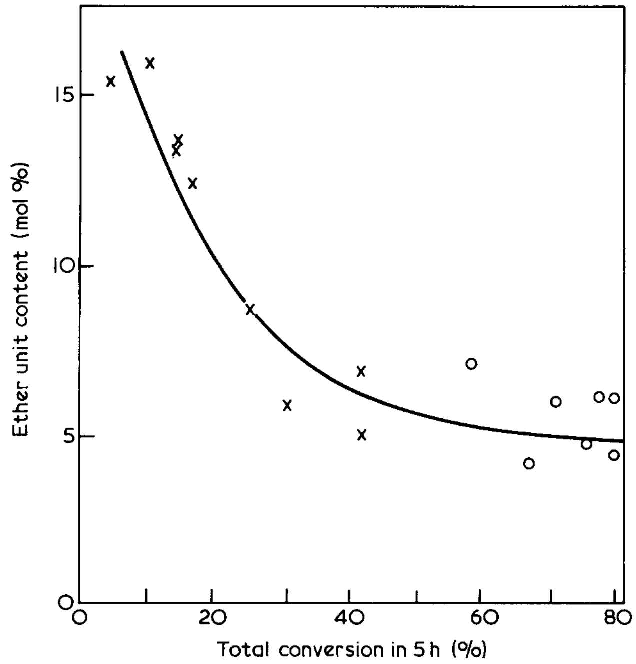


Figure 10 Effect of conversion rate on ether link content of polymer. Catalysts as *Figure 9*. Various reaction temperatures and oxiran partial pressures.

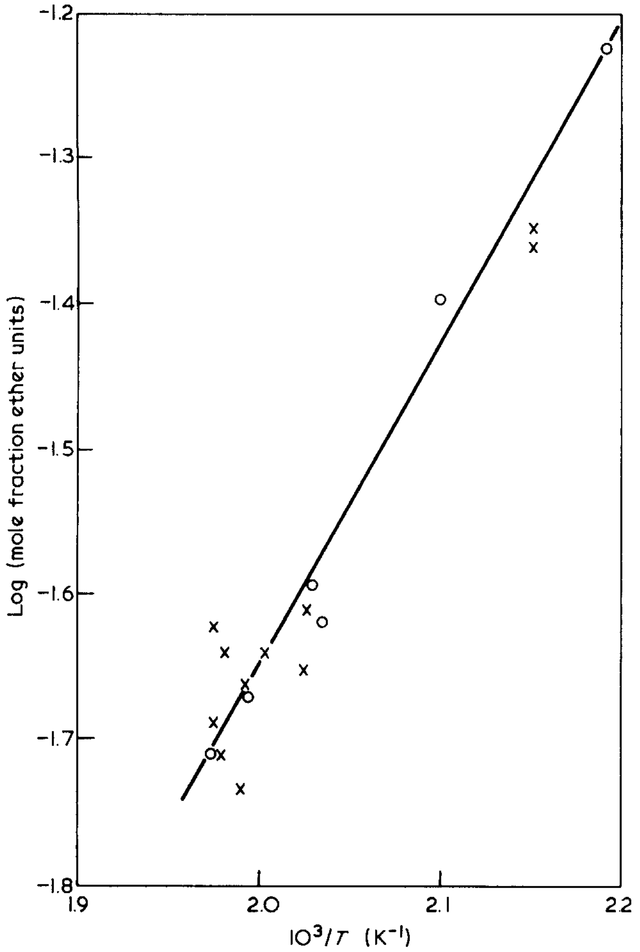


Figure 11 Relationship between ether link content of polymer and mean reaction temperature. Catalysts: antimony trioxide (0.024 mol%) + triphenyl phosphine (0.63 mol%)

(ii) antimony trioxide + triphenyl phosphine at 230°C;
(iii) antimony trioxide + phosphorous acid at 230°C;
(iv) phosphorous acid alone at 230°C.

The rates of conversion were compared over a fixed period of time such that the highest conversion was about 50%. System (i) was most fully examined, over a range of partial pressures from 0.167 to 0.5 bar. *Figure 12* shows that the rate of conversion was approximately proportional to the square of the partial pressure of oxiran. Only two or three partial pressures were examined for systems (ii)–(iv). In each case the order of dependence of conversion rate upon partial pressure was greater than unity.

Acids other than terephthalic acid

Formation of polyester by reaction of other dicarboxylic acids with oxiran under conditions similar to those used for terephthalic acid proved possible provided that both the dicarboxylic acid and the polyester produced were of sufficiently high melting point not to fuse during the process. Polyesters were made in this way from oxiran and

1,2-bis-(4-carboxyphenoxy)ethane (CPE), naphthalene-2,6-dicarboxylic acid (N),
diphenylsulphone-4,4′-dicarboxylic acid (BSO_2B),
biphenyl-4,4′-dicarboxylic acid (BB).

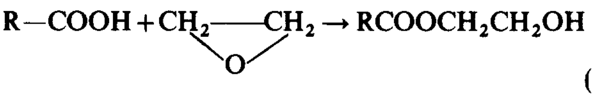
All four polymers were synthesized by reaction with oxiran (partial pressure 0.25 bar) at 200°–205°C in the presence initially of tetra-isopropyl titanate (0.2% by weight) and triphenyl phosphine (1% by weight). The conversion rates for CPE and N were higher than that for terephthalic acid under the same conditions, and complete conversion was obtained in 15–20 h. The product from CPE after 20 h reaction had a limiting viscosity number of 0.71 and melting point 241°C; that from N had a viscosity ratio of 1.66 and melting point 258°C. The conversion rates for BSO_2B and BB were slower; in 20 h, conversions were 80% and 23.7% respectively and due to loss of triphenyl phosphine the reaction rates had become very slow. Polymer isolated from the BSO_2B reaction product had melting point 305°C. All four polymers had unusually high diethylene glycol contents, ranging from 16.5 to 24.0 mol%, due to use of a titanium ester catalyst.

The CPE and BB polyesters were also synthesized by reaction with oxiran (partial pressure 0.25 bar) in the presence of antimony trioxide (0.05% by weight) and continuous feed of triphenyl phosphine (4×10^{-3} g min^{-1}). Complete conversion of CPE was obtained in 10 h at 205°C; the polyester had a limiting viscosity number of 0.73 and diethylene glycol content of 3.3%. Complete conversion of BB was obtained in 20 h at 240°C; the polyester would not dissolve in *o*-chlorophenol and had a melting point of 340°C.

DISCUSSION

There are at least two distinct types of reaction in the conversion of terephthalic acid into poly(ethylene terephthalate) by this method:

(i) hydroxyethylation by oxiran (reaction (1))



$$R{-}COOH + \underbrace{CH_2{-}CH_2}_{O} \rightarrow RCOOCH_2CH_2OH \qquad (1)$$

(ii) polycondensation with elimination of water (reaction (2)) or of ethan-1,2-diol (reaction (3))

$$R{-}COOH + HOCH_2CH_2OOCR \rightarrow RCOOCH_2CH_2OOCR + H_2O \qquad (2)$$

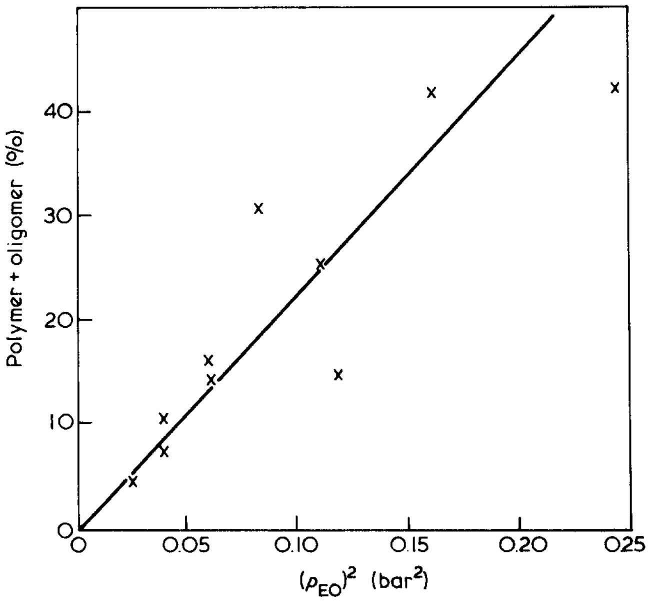


Figure 12 Dependence of rate of conversion upon oxiran partial pressure at 200°C. Catalysts: tetra-isopropyl titanate (0.12 mol%) + triphenyl phosphine (0.63 mol%)

$$2\,RCOOCH_2CH_2OH \rightarrow RCOOCH_2CH_2OOCR + HOCH_2CH_2OH \qquad (3)$$

The original concept underlying the development was that if reactions (1) and (2) occurred simultaneously at rates such that the hydroxyethyl-ended product of reaction (1) was rapidly removed by reaction (2), then hydroxyethyl-ended intermediates would never attain a high concentration and the early stages of polycondensation would proceed through the very much higher-melting carboxyl-ended oligomers (*Figure 1*). It would therefore be possible to keep the reaction medium solid, or more accurately particulate, throughout. There is an obvious alternative, however, in that even if reaction (2) does not occur at all, reaction (3) may be caused to remove hydroxyethyl end-groups rapidly enough to achieve the same effect, although with the disadvantage that ethan-1,2-diol will then be formed as a by-product.

The first effective catalysts found for the hydroxyethylation stage were phosphorus and nitrogen bases, of which triphenyl phosphine was examined more fully. If reaction temperatures were high enough, polycondensation also took place and polymer was formed without loss of the particulate form. Only low conversions into polyester could be attained if the catalyst was supplied only by initial mixing with the terephthalic acid, because at temperatures high enough to give substantial polycondensation rates the catalyst was volatile enough to be stripped out of the reaction bed. When the catalyst was continuously supplied in the fluidizing gas stream, complete conversion into solid polyester could be attained at 235°C. The rate of conversion was higher the greater the triphenyl phosphine concentration in the feed gas, but progress in this direction was limited by sintering of the particles and production of an agglomerated mass.

A combination of triphenyl phosphine with tetra-isopropyl titanate enabled complete conversion into polyester to be achieved at 200°C without continuous supply of triphenyl phosphine. In this case the titanate particularly catalyses the polycondensation stage, although it was found to possess significant catalytic activity for the ethoxylation stage.

With antimony trioxide as polycondensation catalyst instead of the titanate, a higher reaction temperature was required and consequently it was necessary to feed triphenyl phosphine continuously to avoid depletion of its concentration in the bed. The reaction time for complete conversion into polymer was shorter the higher the triphenyl phosphine feed rate.

Phosphorous acid proved to be effective, although at rather high concentrations, as a catalyst for both ethoxylation and polycondensation at 230°C. This result is unexpected since phosphorous acid is not considered to be a useful catalyst for melt polymerization of poly(ethylene terephthalate). Antimony trioxide was an antagonist for this catalytic activity, presumably because of an oxidation–reduction reaction between it and the phosphorous acid. Phosphoric acid and metallic antimony, the probable products of this reaction, both have low catalytic activity.

An important side-reaction in commercial production of poly(ethylene terephthalate) is formation of ether linkages in the chain. Ether formation also occurred in this route to the polymer, but could be brought below 2 mol%, and therefore into an acceptable range for fibre formation, by using antimony trioxide as polycondensation catalyst along with a basic ethoxylation catalyst at a temperature above about 230°C.

Reaction rates depended not only upon catalyst concentrations but also upon the partial pressure of oxiran in the gas stream. Although the order of reaction with respect to oxiran could not be precisely determined from the data, it was certainly greater than 1 and possibly about 2. The range of oxiran pressures used was limited by consideration of potential explosion hazard to 0.5 bar, so it was not possible to determine whether still higher reaction rates could be obtained by operating with oxiran at atmospheric pressure or above.

The scope of the reaction was shown to include the preparation of polyesters of acids other than terephthalic acid where both the acid and the polyester produced were of high melting point. Attempts to make copolyesters by using terephthalic acid together with 10–20 mol% of other, low-melting acids led to sintering and agglomeration.

A feature of this heterogeneous polycondensation process is the presence in the reacting mixture at one and the same time of unreacted starting material (terephthalic acid) and polyester of high molecular weight. Such behaviour is characteristic of vinyl polymerizations but not of polycondensation reactions as normally conducted.

CONCLUSIONS

Aromatic dicarboxylic acids with sufficiently high melting points react with oxiran in the presence of catalysts at temperatures above about 180°C to produce the corresponding poly(ethylene arylenedicarboxylate) without loss of particulate form.

Effective catalysts include triphenyl phosphine as oxyethylation catalyst in combination with a tetra-alkyl titanate or antimony trioxide as polycondensation catalyst.

Phosphorous acid catalyses both stages of the reaction.

With terephthalic acid, the proportion of ether link impurity formed in the polymer chain is below 2 mol% with a triphenyl phosphine/antimony trioxide catalyst system used at a reaction temperature above about 230°C.

Unlike homogeneous polycondensation reactions, this synthesis produces polymer of high molecular weight while unchanged aromatic dicarboxylic acid is still present.

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