Polymerization in the Solid Phase: a Polycondensation Reaction

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The solid-phase polycondensation (ester interchange) reaction leading to the formation of polyethylene terephthalate has been studied. Two types of material were polymerized: the monomer, dihydroxyethyl terephthalate (DHET), and polymeric samples. In the former case reaction only occurs at temperatures close to the melting point and the reaction rate is critically dependent on the temperature in this temperature region; the nature of the dependence is related to increase in mobility of molecules within the crystal lattice, and the presence of impurities used as catalysts broadens the region over which reaction may occur. Polymer reacts over a wider temperature range (e.g. perceptible reaction takes place at 150°C with polymer melting at ca. 260°C) and the activation energy for the reaction is approximately the same as that obtained for melt polymerization. From the kinetic data it is deduced that polymerization occurs only within a limited depth from the surface of each polymer particle. The velocity coefficients for the reaction are much greater than the velocity coefficients for melt polymerization extrapolated to the temperatures used for the solid phase studies. Suggestions are made about ways in which these increased rate constants could arise. The molecular weight distribution of polymer prepared in the solid phase is thought to be abnormal, both from kinetic and other evidence. This abnormality appears to arise from a spatial heterogeneity and differential thermal analysis confirms that the polymer is inhomogeneous.

1. INTRODUCTION

SOLID-PHASE addition polymerization has been extensively studied in recent years and much attention has been paid to the influence of crystal structure and lattice defects on the rate of reaction[1]. Condensation polymerization in the solid phase has received less attention, although it is well-known that reactions of this type proceed at temperatures below the melting points of the polymerizing materials, in both polyamides[2] and polyesters[3]. Several references to the solid-phase polymerization of ethylene terephthalate exist in the patent literature[4].

This paper describes an investigation of the formation of polyethylene terephthalate in the solid phase, with particular reference to the influence of physical parameters on the kinetics of the reaction. Two distinct starting materials may be employed in a study of polycondensation reactions —either the true monomer, or a sample that has already been polymerized to some extent. In the present case, use of the starting materials, which have widely differing melting points, allowed the investigations to be made in two temperature regions.

The monomer used was dihydroxethyl terephthalate (I) (referred to as DHET in the rest of this paper). Reaction of two molecules of DHET (I), with elimination of one molecule of ethylene glycol, forms the dimer, and the subsequent reaction is also an ester interchange process in which glycol is eliminated [equation (1)].

Earlier work[5,6] on polyethylene terephthalate has shown that although

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(I)

the intrinsic viscosity may increase on heating in the solid phase, there is a limit to the increase in $[\eta]$ which can be obtained with any given initial polymer. If, after the solid-phase reaction, a specimen which has reached its limiting $[\eta]$ is remelted and quenched rapidly, then broken up, further polymerization becomes possible. Further, sections cut by microtome from a chip of polymer after solid-phase reaction, show decreasing intrinsic viscosity with increasing penetration towards the middle of the chip[5]. These observations are consistent with the view that, in the solid phase, reaction occurs preferentially near the surface of the particle. The main polymerization process is the reaction

$$\sim\mathrm{COOCH_2CH_2OH} + \mathrm{HOCH_2CH_2OOC}\sim \longrightarrow \sim\mathrm{COOCH_2CH_2OOC}\sim + \mathrm{HOCH_2CH_2OH} \qquad (1)$$

The diffusion of glycol formed can influence the progress of the reaction, which is reversible, and since the glycol concentration is generally lowest near the surface the apparently preferential polymerization in this region is understandable. We shall see later that kinetic observations strongly support these ideas.

It follows from the above that the molecular weight distribution of polymer formed in the solid phase must differ from that obtained in the melt, so that no single relation between $[\eta]$ and end-group concentration (i.e. effectively the number-average degree of polymerization) can be expected. This fact complicates attempts to measure the rate of reaction by intrinsic viscosity determinations, except in special circumstances which will be mentioned in § 4.2.

2. EXPERIMENTAL

2.1. *Materials*

Polymerization in the solid phase may be influenced by crystal structure and lattice defects, molecular mobility and similar physical parameters. It is, therefore, desirable (although not always possible) that any monomer employed should be (*a*) readily identifiable, (*b*) homogeneous, and possibly (*c*) in the form of single crystals. For these reasons, the monomer first employed was DHET in the absence of catalyst. This was obtained from I.C.I. Fibres Ltd; it had been prepared by the action of ethylene oxide on terephthalic acid and recrystallized from water in the presence of activated charcoal. Evidence is presented in § 3 that DHET polymerizes in the solid phase when no catalyst is present. However, the process is very slow, and it was decided to find a way of introducing suitable catalysts into the monomer.

One possible method of catalysis involves replacing a number of the —OH groups in DHET by —ONa. This was first attempted by dissolving DHET in hot glycol and adding a small amount either of sodium methoxide in methanol or of hot glycol in which a little sodium had been dissolved. Great difficulty was experienced in recrystallization and filtration from glycol solutions and the method was abandoned. Instead, toluene was used as a solvent, from which DHET could be recrystallized in flakes. The toluene solution was refluxed with sodium metal for two hours, filtered hot and then cooled. The resultant crystals could be polymerized in the melt at 115°C, as evidenced by the formation of a solid mass at this temperature; tests for polymerization in the solid phase were less conclusive.

A more satisfactory method of preparing a monomer specimen incorporating catalyst is to dissolve titanium tetrabutoxide in molten DHET at a temperature close to the melting point, rapidly quench, and crush the solid mass. In this way a known concentration of catalyst can be introduced into DHET. Unfortunately, the nature of the particles prepared in this way is not well-defined. Recrystallization should provide larger and more homogeneous crystals, although solvents such as water, methanol or acetone seem unsuitable since they react, when hot, with the monomer containing catalyst.

A number of polyethylene terephthalates of differing initial molecular weights (I.C.I. Fibres Ltd) were used as the polymeric starting materials. The polymer was generally powdered and in some cases also sieved and graded, although in certain experiments designed to investigate the effects of fibre orientation on reaction, drawn and undrawn yarns were used. The catalyst system was always present in the polymer supplied, and was usually 0·06 per cent antimony oxide.

All other reagents were of analytical reagent quality.

2.2. *Experimental methods*

2.2.1. Temperature control—Reactions were carried out in vessels immersed in a heated silicone oil bath. The temperature of the bath was maintained constant to within ±0·15 deg. C by the use of two rates of heating. In certain experiments which occupied only a few minutes, the bath was allowed to heat up slowly (usually 0·2 deg. C in the interval) and the temperature of the bath was taken to be the average of the temperatures at the beginning and end of the experiment.

2.2.2. Rates of reaction—Quantitative determinations of the rate of polymerization were made by measurement of the rate of glycol evolution.

Rates of polymerization are expressed as rates of decrease of end-group (OH) concentration: one mole of glycol is evolved for every two end groups consumed. If the density of monomer is δ g cm^{-3}, and the rate of glycol evolution from a reaction mass of m g is z g s^{-1} then the rate of reaction is given by

$$dx/dt=(2z/62)(10^{3}\delta/m) \quad \text{mole l}^{-1}\text{s}^{-1} \qquad (2)$$

where x (mole l^{-1}) is the decrease in end group concentration after time t. The value of δ depends on whether DHET or polymer is used as the starting material, and is taken as 1·2 g cm^{-3}, 1·4 g cm^{-3} in the two cases, respectively.

In experiments with DHET, it is found that the rate of evolution of glycol remains constant over a considerable period, so that it is possible to make several measurements with the same sample. This means that the quantity of glycol evolved represents an insignificant change in the hydroxyethyl end-group concentration in DHET. In polymer, of course, the hydroxyethyl end-group concentration is much lower, and, indeed, it was found that the rate of glycol evolution decayed appreciably with time. Measurements cannot be made immediately the reaction vessel is put into the hot oil bath since the reaction mixture must have time to come to thermal equilibrium, and it therefore became necessary to use an alternative method of treating the experimental data. If the rate constant and initial concentration of end groups in reaction (1) are represented by k, a, respectively, the rate of reaction given (for a second order process) by

$$\omega \equiv \mathrm{d}x/\mathrm{d}t = k\,(a-x)^2 \tag{3}$$

may be expressed as a function of time by the relation

$$\omega = ka^2/(1+akt)^2 \tag{4}$$

A plot of $\omega^{-\frac{1}{2}}$ against t should, therefore, be linear with a slope of $k^{\frac{1}{2}}$. It is thus possible to measure the rate constant directly, without explicit knowledge of the initial end-group concentration. This method is the one that has been used, except where otherwise stated, for measuring rate constants from rates of glycol evolution in experiments with polymer.

Two methods of glycol estimation were employed. In the first, the glycol evolved was condensed in a cold trap (at liquid nitrogen temperature), and then washed out with water at the end of a specified period. The aqueous solution of glycol was then added to 2 ml of a mixture of 2 ml conc. HNO_3 + 2 ml 10 per cent aqueous $AgNO_3$ + 25 ml 2 per cent aqueous KIO_4 and allowed to stand for 15 minutes. Silver iodate was precipitated, one mole per mole of glycol, and was determined gravimetrically. The method is not economical of time, each separate run occupying about one day.

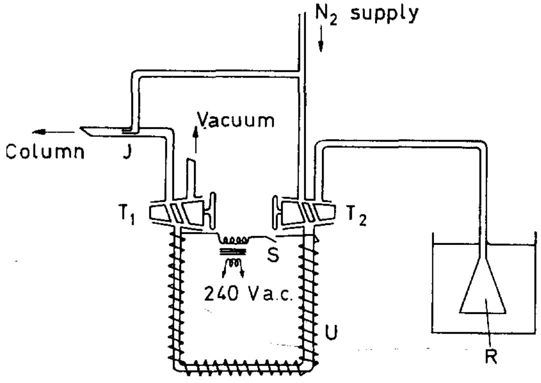


Figure 1—Reaction vessel and sampling system. R reaction cell in oil bath; T_1, T_2 two-way taps; U sampling U-tube with heating coil controlled by switch S; J capillary jet. All parts of the apparatus other than U were heated continuously to 120°C, approximately

A gas chromatographic technique was therefore devised for determining the glycol evolved during the course of reaction. A column approximately 0·2 m long of polyethylene glycol adipate supported on celite at 135°C was used with nitrogen as carrier gas; detection was by flame ionization after injection of hydrogen. Since the reaction was conducted at a pressure around 10^{-5} mm Hg, it was decided to use two-way glass taps in the sampling system, and the arrangement shown in *Figure 1* was employed. The **U**-tube was immersed in liquid nitrogen during the sampling period, with switch S open, and the taps T_1, T_2 open to the vacuum line and reaction flask respectively. T_1 was then closed completely, and T_2 was opened to the nitrogen supply; the coolant was then removed and S closed. The glycol was thus vaporized, after which T_1 was opened to the column. It was necessary to provide a small nitrogen flow through the column at all times, and with the arrangement of two-way taps described, this can only be accomplished by a small nitrogen bleed through a capillary. When a conventional capillary bleed was used, connected by a **T**-junction to the column, some difficulty was experienced arising from diffusion of glycol into the cold regions and condensation. For this reason the capillary jet system shown in *Figure 1* was employed: in this way, the capillary itself J is heated and glycol cannot condense. Edwards' Silicone grease was used on all heated ground surfaces and proved satisfactory at the temperatures employed.

The apparatus was calibrated by introducing known volumes of dilute glycol solutions into the reaction cell with a micro-syringe and sampling in the normal manner.

Molecular weights of amorphous polyethylene terephthalate may be calculated from intrinsic viscosities measured in solutions of the polymer in *o*-chlorphenol by the relation[7]

$$[\eta] = 1{\cdot}7 \times 10^{-4} \bar{M}_n^{0{\cdot}83} \tag{5}$$

in which $[\eta]$ is expressed in dl g^{-1}. However, polymer which has been held at the temperatures employed for polymerization rapidly becomes highly crystalline, and is then insoluble in *o*-chlorphenol (OCP). To overcome this difficulty, the relative viscosities of one per cent solutions (one per cent RV) of the polymer in dichloracetic acid (DCA) were determined, and converted into intrinsic viscosities in *o*-chlorphenol by the empirical relation[5]

$$[\eta]\,(\text{OCP}) = 0{\cdot}715\ (1\%\ \text{RV in DCA}) - 0{\cdot}666 \tag{6}$$

which was obtained by the simultaneous determination of $[\eta]$ in OCP and the one per cent RV in DCA of amorphous polymers soluble in both liquids. All subsequent references to $[\eta]$ should be taken to mean the value in OCP estimated from equation (6).

The molecular weight distribution of polymer prepared in the solid phase differs from that of 'normal' polymer as already discussed (§ 1), and it is important to know whether the process of dissolving the polymer in dichloracetic acid at elevated temperatures leads to re-equilibration of 'abnormal' polymer. To test this, two polymers with intrinsic viscosities 0·45, 0·85, respectively, were blended to give a measured initial $[\eta]$ of 0·66. The solutions were held at 100°C for various periods. A standard melt-polymerized sample with $[\eta] = 0{\cdot}66$ was dissolved in DCA and held at the same temperature for comparison. Results[5] are shown in *Table 1*.

Table 1. Intrinsic viscosities of blended polymer

Time at 100°C, min	*Intrinsic viscosity of blended polymer*	*Intrinsic viscosity of standard polymer*
30	0·655	0·660
60	0·650	0·650
120	0·620	0·625

Thus polymer which is known to have an abnormal molecular weight distribution behaves in the same way as normal polymer (the decrease in intrinsic viscosity with normal polymer may be ascribed to slow degradation). It seems, therefore, that intrinsic viscosity measurements may be made on abnormal polymer without re-equilibration occurring, although, of course, the relation between intrinsic viscosity and molecular weight may no longer apply.

2.2.3. Differential thermal analysis—Differential thermal analysis (DTA) curves were obtained on a DuPont model 900 thermal analyser, made available by courtesy of I.C.I. Ltd, Petrochemical and Polymer Laboratory.

2.2.4. Other techniques—A conventional high vacuum system was used, pressures of less than 10^{-5} mm Hg being attainable.

Other techniques are described in § 3 as the need arises.

3. RESULTS

The polycondensation reactions in DHET and in polymer are considered separately.

3.1. Solid phase reaction of DHET

3.1.1. Polymerization in the absence of catalyst—Polymerization in the solid phase is frequently accompanied by a loss of birefringence (see, for example, ref. 1). Crystals of DHET, recrystallized either from the melt or from aqueous solution, are birefringent and some preliminary investigations of the solid phase polymerization of DHET were made by studying its birefringence. The birefringence of crystals prepared in either manner was found to disappear in about thirty minutes if the sample was heated on a microscope slide to 105°C under vacuum. No change in birefringence was observed either when the crystals were heated at atmospheric pressure, or when they were placed in vacuum without heating, and this indicated that the loss in birefringence was indeed a result of polymerization. However, from later quantitative measurements of the rate of polymerization, it is clear that very little polymerization could have occurred during the times employed in the above experiments. The reason for the loss of birefringence is still not understood, although it is possible either that very small amounts of chemical reaction can greatly disorder a crystalline system, or that the crystalline layers become very thin as a result of the sublimation of DHET under vacuum.

Heating the DHET on the microscope slide under vacuum for much longer periods (of the order of hours at 105°C) resulted in the formation of a material which had a melting point considerably higher than that of the monomer (*ca*, 150°C). It was thought that melting point determination might, indeed, be a suitable method for studying the course of polymerization. However, it appears that the material formed is soluble in the molten monomer, so that no significant change in melting point occurs until a considerable fraction of the monomer has been consumed.

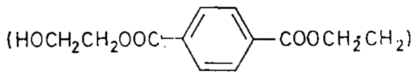
On a larger scale, DHET without catalyst (2 g) was heated for 240 h at 103 °C at pressures not greater than 10^{-4} mm Hg. The reaction was carried out in a sublimation vessel, with the collecting finger cooled by liquid nitrogen. Thus unreacted monomer was slowly removed from the reaction mixture so that, in the end, only reacted material remained behind. The melting point of the product was about 170 °C, and 300 mg remained in the reaction vessel.

Elemental analysis of the monomer and of the product was carrried out with results shown in *Table 2*. The melting point of the product corresponds fairly well with that of dimer (172° to 175 °C), and the elemental analysis for carbon would indicate that the product is approximately dimeric. Hydrogen analyses may be too high as a result of water absorption by the sample, but the good agreement between the experimental and calculated values for the monomer suggests that the figures for the product may also be reliable.

Table 2. Elemental analysis of monomer and product, percentage basis

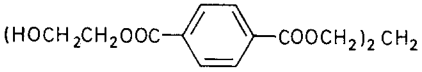
	Monomer		*Product,*	*Dimer,*
	found	*calc.*	*found*	*calc.*
C	56·43	56·69	59·43	59·19
H	5·54	5·51	5·33	4·93

A minute quantity of liquid could be condensed out during reaction of the (well-dried) DHET. This had a melting point of about −3 °C, which suggests that it was substantially water, and not glycol. Elimination of water, with the formation of an ether link, would result in a dimer of structure (II)



(II)

Although this gives better agreement with the elemental analysis no other evidence for such a structure was obtained. X-Ray diffraction studies showed the product to be dimer or trimer, and, although there was an unexplained reflection at $\theta = 10{\cdot}3$, there was no other unusual feature. Infra-red spectroscopy yielded substantially the same result, with no absorption by ether linkages. Hydrolysis of the sample, followed by gas phase chromatographic analysis of the product, showed very little diglycol ($HOCH_2CH_2{-}O{-}CH_2CH_2OH$). Elimination of both water and formaldehyde gives the dimer (III)



(III)

corresponding to C = 60·0, H = 5·2 per cent. These values are in quite good agreement with the experimental ones, but it must be stressed that no further evidence for this structure has yet been obtained. It may, however, be feasible to detect propylene glycol in the hydrolysis products.

Experiments to determine the rate of reaction, with the apparatus described, show that the rate of glycol evolution is very small compared with the rate in catalysed systems. However, moderate quantities of a more volatile material (other than water) are formed, which has not, so far, been identified. It appears that this volatile substance is liberated at about the same rate in catalysed reactions, and we suggest that the reaction which occurs in the absence of catalyst is independent of the catalysed reaction, and proceeds at the same rate whatever the catalyst concentration.

At any rate, it is clear that the uncatalysed reaction is not a straightforward polycondensation process, and further studies have been mainly on the catalysed reactions.

3.1.2. Polymerization of DHET catalysed by titanium tetrabutoxide [Ti (OBu)$_4$]—The rate of glycol evolution from 2 g samples of DHET containing one per cent by weight of Ti (OBu)$_4$ was initially determined by the periodate method described in § 2.2.2.

At first a certain amount of glycol was rapidly evolved (this is probably the glycol produced during the introduction of the catalyst to the molten DHET), after which the rate of glycol production was substantially independent of the time (up to about 5 h). *Table 3* shows the rate of glycol formation at different temperatures.

Table 3. Rate of glycol formation from DHET containing Ti(OBu)$_4$ (1% w/w)

Average temperature, °C	100·5	103·5	104·5	105·0	105·5
10^6 Rate of polymerization mole l^{-1} s^{-1}	1·3	7·4	9·6	9·7	18·6

Only small quantities of glycol are formed in relatively large time intervals, and the transfer of the glycol could easily lead to errors in estimation: the gas chromatographic technique was used for all subsequent rate determinations.

The high sensitivity of the chromatographic method makes possible rate determinations without significant conversion of the monomer. At the highest rate measured ten per cent conversion to dimer would occur in about 100 minutes; the sample was reacting at this rate for 15 to 20 minutes. In general, reaction rates and conversions were much lower, and, in these experiments, the same sample of DHET was used at all temperatures, thus eliminating variation of physical parameters, such as particle size and surface area, between samples. As in the earlier experiments, it was found that relatively large amounts of glycol were released at first. No rate measurements were accepted, therefore, until the rate of glycol evolution remained constant over a series of determinations.

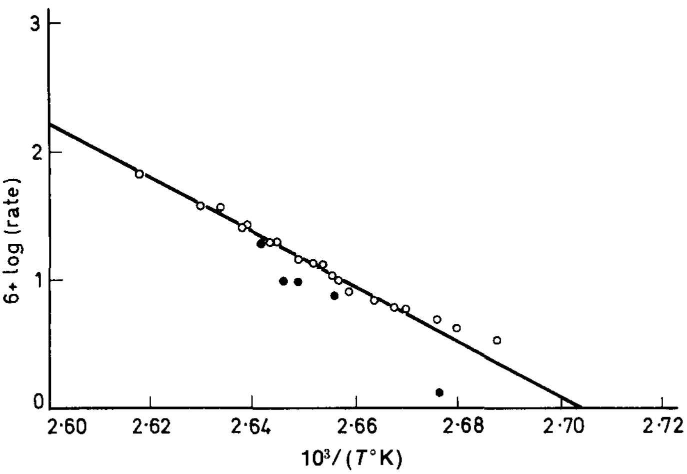


Figure 2—Arrhenius plot for polymerization of DHET in the solid phase. Catalyst $Ti(OBu)_4$, 1% w/w. ○ determinations by gas chromatography. ● determinations by periodate method

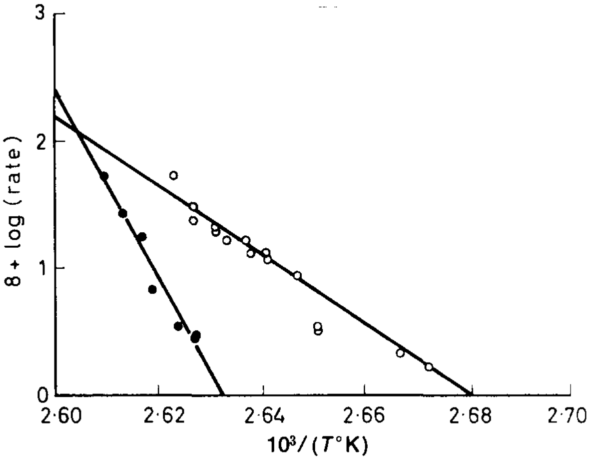


Figure 3—Arrhenius plots for polymerization of DHET in the solid phase. Catalyst $Ti(OBu)_4$. ○ 0·1% w/w; ● 0·01% w/w

In *Figures 2* and *3* the logarithms of the rates of glycol evolution are plotted against the reciprocals of the absolute temperatures for three catalyst concentrations [1 per cent, 0·1 per cent and 0·01 per cent $Ti(OBu)_4$]. In each case an approximately linear graph is obtained. *Figure 2* also displays the rates shown in *Table 2*, obtained by the periodate method. *Table 4* shows the apparent activation energies obtained from *Figures 2* and *3* if the rates are assumed to obey the Arrhenius law.

It was of interest to determine the activation energy for the polymerization of DHET just above its melting point. *Table 5* shows the rate of

Table 4. Apparent activation energies for the solid-phase polymerization of DHET

$\%Ti(OBu)_4$ w/w	1	0·1	0·01
Activation energy, kJ mole^{-1}	410	526	1405

glycol evolution at different temperatures, and *Figure 4* is an Arrhenius plot of these results.

Table 5. Rate of polymerization of molten DHET containing $Ti(OBu)_4$, 0·1% w/w

Temperature, °C	109·6	111·2	113·0	114·2	117·7
Rate × 10^6 mole l^{-1} s^{-1}	1·3	1·6	1·7	2·1	2·6

The nearly linear plot of *Figure 4* gives an activation energy of 117·5 kJ mole^{-1}. This may be compared with the values between 92 and 115 kJ mole^{-1} obtained in a much higher temperature range[5,8] by a different technique, and it may be concluded that the reaction in the melt is identical in the two temperature ranges.

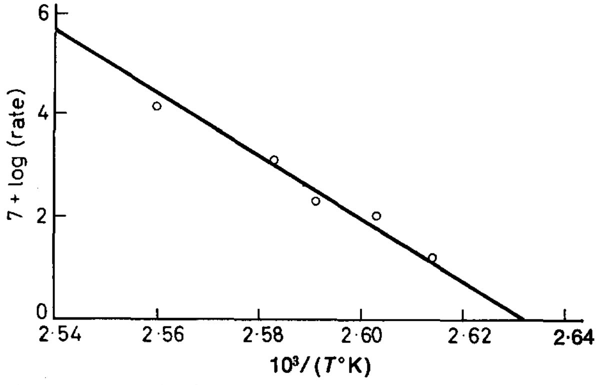


Figure 4—Arrhenius plot for melt polymerization of DHET. Catalyst $Ti(OBu)_4$ 0·1% w/w

After heating DHET in the presence of 1 per cent Ti $(OBu)_4$ for 24 hours at 103 °C under vacuum, the product has a melting point of about 150°C, although there are fractions melting above and below this temperature. Extraction with cold acetone leaves a residue which melts at about 170°C, and is almost certainly dimer.

3.1.3. Differential thermal analysis of DHET—Thermograms were obtained for purified DHET, and for the DHET–catalyst systems with 0·01 per cent Ti $(OBu)_4$ and with 1 per cent Ti $(OBu)_4$, in a temperature range including the melting region. The curves are shown in *Figure 5.*

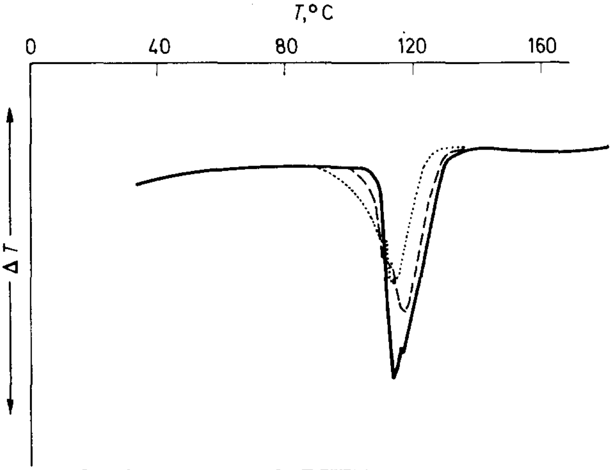


Figure 5—Thermogram of DHET: ——— pure DHET; - - - - - DHET+Ti(OBu)$_4$ 0·01% w/w; . . . . . DHET+Ti(OBu)$_4$ 1% w/w. Rate of heating 20 deg. C/min; sample weight *ca.* 20 mg

3.2 Solid phase reactions of polymer: kinetics with 'low' molecular weight polymer

A relatively high rate of glycol evolution is required for the accurate determination of rates of reaction. For this reason we generally employed relatively low molecular weight polymer $[\eta]=0{\cdot}24$ for kinetic measurements, since high rates might be expected with high end-group concentration. Experiments in which polymer of higher molecular weight was used are described separately (§ 3.3); the present section is concerned with polymers with $[\eta]=0{\cdot}24$ except where otherwise stated.

A typical set of experimental points for the rate of glycol evolution as a function of time is shown in curve (a) of *Figure 6;* curve (b) shows that $\omega^{-\frac{1}{2}}$ is an approximately linear function of time, as expected from equation (4).

3.2.1. The activation energy of the solid phase reaction—The rate constant was measured by the glycol evolution method described above at a series of different temperatures in the range 170°C to 250°C. Line (a) of *Figure 7* shows that the rate constants obey an Arrhenius law in which the activation energy is 81·5 kJ mole^{-1}.

The rate constants were also determined at two temperatures for a different low molecular weight sample $[\eta]=0{\cdot}297$, with beads of particle size 14 to 25 BSS mesh. At 206°C, $k=3{\cdot}81\times10^{-3}$ mole^{-1} l. s^{-1} and at 240°C, $k=14{\cdot}5\times10^{-3}$ mole^{-1} l. s^{-1}. From these two results the calculated activation energy is 85·5 kJ mole^{-1}.

The rate constants determined above lie between 10^{-4} and 10^{-2} mole^{-1} l. s^{-1}, approximately, values which seem abnormally high when compared with those obtained at similar temperatures in the melt[5,8]. The possibility arises that the present results are too high (*i*) as a result of occluded glycol in the starting material, or (*ii*) because of hydrolysis by

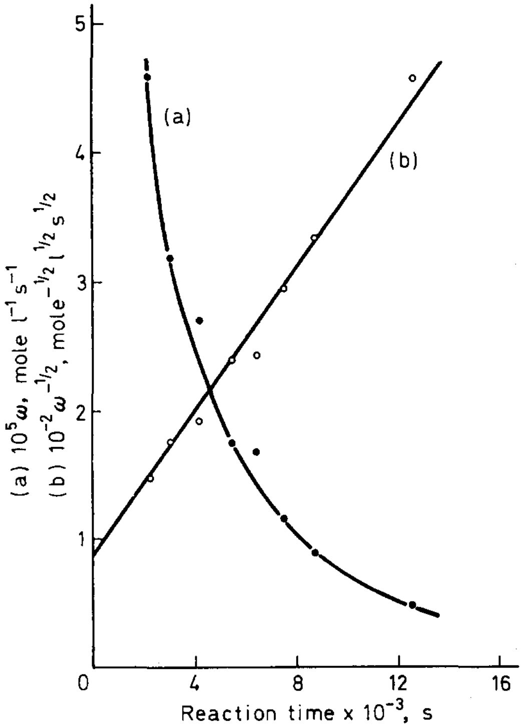


Figure 6—Solid phase polymerization of low polymer ([η]= 0·24). Temperature 180°C. (a) ω versus reaction time; (b) $\omega^{-\frac{1}{2}}$ versus reaction time

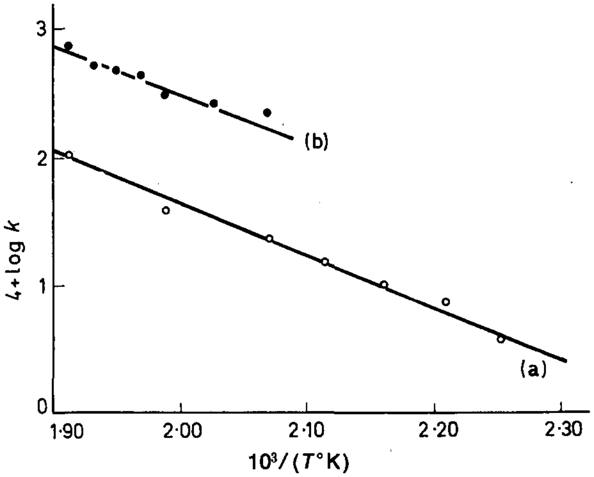


Figure 7—Arrhenius plot for solid phase polymerization. (a) initial polymer [η]=0·24; (b) initial polymer [η]=0·675

water. The first hypothesis was tested by refluxing the polymer first with alcohol and then with acetone; no change in rate was detected. However, since the washing temperature with these solvents is lower than the glass transition temperature of the polymer it is possible that *occluded* glycol could still be trapped within the polymer. We therefore refluxed the polymer with methyl ethyl ketone. Polymer washed in this way gave rates of glycol evolution somewhat lower than previously determined, although the rate constants themselves were unaffected. It should be noted that the decrease in rate of glycol evolution cannot be ascribed to the occurrence of polymerization during the high temperature washing process, since there is no evidence for a change in the intrinsic viscosity of the polymer after washing. We tested hypothesis (ii) by the addition of several millilitres of water to a reaction mixture; no significant change in rate occurred.

3.2.2 *Rates of reaction determined by intrinsic viscosity changes*—A series of samples was polymerized for different times over a period in which the rate constant had been measured and was known to be constant, and the intrinsic viscosities of these samples were measured; the end-group concentrations were then calculated from the molecular weights with the aid of (6).

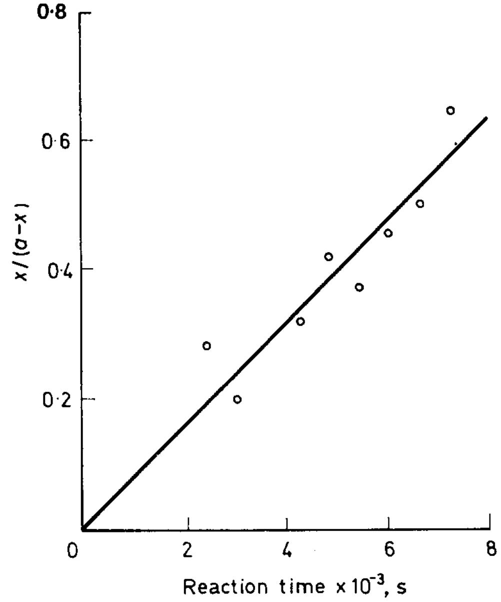


Figure 8—Solid phase polymerization of low polymer ($[\eta]=0{\cdot}24$) at 180°C. $x/(a-x)$ as a function of reaction time. Concentrations were determined from measurements of $[\eta]$

Figure 8 shows a plot of $x/(a-x)$ against t which is as near to a straight line as might be expected for this kind of experiment. The slope (ak) is $0{\cdot}8\times10^{-4}$ s^{-1} and since $a=0{\cdot}480$ mole l^{-1}, $k=1{\cdot}7\times10^{-4}$ mole^{-1} l. s^{-1}. This value is smaller by a factor of about four than that measured by glycol evolution. The origin of this discrepancy will be clear from the discussion in § 1; the matter is considered further in § 4.2.

An attempt to measure the end-group concentrations directly, by titration after treatment with succinic anhydride, so that the molecular weight/intrinsic viscosity relationship need not be used, was not successful. Although the concentration of hydroxyl ends was approximately that expected for a polymer of initial $[\eta]=0{\cdot}24$, the scatter was greater than the change in concentration over a three hour polymerization period.

3.2.3. The effect of particle size—The importance of glycol diffusion, mentioned in § 1, is illustrated by the results described in this and the following section.

By using sieved samples of the starting polymer it was possible to investigate the variation of rate of polymerization with particle size. Although fairly large scatter was obtained for these results (probably because the sieving operation is inefficient, and different samples contain different proportions of particle sizes within a grade) it was possible to obtain consistent results by taking averages of four or five experiments. It immediately became apparent that while the rate constant for the reaction was not significantly affected by changes in particle size, yet the actual rate increased with decrease in particle size. The results are shown in *Table 6*; the rate is expressed as the rate after 50 minutes.

Table 6. Variation of rate and rate constant at 180°C with particle size

Mesh size	*10^4k, mole^{-1} l. s^{-1}*	*10^5 rate at 50 minutes mole l^{-1} s^{-1}*
< 36	7·4	2·2
36–52	6·6	4·8
52–72	5·2	6·5
> 72	7·1	8·7

3.2.4. The effect of the thickness of the polymerizing layer—Since liberated glycol must be removed from the reaction zone, it is possible that the rate of reaction might be dependent on the thickness of the layer of sample. To test this hypothesis, samples of 1, 2 and 3 g of 36–52 mesh polymer were placed in the conical reaction flask, thus giving considerable variation in sample depth. In this series of experiments three separate determinations were made for each sample size, at 180°C. Typical results are presented in *Table 7.*

Table 7. Variation of k with sample size $T=180$°C

Run	*1g*	*2g* *10^4k, mole^{-1} l. s^{-1}*	*3g*
1	6·6	4·3	4·5
2	9·0	6·0	3·6
3	7·5	4·0	3·7
Mean	7·7	4·8	3·9

Although the scatter is significant (probably again a result of variation in particle size), there is clearly a decrease in rate as the sample thickness is increased.

3.2.5. The effect of crystallinity—We prepared highly crystalline polymer in two ways. The first method employed heat treatment of the sample; the polymer was held under dried nitrogen at a pressure just below atmospheric, heated to 230°C and allowed to cool overnight. It also proved possible to recrystallize polyethylene terephthalate from dichloracetic acid, particularly if a non-solvent (e.g. methanol) were present in small proportion. The rate constant for polymerization at 180°C was found to be $7{\cdot}7 \times 10^{-4}$ mole^{-1} l. s^{-1} and $8{\cdot}7 \times 10^{-4}$ mole^{-1} l. s^{-1} in two experiments with a heat-treated sample of particle size >72; the rate constant for the untreated sample is $7{\cdot}1 \times 10^{-4}$ mole^{-1} l. s^{-1} (§ 3.2.3) so the heat treatment described appears not to affect the rate of polymerization to any great extent. On the other hand, polymer recrystallized or reprecipitated from dichloracetic acid polymerizes not at all. It later became apparent that this result arose from the loss of catalyst from the polymer during the recrystallization process, since no antimony could be found by X-ray fluorescence analysis in the recrystallized polymer. Addition of a little antimony oxide to the powdered, recrystallized polymer once again allowed polymerization to proceed, although at a reduced rate, presumably as a result of the highly heterogeneous distribution of catalyst and polymer molecules.

3.2.6. Reactions other than ester interchange—While it is clear from the gas phase chromatographic peaks that the major organic product eliminated during reaction is glycol, yet the flame ionization detector does not detect water vapour. It seemed desirable, therefore, to establish how much water was evolved during reaction. Since the sample may in any case be moist, we dried the polymer carefully before the experiment; nevertheless it should be realized that the conditions for efficient drying are the same as those for polymerization, so any water detected may be merely moisture which has been efficiently held in the solid. However, the total amount of water liberated from the sample at once places an upper limit on the amount of water formed by chemical reaction, and we therefore determined the water evolved at 180°C and at 220°C. The products of reaction were condensed out in a trap over a known period; the trap was sealed off and the water estimated by the method of Karl Fisher (see ref. 9). Glycol formation over the condensation period was calculated from the rate/time curves (already obtained for the various temperatures, i.e. curves such as (a) of *Figure 6*). *Table 8* presents the results obtained, together with the water evolution expressed as a molar percentage of the total water and glycol.

Table 8. Formation of water during reaction

Temperature, °C	*Duration of experiment, min*	*10^4 weight of water, g*	*10^4 weight of glycol, g*	*Mole % of water*
180	60	5·28	36·0	33·9
180	90	6·75	46·5	32·4
180	120	7·85	52·2	34·0
220	60	3·19	88·6	11·0
220	90	4·81	125	11·6

Thus it seems that even if all the water is produced by chemical reaction, the bulk of the polymerization proceeds by ester interchange, particularly at the higher temperature. It is probable that at least some of the water we observe is moisture strongly held within the polymer, although there seems to be no significant dependence of the percentage of water in the reaction products on the duration of the experiment, which suggests that all but the trapped moisture has been removed from the polymer before an experiment begins.

3.3. Solid phase reactions of polymer: kinetics with polymer of higher molecular weight

The polymer used had $[\eta]=0{\cdot}67$ initially and was powdered and sieved. Many of the kinetic features displayed by the lower polymers are also found with the high polymer. In particular, the rate constant appears to be independent of the particle size, although the rate of reaction is greatly increased by a decrease in particle size (cf. § 3.2.3). However, with the high polymer, the rates of polymerization with the larger particle sizes are too small for accurate measurement, so that the lack of dependence of rate constant on particle size can only be demonstrated qualitatively. For other experiments with the high polymer we employed samples with particle size in the range 72–100: these polymerized sufficiently fast for our purposes.

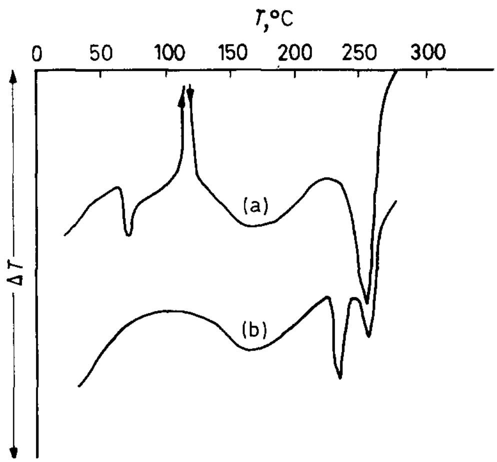
The activation energy of the polymerization reaction was measured for the polymer in the temperature range between 210°C and 250°C; the experimental points for the rate constants at the several temperatures are shown on line (b) of *Figure 7*. From this figure the activation energy is found to be 73·6 kJ mole^{-1}. It should be noted that the rate constants are even higher than those found in the solid phase for low polymer.

The effect of chain orientation on the polymerization may be investigated by the use of drawn and undrawn samples of fibre spun from the high-molecular weight polymer. In order to minimize the influence of surface area, we spun yarns of two diameters, and stretched the thicker one, so that the final diameters of the drawn and undrawn yarns were identical. At 250°C the rate constants for the drawn and undrawn fibres were identical with the value 6×10^{-2} mole^{-1} l. s^{-1}, approximately; this value may be compared with that obtained for the powdered polymer at the same temperature ($7{\cdot}7\times10^{-2}$ mole^{-1} l. s^{-1}).

3.4. Differential thermal analysis of solid-phase-polymerized samples

The amorphous polymer used as the starting material in our experiments possesses normal thermal properties. Thermograms show heat absorption in the glass transition and melting regions, and heat emission during crystallization. However, differential thermal analysis of certain of our solid phase polymerized samples shows rather unusual features. As would be expected, the glass transition and crystallization peaks no longer appear, but in addition to the normal melting peak, a second peak is seen. This is shown in *Figure 9* for a starting polymer of $[\eta]=0{\cdot}24$, polymerized in the solid phase at 180°C. Its magnitude increases and it shifts to higher temperatures with increasing time of polymerization. Similar, but not identical, behaviour is observed with polymer of higher initial molecular weight; in this case the second peak appears at higher, and not lower, temperatures than the normal melting point. In either case, if the sample be taken to temperatures beyond the melting point, cooled, and the thermogram obtained a second time, one peak only appears. Holding the temperatures just below

Figure 9—Thermograms of polyethylene terephthalate. (a) Amorphous polymer, $[\eta]=0{\cdot}24$. (b) After solid-phase polymerization at 180°C for 72 h. Rate of heating 20 deg. C/min; sample weight *ca.* 20 mg



the point of appearance of the second (low temperature) peak obtained from starting polymer of low $[\eta]$ results in the disappearance of the normal melting peak and a shift to higher temperature of the second peak.

4. DISCUSSION

4.1. *Dihydroxyethyl terephthalate*

There seems little doubt that DHET does polymerize in the solid phase, even at temperatures as low as 100°C. Glycol is evolved in the catalysed reaction, although the very slow polymerization reaction in the absence of catalyst appears not to involve the loss of glycol.

The concept of 'activation energy' is probably not particularly meaningful when applied to solid systems such as the present one, even though the values obtained for it may be a satisfactory way of describing the change of rate with temperature. To emphasize the way in which the rate of the solid phase reaction increases rapidly as the melting point is approached, we have plotted the rates for the reaction catalysed by 0·1% $Ti(OBu)_4$ as a direct function of temperature in *Figure 10*. There is no apparent discontinuity in rate between the two phases. The exceedingly large apparent activation energies (*Table 4*) could arise from a correspondingly large temperature dependence on the physical constraints imposed by the solid system; these would disappear when the DHET became molten, the activation energy reverting to the normal value for melt polymerization. Although the exact nature of the constraints is not at present established, they probably affect the mobility of the monomer, the catalyst, or the glycol formed, or a combination of these. Crystal defects and their mobilities may well be of importance, since the catalyst may be concentrated into defect regions, and the reaction may only be able to proceed at all in areas where the crystal lattice is not too well defined. Indeed it would appear from *Figure 10* that the solid-phase polymerization of DHET is extremely slow except in the pre-melting region.

The increase in apparent activation energy with decreasing catalyst concentration could result from a modification (and weakening) of the constraining forces as the catalyst is introduced into the DHET lattice; this

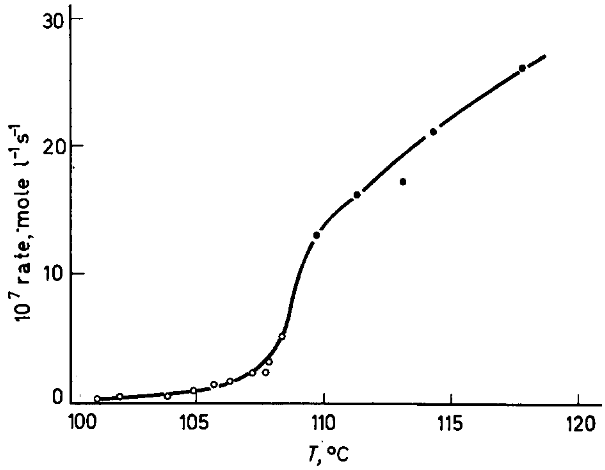


Figure 10—Rate of polymerization of DHET as a function of temperature. Catalyst $Ti(OBu)_4$ 0·1% w/w. ○ solid-phase ● melt

can also be understood as extending the pre-melting region. Alternatively, if the limiting factor is the mobility of catalyst within the solid, it might be that the larger the amount of catalyst, the less mobility is required for it to be effective, and shorter range forces become increasingly important.

The differential thermal analysis data presented in § 3.1.3 seem to confirm the hypothesis that the variation of mobility with temperature is related to the amount of catalyst present in the DHET. Premelting or softening appears on the thermograms as a spreading out of the heat absorption associated with the melting; it can be seen qualitatively that the onset of melting becomes progressively less sharp and its temperature lower, as the concentration of Ti $(OBu)_4$ in the DHET increases from zero to one per cent (*Figure 5*).

4.2 *Polymer*

The activation energies measured for the solid phase polymerization lie between about 71 and 84 kJ mole^{-1}, and are appreciably lower than that for melt polymerization of DHET (117·5 kJ mole^{-1}, § 3.1.2. *Figure 4*), or for polymerization at much higher temperatures[5, 8] (92–115 kJ mole^{-1}). Such a result is to be expected if the rate of diffusion of glycol through the solid or the prevailing molecular mobility[1c] determine, at least partly, the rate of reaction, since neither property is likely to be associated with a large effective activation energy in these systems. The near-normal activation energy contrasts sharply with the results obtained for DHET, in which the molecular mobility increases very rapidly in the premelting region.

We showed in § 3.2.3 that the particle size influences the rate of reaction but has little effect on the rate constant. If the diffusion of glycol out of each polymerizing particle were of importance, the rate of reaction would be expected to increase as the particle size decreases. However, this should be reflected as an increase in both rate and rate constant; the fact that the rate alone increases with decrease of particle size indicates a more complex situation. The straightforward kinetic interpretation to be placed on an increase in rate with a steady rate constant is, of course, that the concentration of reactant has increased. If the concentration of end groups is increased by decreasing the particle size, it further follows that the end groups concerned with reaction must all be near the surface of the particle. Any glycol liberated below the surface of the particle must diffuse through the mass of polymer to escape at the surface. Indeed, it might be thought unlikely that glycol would ever reach the surface, since the depolymerization reaction [the reverse reaction in equation (1)] has an opportunity to occur on every collision between glycol and a polymer molecule. On this picture, it is only the glycol liberated close to the surface of the particle which is able to escape before undergoing the back reaction, so that the polymerization is confined to a relatively narrow zone near the surface.

Although it is not possible at this stage to give a comprehensive interpretation of the results of our differential thermal analysis on the polymer obtained in the solid-phase reaction, yet it seems clear that the material shows considerable heterogeneity (§ 3.4). Similar thermal behaviour for solid-phase-polymerized samples has been reported by other workers[14, 15]. Evidence of a different kind which supports this view has already been described in § 1. We may also note that Mifune's observations[8] indicate that the ratio $\overline{M}_w/\overline{M}_n$ is different for polymers prepared in the molten and solid phases, but they do not prove that the distribution in the product of the solid-phase reaction is abnormal, since there is disagreement in the literature about the details of the distribution in the polymer prepared in the melt[10–13].

The differences between the rates of polymerization determined from glycol evolution and those obtained from measurements of $[\eta]$ (§ 3.2.2) might be expected to be smaller at short reaction times, since in these circumstances the molecular weight distribution should be disturbed to a relatively small extent. Values of k at 180°C calculated with aid of (3) from end-group concentrations estimated from $[\eta]$ [equation (6)] are shown in *Table 9* for the times for which measurements of $[\eta]$ were available. The values of ω were obtained from the appropriate plot of $\omega^{-\frac{1}{2}}$ against t. The rate constants calculated in this manner decrease with time; the value at

Table 9. Values of k calculated from rates of glycol evolution and end-group concentrations estimated from $[\eta]$

$10^{-3}t$, s	$10^5\omega$, mole l^{-1} s^{-1}	$a-x$, mole l^{-1}	$10^4k = \frac{10^4 w}{(a-x)^2}$ mole^{-1} l. s^{-1}
0	12·34	0·480	5·37
2·4	4·16	0·374	2·97
3·0	3·38	0·400	2·11
4·2	2·40	0·364	1·82
4·8	2·10	0·338	1·84
5·4	1·80	0·350	1·47
6·0	1·55	0·330	1·43
6·6	1·37	0·320	1·35
7·2	1·23	0·302	1·35
7·8	1·08	0·292	1·25

zero time is, in fact, quite close to that calculated directly from the rate of glycol evolution [approximately $5{\cdot}3 \times 10^{-4}$ mole^{-1} l. s^{-1} at 180°C from the results in *Figure 6*].

A further complication arises if glycol is not the only product of reaction. If water is eliminated by the interaction of carboxyl and hydroxyl ends, an increase in $[\eta]$ would occur and the overall rate of polymerization would be greater than that expected from the determinations of the rate of glycol evolution alone. The present results, in fact, show the reverse trend; and we have shown that in any case direct esterification is of relatively minor importance (§ 3.2.6).

The rate constants measured by either method are, however, greater than those expected from extrapolation of melt polymerization kinetics[8]. The observation that the rate in the melt is lower than that in the solid at the same temperature is completely unexpected and can be explained only by the postulation of an effect leading either to concentration or to favourable orientation of the end groups in the solid, although straightforward chain orientation does not itself lead to any considerable increase in rate of reaction (§ 3.3). It could be argued that crystallization during the course of polymerization might lead to a concentration of end groups within the remaining amorphous regions of the polymer. This would increase the apparent rate constant, since the rate constant is calculated on the basis of a random distribution of end groups through the total volume. The use of highly crystalline starting polymer has virtually no effect on the rate constant (§ 3.2.5), but this does not argue against the concentration process described, since it is known that primary crystallization occurs very rapidly (within a few minutes) at the temperatures we used for polymerization[16]; in fact, therefore, all the polymers used are probably highly crystalline.

Observations made in melt polymerization systems do, however, show certain anomalous features which may have some relevance to the problems of the increased rate constants observed in the solid phase. Challa[8] reports that the reactivity of monomer is less by a factor of about two than that of polymer, and that the rate of polymerization increases with an increase in conversion. It is demonstrated that the energy of activation for the reaction of monomer is virtually identical with that for polymer, and that the entropies of activation are about -41 e.u. and -38 e.u. [1 e.u. = $4{\cdot}184$ J (deg. K)$^{-1}$ mole $^{-1}$] in the two cases respectively; Challa suggests that the monomer loses more entropy on entering into the transition state than do the longer molecules. A similar argument could be advanced to account for the relatively high rate constants observed in the solid-phase reaction, but its validity would depend critically on the details of the model assumed.

In conclusion, then, we may say that polyethylene terephthalate undergoes polymerization in the solid phase, and the rate constants determined for the reaction are considerably higher than anticipated from extrapolated melt polymerization data. The polymerization is confined to a layer near to the surface of each particle and appears to lead to an inhomogeneous polymer of abnormal molecular weight distribution.

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REFERENCES

[1] For reviews see (a) BRUK, M. A. *Usp. Khim. Polim.* 1966, 42
(b) TABATA, Y. in *Advances in Macromolecular Chemistry*, Ed. W. PASIKA, Vol. I, p 283. Academic Press: London, 1968
(c) BAMFORD, C. H. and EASTMOND, G. C. *Quart.* 1969, **23**, 271
[2] CHAMBRET, F. *Bull. Soc. chim. Fr.* 1947, 283
OYA, S., TOMIOKA, M. and ARAKI, T. *Kobunshi Kogaku*, 1966, **23**, 415
[3] MIFUNE, A. *J. chem. Soc., Japan*, 1962, **65**, 996
[4] e.g. *U.S. Pat. Nos. 3 075 952 and 3 117 950*
[5] ICI Fibres Ltd. Private communication
[6] HARTLEY, F. D. Private communication
[7] RAVENS, D. A. S. and WARD, I. M. *Trans. Faraday Soc.* 1961, **57**, 150
[8] CHALLA, G. *Makromol. Chem.* 1960, **38**, 123
[9] WELCHER, F. J. *Standard Methods of Chemical Analysis*, 6th ed., p 526. Van Nostrand: Princeton, N.J., 1963
[10] TURSKA, E., SKWARSKI, T. and SZAPIRO, S. *J. Polym. Sci.* 1958, **A30**, 391
[11] KEOPP, H. M. and WERNER, H. *Makromol. Chem.* 1959, **32**, 79
[12] CHALLA, G. *Makromol. Chem.* 1960, **38**, 105
[13] KORSHAK, V. V. *Faserforsch. Textiltech.* 1955, **6**, 241
[14] SCHULKEN JR, R. M., BOY JR, R. E. and COX, R. H. *J. Polym. Sci.* 1964, **C6**, 17
[15] Japanese Pat. Applic. 1964, 10489
[16] HARTLEY, F. D., LORD, F. W. and MORGAN, L. B. *Phil. Trans*, 1954, **A247**, 23