Solid state polycondensation of poly(butylene terephthalate)

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Solid state polycondensation of poly(butylene terephthalate) has been studied under vacuum at 200°C for various particle sizes. The effect of the process on intrinsic viscosity and number of end groups has been examined. The results suggest that the increasing of the number average molecular weight can be explained by a mechanism involving hydroxyl groups, which approach each other by diffusion until a limiting value of their concentration is attained.

INTRODUCTION

Polycondensation in the solid state has been long since studied, in view of its technological interest. In fact, by this process high molecular weights can be attained for various polymers, such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). It may be remembered that high molecular weights, which are often necessary for special uses, cannot be obtained in the molten state.

A survey of the literature, however, shows that this process has been studied until now with the only aim of finding out the best operating conditions, and most of the work has been published in patents[1-6].

Our studies on PBT[7-9] lead us to examine its solid state polycondensation, in order to ascertain and evaluate the effect of the experimental conditions on the process, with the ultimate aim of elucidating the reaction mechanism.

EXPERIMENTAL

Products

A former sample of PBT (denoted as A) was obtained by the usual reaction of *trans*-esterification from dimethyl terephthalate and 1,4-butanediol, in the presence of titanium tetrabutylate as catalyst[7]. This product, analysed by the methods described below, showed the following characteristics: end–COOH content: 61.0 mmol kg^{-1}; end–OH content: 26.0 mmol kg^{-1}; $[\eta] = 0.955$; ash content <200 ppm; Ti content: 58 ppm. Product A was ground and sieved; particles were collected in the following size ranges (average diameters in mm): 0.18–0.075; 0.5–0.3; 1.0–0.5. Chips ($4 \times 4 \times 2.5$ mm) were also considered.

Another sample (denoted as B) was obtained from the former one by partial glycolysis with 1,4-butanediol at about 250°C: 100 g of A were allowed to melt under stirring in a stream of nitrogen; 0.68 g of 1,4-butanediol were afterwards added, and stirring was continued for 30 min. The polymer was dissolved in 1,1,2,2-tetrachloroethane (TCE) at ~110°C, on cooling it was recovered in powder form. Its characteristics were: end–COOH content: 84.6 mmol kg^{-1}; end–OH content: 31.4 mmol kg^{-1}; $[\eta] = 0.602$; ash content <200 ppm; Ti content: 58 ppm. This product was not ground, since it was formed by small, brittle particles (average diameter less than 1 mm).

Polycondensation technique

Samples (about 4 g) after a thorough drying (6 h at 120°C under vacuum) underwent postpolymerization in glass vessels placed in a thermostatic bath at 200°C, under dynamic vacuum ($<7 \times 10^{-5}$ bars) for different times ranging from 4 to 40 h.

End groups analysis

Carboxyl content was determined according to the method of Pohl[10].

The number of end groups (COOH and OH) was obtained with the method of Borman[11], by esterification of the OH end groups with succinic anhydride. After such treatment, samples were purified by standardized procedure, involving four washings with acetone; they were recovered each time by centrifugation and finally dried. They were then dissolved in freshly distilled benzyl alcohol at a temperature not above 160°C and titrated immediately (to prevent precipitation) with a sodium hydroxyde alcoholic solution.

Viscometry

Viscosity measurements were carried out by means of an Ubbelohde viscometer, at 30.00 ± 0.05°C, in a mixture of phenol and TCE 60/40 by weight as a solvent.

Volatile products

Some attempt made to evaluate the amount of volatile products showed that weight losses are quite small. However, some material was observed to condense by sublimation outside the high-temperature region of the vessel. Some tests performed with HPLC allowed us to identify terephthalic acid as minor component among other unidentified products.

RESULTS AND DISCUSSION

In principle, when PBT undergoes postpolymerization, the following reactions must be considered:

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Table 1 Experimental data of postpolymerization (T = 200°C)

	Particle size (average diameter) (mm)	Time (h)	Chain end groups[a]		$[\eta]$[b] (dl g^{-1})
			-(COOH) (mmol kg^{-1})	total (mmol kg^{-1})	
Sample *A*	0.18–0.075	0	60.8	87.4	0.955
		4	56.5	63.8	1.066
		8	51.8	59.5	1.10
		24	48.8	56.7	1.16
		40	50.1	61.6	1.17
	0.5–0.3	0	61.3	86.4	0.955
		4	57.1	66.9	1.072
		24	49.7	57.9	1.163
	1.0–0.5	4	55.7	70.3	1.060
		24	50.0	62.8	1.175
	Chips	4	60.0	81.3	1.010
		24	57.3	66.8	1.075
		40	59.7	60.3	1.118
Sample *B*	Powder	0	84.7	116.0	0.602
		4	79.4	82.1	0.730
		24	66.6	73.7	0.796
		40	61.6	66.4	0.802

[a] Reported data are mean values of at least two measurements, actual deviations never exceeding 5%

[b] Data were evaluated by measurements on at least four different concentrations

$$\text{(I)}\quad \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OH} + \sim\!(\mathrm{M})_{n''}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OH} \rightleftharpoons \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{O}-(\mathrm{M})_{n''}\!\sim + \mathrm{HO}-(\mathrm{CH_2})_4-\mathrm{OH}$$

$$\text{(II)}\quad \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OH} + \sim\!(\mathrm{M})_{n''}\!-\mathrm{OH} \rightleftharpoons \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{O}-(\mathrm{M})_{n''}\!\sim + \mathrm{H_2O}$$

$$\text{(III)}\quad \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OOC(C_6H_4)COOH} + \sim\!(\mathrm{M})_{n''}\!-\mathrm{OH} \rightleftharpoons \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{O}-(\mathrm{M})_{n''}\!\sim + \mathrm{HOOC(C_6H_4)COOH}$$

$$\text{(IV)}\quad \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OH} + \sim\!(\mathrm{M})_{n''}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{O}-(\mathrm{M})_{n'''}\!\sim \rightleftharpoons \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{O}-(\mathrm{M})_{n'''}\!\sim + \sim\!(\mathrm{M})_{n''}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OH}$$

$$\text{(V)}\quad \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{O}-(\mathrm{M})_{n''}\!\sim \rightarrow \sim\!(\mathrm{M})_{n'}\!-\mathrm{OH} + \sim\!(\mathrm{M})_{n''}\!-\mathrm{OH} + \mathrm{CH_2{=}CH{-}CH{=}CH_2}$$

$$\text{(VI)}\quad \sim\!(\mathrm{M})_{n'}\!-\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OH} \longrightarrow \sim\!(\mathrm{M})_{n'}\!-\mathrm{OH} + \mathrm{THF}$$

$$\text{where } -(\mathrm{M})- = -\mathrm{O}-(\mathrm{CH_2})_4-\mathrm{OOC(C_6H_4)CO}-$$

Reactions I, II, III and IV may occur both intra- and intermolecularly. In the former case, volatile products and macrocycles may be formed, consequently the decrease of the number of end groups is not accompanied by an increase of the number-average molecular weight. However, these macrocycles can further react with the end groups of neighbouring chains. The molecular weight increases without any decrease of the number of end groups. For these reasons, as soon as an equilibrium concentration of cyclic macromolecules is attained, the intramolecular reactions do not affect either the molecular weight or the number of end groups. However, if the cyclic products are volatile and can continuously evaporate, only a slight decrease of the molecular weight may occur without any decrease in the number of end groups.

If reactions I–IV take place between different molecules, they bring about an increase of the number-average molecular weight and a decrease in the number of end groups, provided that volatile products are formed, and are removed by diffusion. In *Table 1* all experimental results are collected. *Figure 1* shows the effect of postpolymerization on polymer A (average diameter of particles comprised between 0.18 and 0.075 mm) and on B. The remarkable increase of the intrinsic viscosity in both cases finds its counterpart in the strong decrease of the total number of end groups. This decrease can be attributed to the disappearing of the hydroxyl groups, since carboxyl groups show a slower decrease.

Previous investigations[7–9] enable us to predict that reactions V and VI in this temperature range have little effect on the number of COOH groups, because of the low value of k_V and (for reaction VI) the small amount of OH end groups in our samples. Therefore, the nearly constant number of COOH groups cannot be ascribed to opposite effects arising from reactions V, VI and II; on the other hand terephthalic acid has been identified in small amounts among the volatile products. It may arise from reaction III or from reaction V during the previous polymerization process in the molten state. Consequently, the molecular weight increase is mainly related to the presence of OH groups, i.e. it depends mainly upon reaction I. Furthermore, the intrinsic viscosity tends to an upper limit when hydroxyl content tends to a minimum value. This is true for both samples, in spite of their different carboxyl and hydroxyl contents. While for *A* and *B* the intrinsic viscosity tends to different limits, the number of OH groups tends nearly to the same limit.

A model of mechanism for the increasing of molecular weight may be proposed, based on the occurrence of reaction I by a diffusive rearrangement of the hydroxyl groups. Such a process is hindered as soon as a limiting value in the concentration of these groups is attained. Carboxyl groups are perhaps less mobile in which case, direct esterification is unfavoured. All reactions take place generally in the amorphous regions[6], where the highest concentration of end groups is likely to be found. Conclusions of the same kind may be drawn from *Figure 2*. Here the effect of different particle sizes on the

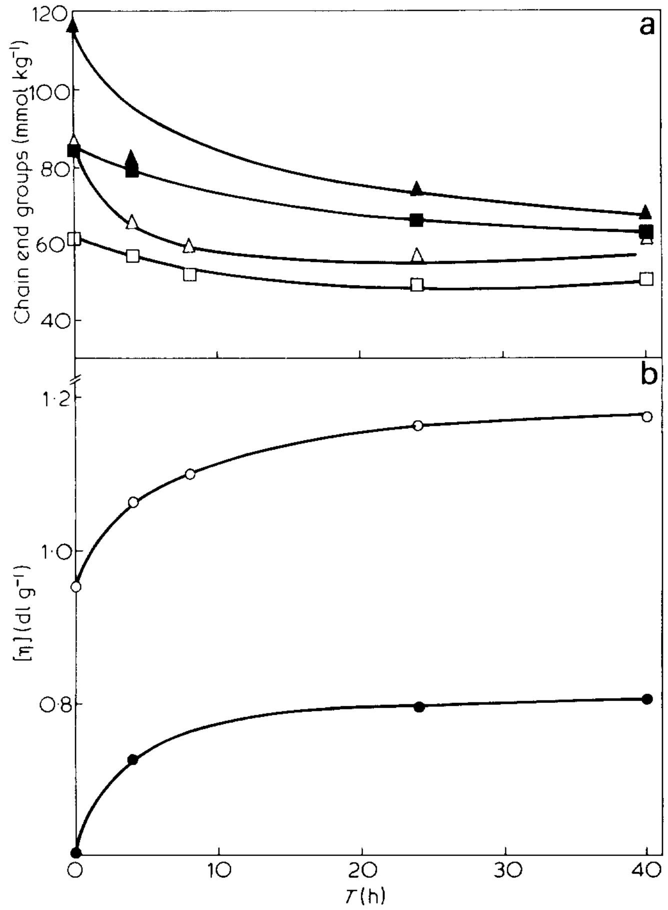

Figure 1 (a) End groups at various times of polycondensation. Sample *A*: △ total end groups, □ carboxyl end groups; sample *B*: ▲ total end groups, ■ carboxyl end groups. (b) Intrinsic viscosity at various times of polycondensation. Sample *A* ○; sample *B* ●

parameters under examination are shown. The intrinsic viscosity is almost independent of the particle size (except in the case of chips); the number of COOH end groups follows a similar trend, whereas the number of total end groups undergoes a continuous increase as particle size increases, for a given time of polycondensation. These facts can be explained in terms of a preferential diffusion of glycol and of oligomers having hydroxyl end groups. In this way reversible reactions I, II and IV shift to the right, better than III. For the last reaction more drastic conditions, such as a stream of an inert gas for removing terephthalic acid, are perhaps effective.

From the same Figure, it appears that samples having a different end group content have the same intrinsic viscosity. It may be inferred that the diffusion of oligomers and of 1,4-butanediol from the amorphous regions, although it depends upon the particle size, always take place at a higher rate than reaction I, which is controlled by the diffusive rearrangement of the hydroxyl groups. Therefore the concentration of the smallest oligomers is lower than the equilibrium one. Also, in view of the prolonged times and relatively high temperatures of polycondensation, it is reasonable to suppose that some ester groups can accomodate themselves in the ordered regions as soon as they are formed in reaction I, and leave the equilibrium. Thus, for small particles I becomes a non-equilibrium reaction, and it may be understood why intrinsic viscosity has no relationship with particle size, except for chips.

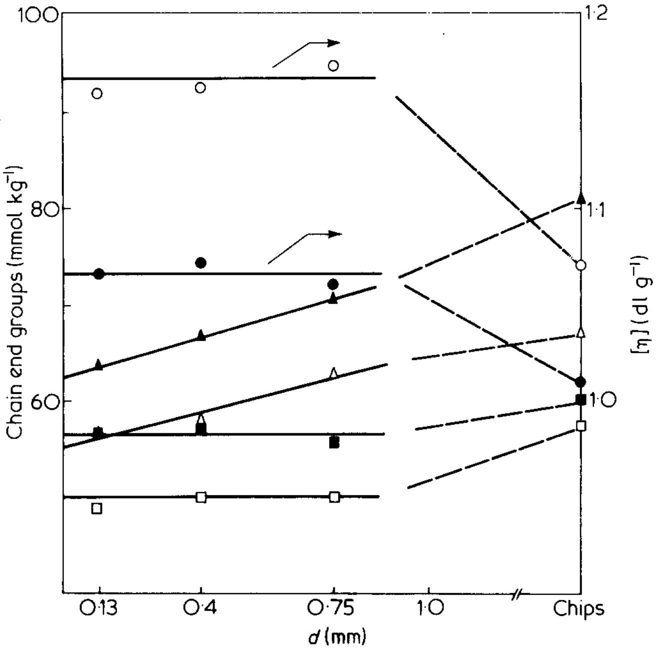

Figure 2 Effect of particle size on various parameters during polycondensation. Intrinsic viscosity: after 4 h ●, after 24 h ○. Total end groups: after 4 h ▲, after 24 h △. Carboxyl end groups: after 4 h ■, after 24 h □

CONCLUSIONS

The results lead us to conclude that in the above specified conditions postpolymerization takes place by a reaction between the OH end groups. It may be inferred that polymers having a low COOH content are especially suitable for this process, although carboxyl groups can arise from reaction VI. In different conditions (e.g. under a stream of nitrogen or other inert gas) higher molecular weights can be obtained by elimination of small molecules containing carboxyl end groups, such as terephthalic acid. In this case other reactions, and in particular reaction III, may become important. This point shall be considered in a further research.

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