# Polycondensation kinetics of poly(ethylene terephthalate) and poly(butylene terephthalate)

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The polycondensation kinetics of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) in the absence of catalyst are found to be of different nature. By means of a set of multiparameter kinetic equations, the kinetic behaviour of PET polycondensation can be simulated numerically; the cause of the disparity is found to be due to the difference in reactivity between monomer and higher oligomers. In the case of PBT, the reactivities of its monomer and higher oligomers are found to be quite similar; however, the reaction kinetics turn out to be too complicated on account of many side reactions.

**(Keywords: polymerization; kinetics; poly(ethylene terephthalate); poly(butylene terephthalate); computer simulation)**

## INTRODUCTION

In view of the success of polycondensation kinetics with multiparameter equations in the case of poly(phenylene ether sulphone)[1], we have been testing many systems, among which the polycondensation of bis(hydroxyethyl)terephthalate (BHET) into poly(ethylene terephthalate (PET) and bis(hydroxybutyl)terephthalate (BHBT) are most illustrative.

Although there are many reports regarding the polycondensation kinetics of PET, only a few of them are carried out in the absence of catalyst[2,3]. As pointed out by Hoftyzer[3], the presence of catalyst not only accelerates the rate of reaction but also increases the degree of degradation. The degradation products may further catalyse the reactions if it is a Lewis acid and, at the same time, may reduce the concentration of reactants, thus making the kinetics more complex. Hence, in the present investigation, we did not use any kind of Lewis acid and we kept the heating time short in order to lessen degradation, even though the study of polycondensation of poly(butylene terephthalate) (PBT) was still subject to large errors due to its much easier decomposition into free carboxylic acid than the case of PET on account of the tetramethylene unit.

As most reports in the literature on the kinetics of polycondensation of PET are working in the presence of catalyst, some of their results are valuable here and agree with our investigations. First of all, the necessity to remove the volatile components in order to check the backward reaction was stressed. For example, Tomita[4] showed that agitation has a marked effect on the kinetics. Secondly, Challa[5] suggested that the monomer is more active than the polymer, and Chegolya[6] pointed out that cyclic PET oligomer has an accelerating effect toward PET formation; both of these experiments were carried out under catalysed conditions.

It is evident that the polycondensation kinetics of PET and PBT are bimolecular nucleophilic substitution reactions, but a plot of $1/(1-p)$ against time is not a straight line, particularly at the beginning of the reaction. We studied the polycondensation kinetics of PET under conditions in which there is no catalyst present and the reaction is kept irreversible. The results obtained were treated with multiparameter kinetics, and good agreement was found by simulation. In the case of PBT, since there are too many side reactions, especially the appearance of carboxylic acid serving as catalyst, the system becomes very complicated. Our studies show that there is no difference in reactivity between the monomer and the higher oligomers, as shown by the similarity in activation energy of polycondensation. Since the oligomers formed contain the ester of butane-1,4-diol, the latter is readily decomposed by heating into a carboxylic acid, which catalyses the polycondensation and makes the kinetics of the whole process very complicated.

A study with high-pressure gel permeation chromatography (h.p.g.p.c.) shows that the molecular weight distributions in PET and PBT formed follow the Flory distribution, which means that ester exchange is present in both cases.

## EXPERIMENTAL

### *Syntheses and purification of raw materials*

*BHET* was prepared by reacting dimethyl terephthalate with excess ethylene glycol using tri-n-butylamine as catalyst. The product after recrystallization melts at 110–110.5°C.

*Analysis.* $C_{12}H_{14}O_6$
Calculated C, 56.9; H, 5.7
Found C, 56.7; H, 5.5

*PET* oligomer containing no BHET was made by heating BHET at 260°C without catalyst. It was repeatedly extracted with boiling water to remove the unreacted BHET. The product was analysed with high-pressure liquid chromatography (h.p.l.c.) to ensure that

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there is no BHET present. The average degree of polymerization is $\bar{x}_n = 2.3$–$2.5$.

*BHBT* was synthesized from terephthaloyl chloride and butane-1,4-diol in tetrahydrofuran as solvent in the presence of pyridine[7]. The product was extracted with boiling water, from which pure BHBT was obtained: m.p. 72°C; analysed by h.p.l.c., the BHBT content amounted to 99.8%.

*Analysis.* $C_{16}H_{22}O_6$
Calculated C, 62.19; H, 7.09
Found C, 61.93; H, 7.15

*PBT* dimer was obtained in the residue after boiling water extraction in BHBT purification. It was repeatedly recrystallized from alcohol. The product is PBT dimer with trace of higher oligomers: m.p. 136–137°C (the m.p. of pure dimer is 138°C). By means of h.p.l.c. analysis, the content of BHBT was less than 0.1%.

*Analysis.* $C_{28}H_{34}O_{16}$
Calculated C, 63.16; H, 6.31
Found C, 63.38; H, 6.46

### *Kinetic study*

A 50 ml round-bottomed flask was fitted with a stirrer, dry nitrogen inlet tube and distilling condenser. The flask was placed in a thermostated silicone oil bath (±1°C) and evacuated. In the vacuum line, a 3000 ml buffer bottle was installed so that after shutting off the vacuum in the flask for sampling, the vacuum can be restored quickly in order to lessen the disturbance in kinetic study.

A certain amount of the samples was introduced into the thermostated flask with stirring, so that the contents were heated up to the desired temperature and vacuum in a very short time (about 5–6 min). Samples of 0.5–1.0 g were taken out at intervals, and were analysed for terminal hydroxyl groups to determine the degree of polymerization $\bar{x}_n = 1/(1-p)$. From the slope of the $\bar{x}_n$ vs. $t$ plot, the velocity constant $k$ could be calculated.

In this investigation, the rate determination was up to $\bar{x}_n = 10$. The viscosity of reactants at this time is not so large that the small molecules could escape easily and the reaction is kept irreversible.

### *Analysis of terminal OH group*

The method of semimicroanalysis was used[8] with some modifications. With dimethylsulphoxide as solvent, pyromellitic acid anhydride as acylating agent and imidazole as catalyst, the acylation was run at 100–150°C for 20–25 min, and back-titrated with 0.15 N KOH up to pH 9.75.

### *H.p.g.p.c. analysis*

The apparatus used[9] was a Shimadzu LC-3A with UVD-2 ultra-violet detector, and Zorbax-PSM$_{60s}$ filler; dimension of column, 6.2 mm × 25 cm. The solvent used was chloroform when $\bar{x}_n < 3$, and a mixture of tetrachloroethane and chloroform when $\bar{x}_n > 3$. When tetrachloroethane was used as solvent, it showed a chromatograph peak in our experiment, so its value must be deducted, and the method of preparing the sample should be quantitative in this case.

## RESULTS AND DISCUSSION

### *PET system*

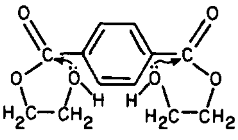
We started the polycondensation using BHET monomer as well as its oligomers containing no monomer in the absence of catalyst and under irreversible conditions. The reaction velocity constants between monomers $k_{11}$ and between higher oligomers $k_{mn}$ at four different temperatures were measured. The results are shown in *Table 1*. All the rate constants in this paper are in the unit $10^{-8}\ m^3\ mol^{-1}\ s^{-1}$. From this table, $k_{11}$ is about 16 times less than $k_{mn}$; this means that the activity of monomer is much less than that of higher oligomers. This phenomenon is not present in the case of PBT. It clearly shows that the hydroxyl group in monomer is less active than that when one of them in higher oligomers is esterified. Since the two hydroxyethylcarbonyl groups in monomer are in the *para* positions of a benzene ring, they would deactivate each other. Hence it is natural that the rate constant between monomer and higher oligomers $k_{1n}$ is intermediate between that of $k_{11}$ and $k_{mn}$. Thus, we can use the same scheme to simulate the experimental values as we did in poly(phenylene ether sulphone)[1]. Let us use the subscript 1 to denote monomer and *m*, *n*, *p*, *q* for higher oligomers; thus

$$P_1 + P_1 \xrightarrow{k_{11}} P_2$$

$$P_1 + P_n \xrightarrow{k_{1n}} P_{n+1}$$

$$P_m + P_n \xrightarrow{k_{mn}} P_{m+n} \qquad m,n = 2,3,4,\ldots$$

The difference in reactivity between the free hydroxyethyl radical and the esterified group might be due to coordination of the hydroxyl group with the neighbouring carbonyl group, which is unlikely in esterified species of higher oligomers.



BHET

Owing to the fact that the electronic effects of both hydroxyethylcarbonyl groups in monomer mutually deactivate each other through the benzene ring, the monomer is the most unreactive one, and we can predict that $k_{11} < k_{1n} < k_{mn}$.

Furthermore, there is still the possibility that the monomer may react with polymers through trans-esterification, i.e.

$$P_1 + P_{qn} \xrightarrow{k_{1qn}} P_{1+q} + P_n \qquad q = 1,2,3,\ldots$$

**Table 1** Rate constants and activation energy (*E*) in polycondensation of BHET and its oligomers

| | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | 235 | 242 | 250 | 262 | $E$ (J mol$^{-1}$) |
| $k_{11}$ | 0.64 | 1.03 | 1.69 | 3.25 | 142 |
| $k_{mn}$ | 10.9 | 16.6 | 26.9 | 51.5 | 126 |

Thus we are in a position to formulate the kinetic equations by means of these constants similar to those in poly(phenylene ether sulphone)[1]:

$$\frac{dZ}{dX} = -R_1Z^2 - R_2Z[Y-Z] - R_3Z[1-2Y+Z]$$

$$\frac{dY}{dX} = -\tfrac{1}{2}R_1Z^2 - R_2Z[Y-Z] - \tfrac{1}{2}[Y-Z]^2$$

This is derived when we let $[P] = \sum_{i=1}^{\infty}[P_i]$ and $[P]_0$ is the initial concentration of the monomer, and

$$X = [P]_0k_{mn}t \qquad R_1 = k_{11}/k_{mn}$$
$$Y = [P]/[P]_0 \qquad R_2 = k_{1n}/k_{mn}$$
$$Z = [P_1]/[P]_0 \qquad R_3 = k_{1qn}/k_{mn}$$

This set of differential equations can be solved numerically by the Runge–Kutta method if the individual rate constants are known. The resulting plot of $1/Y$ against $X$ should conform to the experimental results if such analysis is correct. Or in case where the kinetic relation is set, the rate constants, or at least some of them, can be obtained through simulation of the experimental curve.

In the present case, $R_1 = k_{11}/k_{mn} = 0.064$, but the values of $k_{1n}$ and $k_{1qn}$ are unavailable experimentally. From the analysis of the activity of hydroxyethyl group, we could suggest the relation $k_{mn} > k_{1n} > k_{11} \approx k_{1qn}$. First, we try $R_1 = 0.064$, $R_2$ from 0.5 to 0.9 and $R_3 = 0$, the results are shown in *Figure 1*, in which the experimental curve is close to $R_2 = 0.6$ at the beginning but deviates at a later stage of reaction, which means that, as more oligomers are formed, the part of $k_{1qn}$ could not be ignored. For $R_3 = 0.06$, good agreement was obtained from the simulation as shown in *Figure 1*. Thus we obtained the rate constants of the component reactions at 250°C as $k_{11} = 1.69$, $k_{mn} = 26.9$, $k_{1n} = 16.1$, $k_{1qn} = 1.6$ when there is no catalyst present.

In order to study further the mechanism of polycondensation, the molecular weight distribution of the oligomers was studied by h.p.g.p.c. It is quite unexpected that the *MWD* conforms to the Flory distribution as shown in *Figure 2* at four different degrees of polymerization, although the component reactions are rather complicated as we showed before. It suggests that there is ester exchange among the oligomers formed. As further evidence, when we started with dimer as the raw material, a small amount of monomer was detected by h.p.g.p.c. from the resulting products. This strongly proves that intermolecular ester exchange is present. Thus, a further component reaction must be added which does not or only slightly interferes with the reaction kinetics but alters the *MWD* greatly:

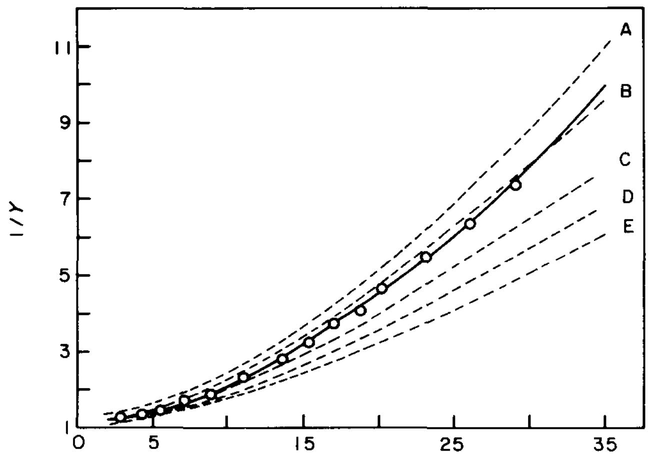


**Figure 1** Computer simulation of the kinetics of PET polycondensation from BHET at 250°C. Broken curves: simulated when $R_1 = 0.064$, $R_3 = 0$; A, $R_2 = 1.0$; B, $R_2 = 0.90$; C, $R_2 = 0.70$; D, $R_2 = 0.60$; E, $R_2 = 0.50$. Full curve: simulated when $R_1 = 0.064$, $R_2 = 0.60$, $R_3 = 0.06$. Open circles: experimental values

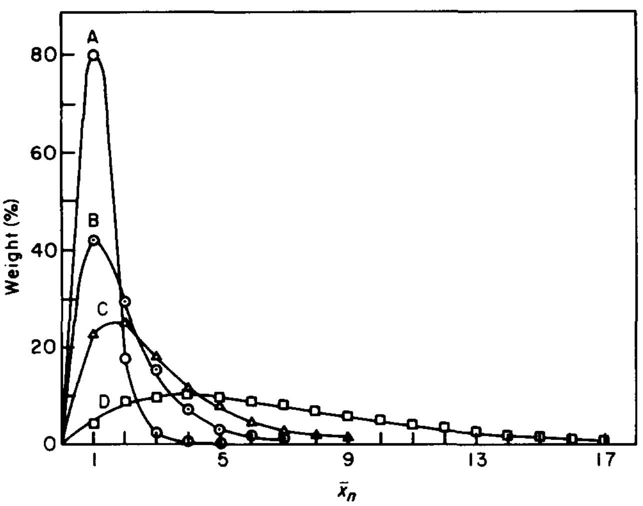


**Figure 2** *MWD* of BHET polycondensation, conforming to the Flory distribution. The points are experimental values. The full curves are: A, $p = 0.1028$; B, $p = 0.3575$; C, $p = 0.5157$; D, $p = 0.7706$

**Table 2** Rate constant and activation energy ($E$) in polycondensation of BHBT and its dimer

| | Temperature (°C) | | | | | |
|---|---|---|---|---|---|---|
| | 195 | 200 | 215 | 230 | 240 | $E$ (J mol$^{-1}$) |
| $k_{11}$ | 0.413 | 0.813 | 1.85 | 5.61 | – | 124 |
| $k_{22}(k_{mn})$ | – | 0.798 | 2.07 | 5.32 | 8.69 | 122 |

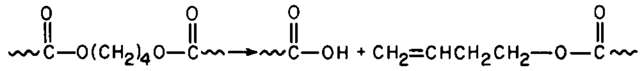
$$P_{m+n} + P_{p+q} \rightarrow P_{m+p} + P_{n+q}$$

in which *m*, *n*, *p*, *q* are integers.

### *PBT system*

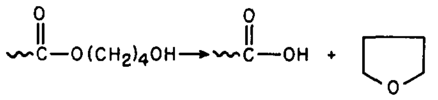
The results of the kinetic study on polycondensation starting from BHBT and its dimer when there is no catalyst present and the reactions are kept irreversible are shown in *Table 2* at four different temperatures. The activation energies show that there is no essential difference between the rate constants $k_{11}$ and $k_{mn}$ (in fact it is $k_{22}$). This clearly shows that unequality of reactivity between monomers and higher oligomers is not present. Based on this fact, the possible coordination of hydroxyethyl group with carbonyl group to form a five-membered ring as in the case of PET is unable to exist. A h.p.g.p.c. experiment shows that the *MWD* of the product strictly follows the Flory distribution.

However, the graph of $1/(1-p)$ against $t$ is still not a straight line although the reactivities of monomer and oligomers are quite close to each other. An explanation[10] has already been given that the product decomposes on heating into an acid, which is not likely to be present in the case of PET:



$$\sim\overset{\overset{O}{\|}}{C}-O(CH_2)_4O-\overset{\overset{O}{\|}}{C}\sim\;\longrightarrow\;\sim\overset{\overset{O}{\|}}{C}-OH + CH_2{=}CHCH_2CH_2-O-\overset{\overset{O}{\|}}{C}\sim$$

and the hydroxybutyl group at the end of the oligomer may also be subject to decomposition at higher temperature forming an acid and tetrahydrofuran:



$$\sim\overset{\overset{O}{\|}}{C}-O(CH_2)_4OH\;\longrightarrow\;\sim\overset{\overset{O}{\|}}{C}-OH\;+$$

In our experiments, the presence of tetrahydrofuran was detected in the distillate by thin later chromatography, and the presence of carboxylate group was identified by i.r. spectroscopy.

Although the amount of carboxyl group produced is rather small, its catalytic activity on transesterification cannot, however, be ignored. Hence it is no longer possible to use the multiparameter equations to simulate its kinetic behaviour. For this reason, in industry, it is advisable to use highly efficient catalyst for the polycondensation in order to avoid the above-mentioned side reactions.

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