Analysis of oligomerization in the reaction of dimethyl terephthalate with ethylene glycol

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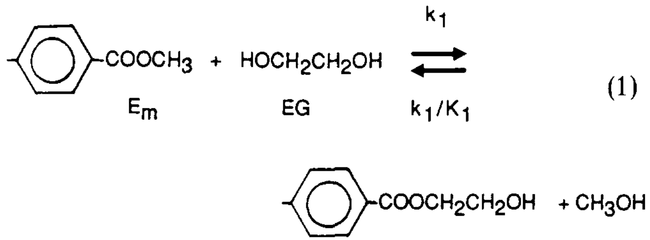
The extent of oligomerization during the reaction between dimethyl terephthalate and ethylene glycol was analysed by measuring by Fourier transform infrared spectroscopy the time evolution of the number of ethylene diester groups produced during reactions at different temperatures. These data together with the methanol withdrawn from the reactor were used for kinetic analysis of the system. Two kinetic models were considered. In the first, the ester interchange reaction and the transesterification reaction were included. In the second, the polycondensation reaction was also included. Both models adequately fitted the experimental data. However, model discrimination has not been possible because no significant differences between the models were found. The effect of reaction temperature and of the ratio of dimethyl terephthalate to ethylene glycol on the chain length distribution was analysed by simulation with the model including the three reactions and the values of the parameters estimated in the kinetic analysis.

(Keywords: dimethyl terephthalate; ethylene glycol; oligomerization; ethylene diester group data)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is produced by polycondensation of bis(2-hydroxyethyl) terephthalate (BHET) or its oligomers. An important process for the synthesis of BHET is the reaction of dimethyl terephthalate (DMT) and ethylene glycol (EG). The main reactions involved in this process are the ester interchange reaction, the transesterification reaction and the polycondensation reaction. In terms of the participating functional groups, these reactions can be written as follows:



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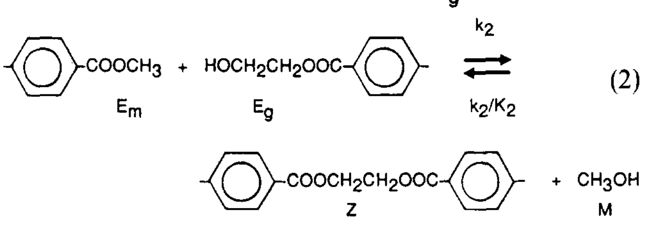

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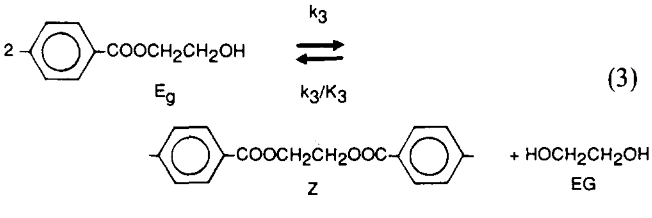

(3)

One of the objectives of this process is to achieve complete reaction of the methyl ester groups. Therefore, methanol is continuously removed from the reactor to shift the reaction to the right. The extent of the reaction has traditionally been followed by measuring the methanol withdrawn from the reactor. It has been shown[1] that methanol data obtained under a wide range of experimental conditions can be accounted for by a simple model including only the ester interchange reaction. Additionally, some attempts at using methanol data to elucidate the existence of oligomerization have been reported[2–4]. These reports conclude that for conversions of DMT of $<88\%$ and EG/DMT ratios >2 oligomerization did not proceed to any significant extent. However, Barandiaran and Asúa[5] have found that a model including reactions (1) and (2) fitted the extensive methanol data reported in Reference 1 better than the model including only the ester interchange reaction. The same holds for a model including reactions (1)–(3)[5]. Note that the better fit might be due to the larger number of parameters involved in these models. Nevertheless, these results show that methanol data do not provide a good reason to neglect the importance of the transesterification and polycondensation reactions. Therefore, it was concluded[5] that the importance of oligomerization reactions cannot be evaluated by using as the only observed variable the methanol withdrawn from the reactor. To investigate this point further, it was pointed out that more information should be available[5].

In this paper, the degree of oligomerization during the reaction of dimethyl terephthalate and ethylene glycol is determined experimentally by measuring the number of ethylene diester groups by Fourier transform infrared spectroscopy (*FT*i.r.). A kinetic analysis of reactions (1)–(3) using the methanol withdrawn from the reactor and the ethylene diester groups as observable variables is also presented. Finally, the effect of the experimental conditions on the chain length distribution of the

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oligomers is studied by simulation, using the values of the parameters estimated in the kinetic analysis.

EXPERIMENTAL

Reactions were carried out in standard equipment provided with a rectification column and mechanical agitation. Details are reported elsewhere[1]. Commercial grade EG and DMT were used without further purification. $Mn(CH_3COO)_2$ was used as catalyst. Experiments were carried out by heating the DMT in the reactor to its melting point ($\approx$140°C). The EG and catalyst were added and the reaction mixture heated until the temperature reached its final value. The internal reactor temperature was continuously measured and recorded. *Table 1* summarizes the experimental conditions. The methanol was collected in a cold trap.

To determine oligomerization qualitatively, thin-layer chromatography (t.l.c.) of samples obtained at different conditions was carried out. The samples were dissolved in the mixture phenol/tetrachloroethane (1/1 weight ratio) and chloroform/ethanol (96/4) was used as eluant in accordance with the system used by Dimov and Terlemezyan[6]. *Figure 1* presents the thin-layer chromatographs obtained at different conversions for the two temperature profiles studied. Oligomers up to pentamers were detected. *Figure 1* shows that oligomerization increases with conversion and reaction temperature.

To determine oligomerization quantitatively, the time evolution of the number of ethylene diester groups in the reaction mixture was determined. The number of moles of $-COOCH_2CH_2OOC-$ groups, z, present in the reaction mixture is:

$$z = z^*(e_m + e_g)/2 \qquad (4)$$

where z^* is the average number of ethylene diester groups per molecule of oligomer and e_m and e_g are the equivalents of methyl ester groups and hydroxyethyl ester groups, respectively. Note that $(e_m + e_g)/2$ is the number of moles of oligomers.

The average number of ethylene diester groups per molecule of oligomer is given by

$$z^* = \frac{(\text{total number of internal} -\text{COO groups})/2}{\text{total number of oligomers}} \qquad (5)$$

The total number of internal –COO groups can be calculated as follows:

$$\text{total number of internal} -\text{COO groups} = T_{COO} - (E_m + E_g) \qquad (6)$$

where T_{COO} is the total number of –COO groups, E_m the number of methyl ester groups and E_g the number of hydroxyethyl ester groups.

The total number of oligomers is:

$$\text{total number of oligomers} = \frac{E_m + E_g}{2} \qquad (7)$$

Table 1 Summary of experimental conditions

DMT: 0.5 mol
EG: 1 mol
Catalyst content: 6.0×10^{-4} mol
Final temperature: 180 and 190°C

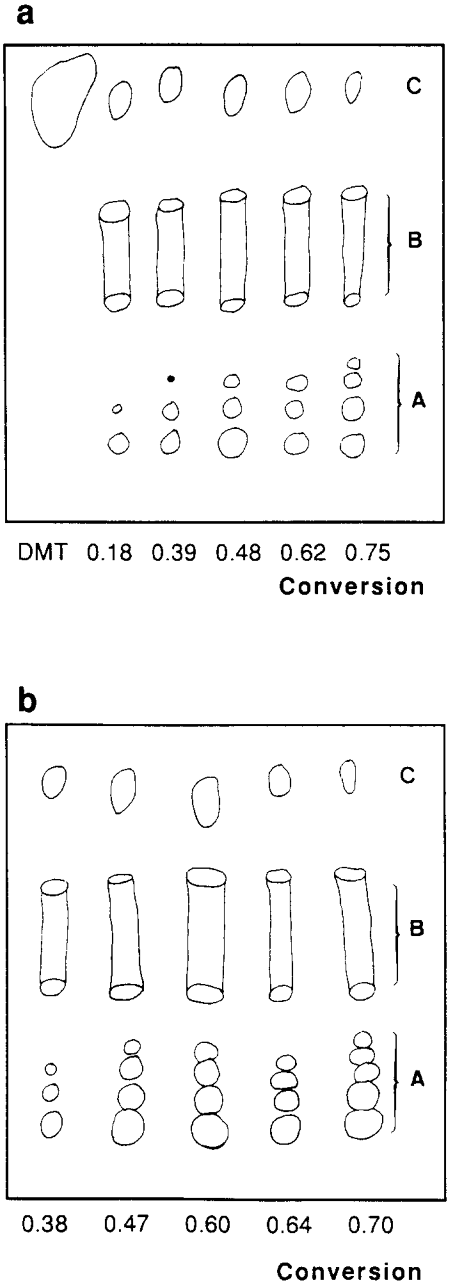


Figure 1 Thin-layer chromatographs of samples at different conversions and two different final temperatures: (a) 180°C; (b) 190°C. A, ester diol oligomers; B, half-transesterificated DMT oligomers; C, DMT

By substituting equations (6) and (7) into equation (5) and rearranging, the following equation is obtained:

$$z^* = \left(\frac{E_m}{T_{COO}} + \frac{E_g}{T_{COO}}\right)^{-1} - 1 \qquad (8)$$

The ratio E_m/T_{COO} is given by

$$\frac{E_m}{T_{COO}} = \frac{e_m}{e_{m0}} \qquad (9)$$

and is calculated by means of the total mass balance. The ratio E_g/T_{COO} can be calculated as follows:

$$\frac{E_g}{T_{COO}} = \frac{-\text{OH groups}}{2 \times \text{phenyl groups}} \qquad (10)$$

The ratio –OH groups/phenyl groups was determined by *FT*i.r. with a Nicolet 5DXC. The samples were first dried under vacuum at 1 mmHg (≈100 Pa) and 40°C, to eliminate all possible traces of methanol, ethylene glycol and humidity. The spectra were recorded over the range 4000–400 cm^{-1}, with a minimum of 64 scans, using KBr pellets. The measured ratio between the absorbance of primary –OH groups at 1070 cm^{-1} and the absorbance of substituted phenyl groups at 720 cm^{-1} was used to determine the ratio –OH groups/phenyl groups from the calibration curve presented in *Figure 2*.

The calibration curve was made by using mixtures of DMT and BHET of different compositions. BHET was synthesized by the reaction of DMT and EG with an EG/DMT ratio of 10 by allowing the system to reach complete conversion of DMT. The unreacted EG was eliminated in a vacuum oven, leaving the system under vacuum at 1 mmHg and 40°C.

The values of z obtained using the calibration curve in *Figure 2* and equations (4)–(10) are presented in *Figure 3*. The difficulty of replicating experiments resulted in some scattering of the experimental data. The reaction mixture is liquid at the reaction temperature but solid at room temperature. This characteristic makes it very difficult to take samples from the reactor and, hence, to follow the reaction continuously. The problem was solved by doing different reactions under the same experimental conditions but stopping them at different reaction times. However, note that, because of the difficulty of reproducing the reaction temperature profile from run to run, this operational procedure increased the scattering of the data. The experimental noise was smoothed by means of a polynomial fitting of the data (solid lines in *Figure 3*). These lines were used as experimental data to estimate the parameters of models during the kinetic analysis.

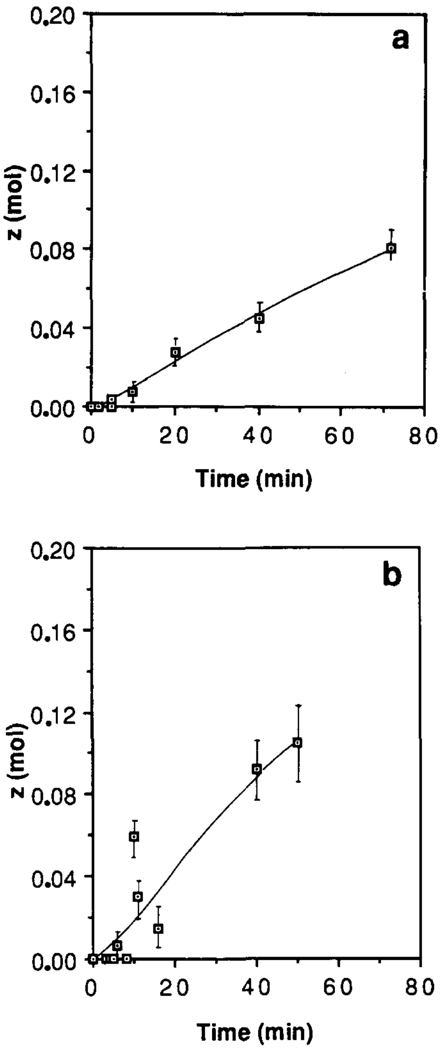


Figure 3 Variation of moles of ethylene diester groups with time for two different temperature profiles: (a) final temperature ≈180°C; (b) final temperature ≈190°C. ———, Polynomial fitting of the experimental points

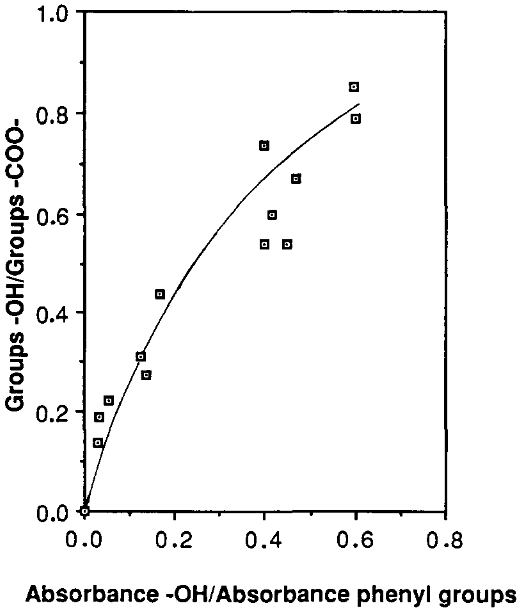


Figure 2 Calibration curve obtained by *FT*i.r

MODEL DESCRIPTION

Due to lack of knowledge about the relative importance of transesterification and polycondensation reactions in the production of oligomers, two different models were developed. The first considered both ester interchange and transesterification reactions. The second also included the polycondensation reaction. To avoid repetition, only the model including the three reactions will be developed. The model including the first two reactions can be obtained by eliminating the terms corresponding to the polycondensation reaction.

Ester interchange, transesterification and polycondensation reactions can be written in terms of participating functional groups as follows:

$$\mathrm{E_m} + \mathrm{EG} \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} \mathrm{E_g} + \mathrm{M} \quad (11)$$

$$\mathrm{E_m} + \mathrm{E_g} \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{Z} + \mathrm{M} \quad (12)$$

$$2\mathrm{E_g} \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} \mathrm{Z} + \mathrm{EG} \quad (13)$$

The material balances for e_m and z are given by:

$$\frac{1}{V}\frac{\mathrm{d}e_m}{\mathrm{d}t}=\left[-k_1\frac{e_m}{V}\left(\frac{2g}{V}\right)^{0.6}+\frac{k_1}{K_1}\frac{e_g}{V}\frac{m}{V}\right.$$
$$\left.-k_2\frac{e_m}{V}\frac{e_g}{V}+\frac{k_2}{K_2}\frac{2z}{V}\frac{m}{V}\right]$$

$$\times\left[\frac{C/V}{1+k(C/V)}\right] \qquad (14)$$

$$\frac{1}{V}\frac{\mathrm{d}z}{\mathrm{d}t}=\left[k_2\frac{e_\mathrm{m}}{V}\frac{e_\mathrm{g}}{V}-\frac{k_2}{K_2}\frac{2z}{V}\frac{m}{V}+k_3\left(\frac{e_\mathrm{g}}{V}\right)^2-\frac{k_3}{K_3}\frac{2z}{V}\left(\frac{2g}{V}\right)\right]$$

$$\times\left[\frac{C/V}{1+k(C/V)}\right] \qquad (15)$$

where e_m, e_g and z are the number of moles of $\mathrm{E_m}$, $\mathrm{E_g}$ and Z groups, respectively; m and g are the number of moles of methanol and ethylene glycol in the reaction mixture, C is the number of moles of catalyst and V the volume of the reaction mixture. In the derivation of equations (14) and (15) it was assumed that the three reactions were reversible and that the dependences with respect to the concentration of the participating species were the same that those obtained by Barandiaran and Asúa[1]. These dependences are first-order reactions with respect to $\mathrm{E_m}$, $\mathrm{E_g}$ and Z, order 0.6 for EG in the ester interchange reaction but first order in the polycondensation reaction, and hyperbolic dependence of the reaction rate on catalyst concentration.

The number of moles of EG and $\mathrm{E_g}$ can be calculated from the balance of functional groups as follows:

$$g=g_0+z-(e_{\mathrm{m}0}-e_\mathrm{m}) \qquad (16)$$

$$e_\mathrm{g}=e_{\mathrm{m}0}-e_\mathrm{m}-2z \qquad (17)$$

The methanol content in the reaction mixture, m, was calculated by assuming that equilibrium between liquid and gas phases was attained:

$$P_\mathrm{T}=P_\mathrm{M}+P_\mathrm{G} \qquad (18)$$

where P_T is the reactor total pressure and P_M and P_G the partial pressure of methanol and ethylene glycol, respectively. These partial pressures were calculated through the Flory–Huggins relationship[7].

PARAMETER ESTIMATION AND MODEL DISCRIMINATION

Parameters for the two models were estimated by means of the modified Gauss–Newton method for differential equations proposed by Hwang and Seinfeld[8]. The convergence was enhanced through a Marquardt like approach[9].

Although in the present study there were two observable variables, namely the methanol withdrawn from the reactor and the number of moles of ethylene diester groups, the number of experimental points was smaller than that in the study using methanol data only[5]. Hence estimation of a large number of parameters should be avoided. The adjustable parameters were the frequency factors and the activation energies of the direct reactions for different values of equilibrium constants.

Model based on ester interchange and transesterification reactions

First, parameters were estimated by using the equilibrium constants given by Challa[10]. *Figure 4* shows that poor agreement between model prediction and experimental data was obtained. Therefore, different values of the equilibrium constants were tried. The equilibrium constants that best fitted the experimental values were:

$$K_1=4\times10^{-4}\exp[6000/RT] \qquad (\mathrm{mol}^{0.4}\,\mathrm{l}^{-0.4}) \qquad (19)$$

$$K_2=0.25 \qquad (20)$$

For these equilibrium constants the following estimated parameters were obtained:

$$k_1=(22.82\pm1.07)$$
$$\times\exp\{-[(8190\pm286)/RT](1/T-1/457)\}$$
$$(\mathrm{l}^{1.6}\,\mathrm{mol}^{-1.6}) \qquad (21)$$

$$k_2=(1.34\pm0.10)$$
$$\times\exp\{-[25060\pm287)/R](1/T-1/457)\}$$
$$(\mathrm{l}^2\,\mathrm{mol}^{-2}\,\mathrm{min}^{-1}) \qquad (22)$$

where 457 (K) is the average temperature of the experiments.

In all cases, the constant included in the function giving the dependence of reaction rate on catalyst concentration was taken to be the same as that reported by Barandiaran and Asúa[1]:

$$k=420 \qquad (\mathrm{l\,mol}^{-1}) \qquad (23)$$

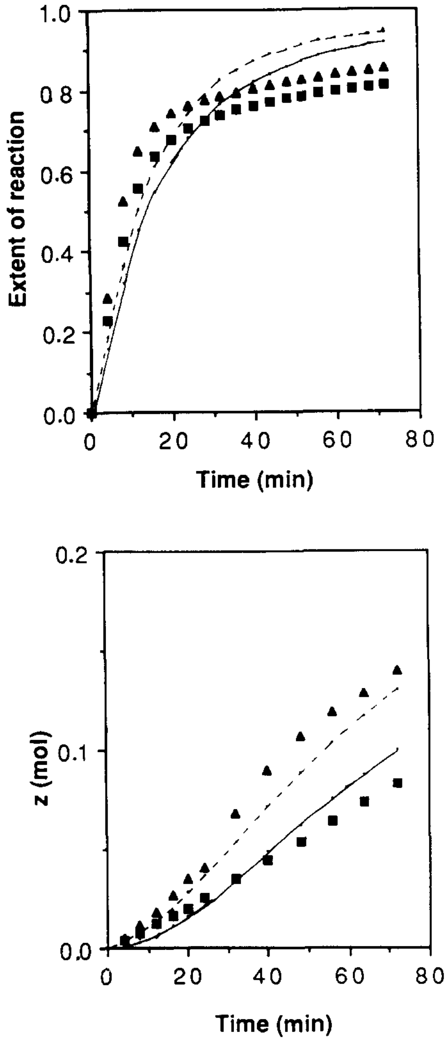


Figure 4 Comparison between experimental results and prediction of the model including ester interchange, transesterification and polycondensation reactions with Challa's equilibrium constants. ■, ———, $T=180$°C; ▲, – – – –, $T=190$°C

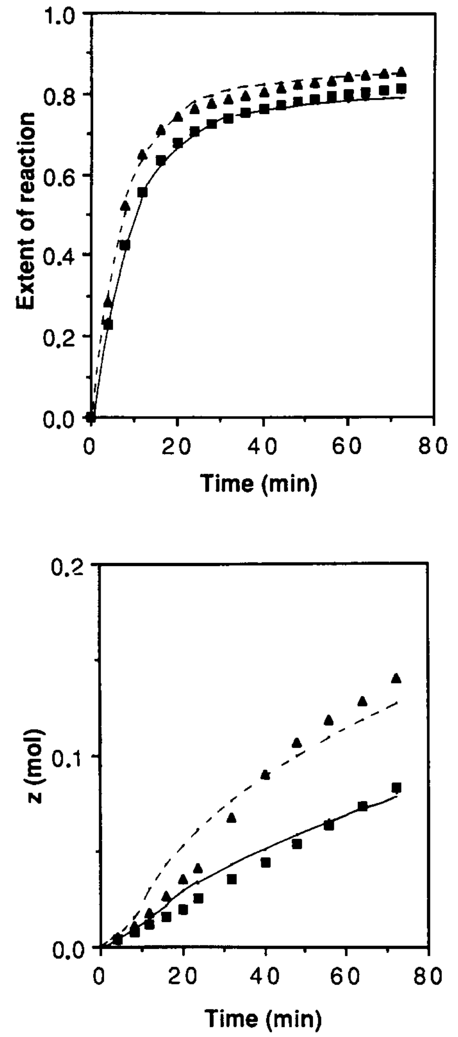


Figure 5 Fit of experimental results by the model including ester interchange and transesterification reactions with equilibrium constants given in equations (19) and (20). ■, ———, $T = 180°C$; ▲, -----, $T = 190°C$

Figure 5 shows the good agreement obtained between model prediction and experimental data using the values of the parameters given by equations (19)–(23).

Model based on ester interchange, transesterification and polycondensation reactions

A similar approach was used to estimate the values of the parameters for the model including the three reactions. Parameters were estimated by keeping $k = 420$ $\mathrm{l\,mol^{-1}}$ and the following values of the estimated parameters were obtained:

$$k_1 = (17.06 \pm 0.91) \times \exp\{-[(8070 \pm 132)/R](1/T - 1/457)\} \quad (\mathrm{l^{1.6}\,mol^{-1.6}\,min^{-1}}) \quad (24)$$

$$k_2 = (0.68 \pm 0.25) \times \exp\{-[(26\,300 \pm 132)/R](1/T - 1/457)\} \quad (\mathrm{l^{2}\,mol^{-2}\,min^{-1}}) \quad (25)$$

$$k_3 = (0.122 \pm 0.10) \times \exp\{-[(10\,990 \pm 154)/R](1/T - 1/457)\} \quad (\mathrm{l^{2}\,mol^{-2}\,min^{-1}}) \quad (26)$$

$$K_1 = 4 \times 10^{-4} \exp(6000/RT) \quad (\mathrm{mol^{0.4}\,l^{-0.4}}) \quad (27)$$

$$K_2 = 0.25 \quad (28)$$

$$K_3 = 0.40 \quad (29)$$

Figure 6 presents a comparison between experimental data and model predictions. It shows that the model including three reactions fits well both types of experimental data: methanol collected and extent of oligomerization.

Model discrimination

To check which of the described models best fits the experimental data, the χ^2 statistical test for model discrimination was applied. *Table 2* shows the data needed to perform the discrimination. The calculated value $\chi_c^2 = 2.36 \times 10^{-4}$ was lower than the value obtained

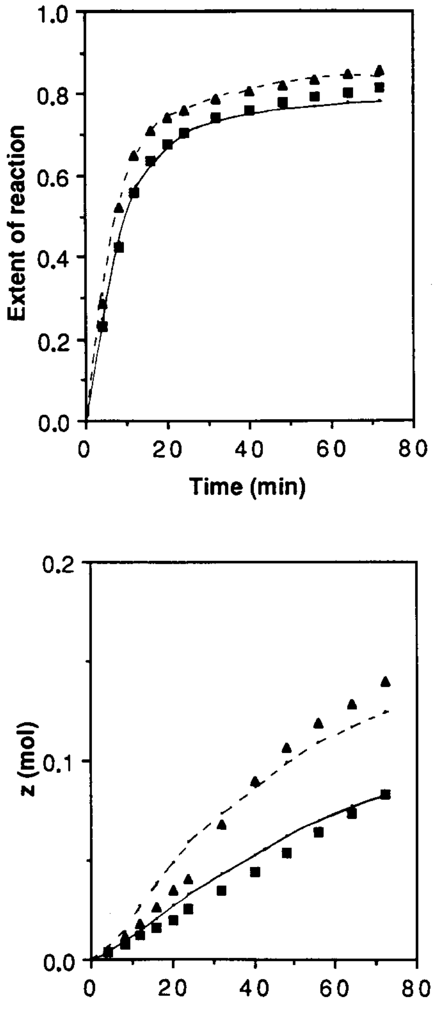


Figure 6 Comparison between experimental results and prediction of the model including ester interchange, transesterification and polycondensation reactions. ■, ———, $T = 180°C$; ▲, -----, $T = 190°C$

Table 2 Data for the χ^2 test of discrimination between models

Model	Parameters	d_f	s^2
Reactions 1 and 2	4	32	3.080×10^{-4}
Reactions 1–3	6	30	3.063×10^{-4}

from the χ^2 distribution with a confidence interval of 95%: $\chi^2(1, 0.95) = 3.84$[11]. Therefore, on a statistical basis, there are no significant differences between the models.

SIMULATION OF THE CHAIN LENGTH DISTRIBUTION

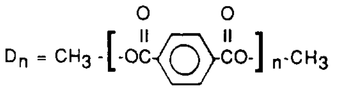
Assuming that the system involves the ester interchange reaction, the transesterification reaction and the polycondensation reaction, the mechanism of the reaction of DMT with EG can be written, in terms of the molecular species as follows.

Reaction with ethylene glycol:

$$\mathrm{D}_n + \mathrm{EG} \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} \mathrm{H}_n + \mathrm{M} \tag{30}$$

$$\mathrm{H}_n + \mathrm{EG} \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} \mathrm{P}_n + \mathrm{M} \tag{31}$$

where k_1 is the kinetic constant for free glycol and k_1/K_1 is the rate coefficient for substitution of one hydroxyethyl ester group by methanol. These kinetic constants are the same as in equation (11). D_n, H_n and P_n are defined as follows: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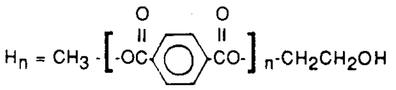
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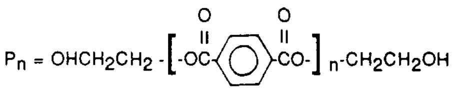
(34)

Note that D_1 is DMT and P_1 is BHET.

Transesterification reaction:

$$\mathrm{D}_n + \mathrm{H}_m \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{D}_{n+m} + \mathrm{M} \tag{35}$$

$$\mathrm{H}_n + \mathrm{H}_m \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{H}_{n+m} + \mathrm{M} \tag{36}$$

$$\mathrm{P}_n + \mathrm{D}_m \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{H}_{n+m} + \mathrm{M} \tag{37}$$

$$\mathrm{P}_n + \mathrm{H}_m \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{P}_{n+m} + \mathrm{M} \tag{38}$$

where k_2 is the kinetic constant for the reaction of methyl ester groups and hydroxyethyl ester groups and k_2/K_2 is the rate constant for the reaction of methanol with ethylene diester groups. These rate coefficients are the same as those in equation (12).

Polycondensation reaction:

$$\mathrm{P}_n + \mathrm{P}_m \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} \mathrm{P}_{n+m} + \mathrm{EG} \tag{39}$$

$$\mathrm{H}_n + \mathrm{H}_m \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} \mathrm{D}_{n+m} + \mathrm{EG} \tag{40}$$

$$\mathrm{P}_n + \mathrm{H}_m \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} \mathrm{H}_{n+m} + \mathrm{EG} \tag{41}$$

where k_3 is the kinetic constant of the reaction involving two hydroxyethyl ester groups and k_3/K_3 is the rate coefficient of the reaction of ethylene glycol with ethylene diester. These rate parameters are the same as in equation (13).

This kinetic scheme differs from that proposed by Gupta and Kumar[12] in equation (41), which was omitted by those authors. In addition, the kinetic constant for the reverse reaction in equation (38) was also different.

The material balance for D_n can be written as follows:

$$\frac{1}{V}\frac{\mathrm{d}D_n}{\mathrm{d}t} = \left[-2k_1 \frac{D_n}{V}\left(\frac{2g}{V}\right)^{0.6} + \frac{k_1}{K_1}\frac{H_n}{V}\frac{m}{V} \right.$$

(equation (30))

$$-2k_2 \frac{D_n}{V} \sum_{m=1}^{N-n} \frac{H_m}{V} - 2(n-1)\frac{k_2}{K_2}\frac{m}{V}\frac{D_n}{V}$$

(equation (35))

$$+2k_2 \sum_{m=1}^{n-1} \frac{D_m}{V}\frac{H_{n-m}}{V} + 2\frac{k_2}{K_2}\frac{m}{V} \sum_{m=n+1}^{N} \frac{D_m}{V}$$

(equation (35))

$$-4k_2 \frac{D_n}{V} \sum_{m=1}^{N-n} \frac{P_m}{V} + \frac{k_2}{K_2}\frac{m}{V} \sum_{m=n+1}^{N} \frac{H_m}{V}$$

(equation (37))

$$+\frac{1}{2}k_3 \sum_{m=1}^{N-1} (\delta_{(m=n/2)} + 1)\frac{H_m}{V}\frac{H_{n-m}}{V}$$

(equation (40))

$$\left. -4(n-1)\frac{k_3}{K_3}\frac{D_n}{V}\frac{g}{V} \right] \frac{C/V}{1+k(C/V)}$$

(equation (40)) (42)

where $\delta_{(m=n/2)}$ is the Dirac δ function, which is equal to one when $m = n/2$ and zero otherwise. N is the maximum oligomer length. This means that reactions between oligomers which would result in oligomers of a length $> N$ are not considered in the simulation.

The material balance for H_n is:

$$\frac{1}{V}\frac{\mathrm{d}H_n}{\mathrm{d}t} = \left[2k_1 \frac{D_n}{V}\left(\frac{2g}{V}\right)^{0.6} - \frac{k_1}{K_1}\frac{H_n}{V}\frac{m}{V} \right.$$

(equation (30))

$$-k_1 \frac{H_n}{V}\left(\frac{2g}{V}\right)^{0.6} + 2\frac{k_1}{K_1}\frac{P_n}{V}\frac{m}{V}$$

(equation (31))

$$-2k_2 \frac{H_n}{V} \sum_{m=1}^{N-n} \frac{D_m}{V} + 2\frac{k_2}{K_2}\frac{m}{V} \sum_{m=n+1}^{N} \frac{D_m}{V}$$

(equation (35))

$$+k_2 \sum_{m=1}^{n-1} (\delta_{(m=n/2)} + 1)\frac{H_m}{V}\frac{H_{n-m}}{V}$$

(equation (36))

$$-2k_2 \frac{H_n}{V} \sum_{m=1}^{N-n} \frac{H_m}{V}$$

(equation (36))

$$-2(n-1)\frac{k_2}{K_2}\frac{m}{V}\frac{H_n}{V}$$

(equations (36), (37))

$$+2\frac{k_2}{K_2}\frac{m}{V}\sum_{m=n+1}^{N}\frac{H_m}{V}$$

(equation (36))

$$+4k_2\sum_{m=1}^{n-1}\frac{P_m}{V}\frac{D_{n-m}}{V}$$

(equation (37))

$$-2k_2\frac{H_n}{V}\sum_{m=1}^{N-n}\frac{P_m}{V}+2\frac{k_2}{K_2}\frac{m}{V}\sum_{m=n+1}^{N}\frac{P_m}{V}$$

(equation (38))

$$-k_3\frac{H_n}{V}\sum_{m=1}^{N-n}\frac{H_m}{V}$$

(equation (40))

$$+8\frac{k_3}{K_3}\frac{g}{V}\sum_{m=n+1}^{N}(1-\tfrac{1}{2}\delta_{(m,n\,\mathrm{even})})\frac{D_m}{V}$$

(equation (40))

$$-2k_3\frac{H_n}{V}\sum_{m=1}^{N-n}\frac{P_m}{V}+2k_3\sum_{m=1}^{n-1}\frac{H_m}{V}\frac{P_{n-m}}{V}$$

(equation (41))

$$-4(n-1)\frac{k_3}{K_3}\frac{H_n}{V}\frac{g}{V}+4\frac{k_3}{K_3}\frac{g}{V}\sum_{m=n+1}^{N}\frac{H_m}{V}\Bigg]$$

(equation (41))

$$\times\frac{C/V}{1+k(C/V)} \qquad (43)$$

The material balance for P_n can be written as follows:

$$\frac{1}{V}\frac{\mathrm{d}P_n}{\mathrm{d}t}=\Bigg[k_1\frac{H_n}{V}\left(\frac{2g}{V}\right)^{0.6}-2\frac{k_1}{K_1}\frac{P_n}{V}\frac{m}{V}$$

(equation (31))

$$-4k_2\frac{P_n}{V}\sum_{m=1}^{N-n}\frac{D_m}{V}+\frac{k_2}{K_2}\frac{m}{V}\sum_{m=n+1}^{N}\frac{H_m}{V}$$

(equation (37))

$$-2k_2\frac{P_n}{V}\sum_{m=1}^{N-n}\frac{H_m}{V}+2k_2\sum_{m=1}^{n-1}\frac{P_m}{V}\frac{H_{n-m}}{V}$$

(equation (38))

$$-2(n-1)\frac{k_2}{K_2}\frac{m}{V}\frac{P_n}{V}+2\frac{k_2}{K_2}\frac{m}{V}\sum_{m=n+1}^{N}\frac{P_m}{V}$$

(equation (38))

$$-4k_3\frac{P_n}{V}\sum_{m=1}^{N-n}\frac{P_m}{V}$$

(equation (39))

$$+2k_3\sum_{m=1}^{n-1}(\delta_{(m=n/2)}+1)\frac{P_m}{V}\frac{P_{n-m}}{V}$$

(equation (39))

$$-4(n-1)\frac{k_3}{K_3}\frac{P_n}{V}\frac{g}{V}$$

(equation (39))

$$+8\frac{k_3}{K_3}\frac{g}{V}\sum_{m=n+1}^{N}(1-\tfrac{1}{2}\delta_{(m,n\,\mathrm{even})})\frac{P_m}{V}$$

(equation (39))

$$-2k_3\frac{P_n}{V}\sum_{m=1}^{N-n}\frac{H_m}{V}+4\frac{k_3}{K_3}\frac{g}{V}\sum_{m=n+1}^{N}\frac{H_m}{V}\Bigg]$$

(equation (41))

$$\times\frac{C/V}{1+k(C/V)} \qquad (44)$$

The material balance for the ethylene glycol is:

$$\frac{1}{V}\frac{\mathrm{d}g}{\mathrm{d}t}=\Bigg[-2k_1\left(\frac{2g}{V}\right)^{0.6}\sum_{m=1}^{N}\frac{D_m}{V}+\frac{k_1}{K_1}\frac{m}{V}\sum_{m=1}^{N}\frac{H_m}{V}$$

(equation (30))

$$-k_1\left(\frac{2g}{V}\right)^{0.6}\sum_{m=1}^{N}\frac{H_m}{V}+2\frac{k_1}{K_1}\frac{m}{V}\sum_{m=1}^{N}\frac{P_m}{V}$$

(equation (31))

$$+2k_3\sum_{m=1}^{N}\sum_{n=1}^{N}\frac{P_n}{V}\frac{P_m}{V}-4\frac{k_3}{K_3}\frac{g}{V}\sum_{n=1}^{N}(n-1)\frac{P_n}{V}$$

(equation (39))

$$+\frac{1}{2}k_3\sum_{m=1}^{N}\sum_{n=1}^{N}\frac{H_n}{V}\frac{H_m}{V}-4\frac{k_3}{K_3}\frac{g}{V}\sum_{n=1}^{N}(n-1)\frac{D_n}{V}$$

(equation (40))

$$+2k_3\sum_{m=1}^{N}\sum_{n=1}^{N}\frac{P_n}{V}\frac{H_m}{V}-4\frac{k_3}{K_3}\frac{g}{V}\sum_{n=1}^{N}(n-1)\frac{H_n}{V}\Bigg]$$

(equation (41))

$$\times\frac{C/V}{1+k(C/V)} \qquad (45)$$

The methanol content in the reaction mixture, m, was calculated as in the case of parameter estimation (equation (18)).

The effect of both reaction temperature and the ratio of DMT and EG in the feed on the chain length distribution was simulated by integrating equations (42)–(45) by means of a fourth-order Runge–Kutta method. The parameters given in equations (24)–(29) were used in the simulations. All the simulations assumed isothermal conditions for the reaction. To make the chain length distribution independent of the maximum oligomer length, simulations using different values of N were carried out. The chain length distribution was found to remain unchanged for $N > 9$. Therefore, this value was used in the simulations. *Figures 7–10* show the effect of reaction temperature on chain length distribution for

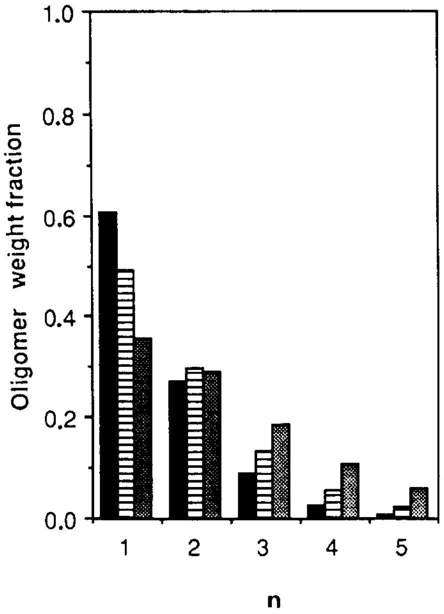

Figure 7 Effect of temperature on chain length distribution for DMT/EG = 1/2.4: ■, 180°C; ⊟, 190°C; ▨, 210°C

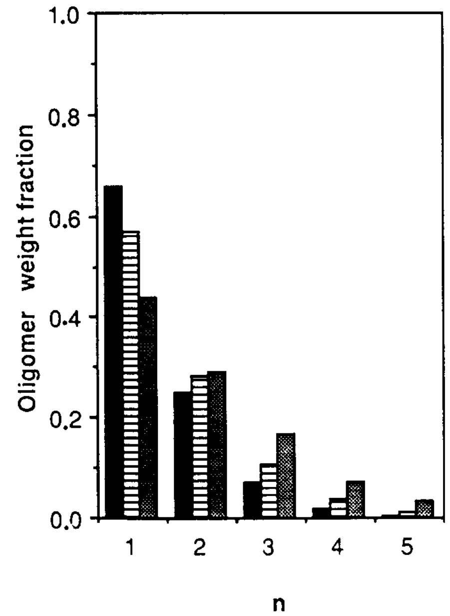

Figure 8 Effect of temperature on chain length distribution for DMT/EG = 1/2: ■, 180°C; ⊟, 190°C; ▨, 210°C

several DMT/EG ratios. It can be seen that, contrary to what has been reported based on methanol data[2–4], significant oligomerization occurs during the reaction of dimethyl terephthalate with ethylene glycol. In addition, it was found that the degree of polymerization increased when the reaction temperature increased and the ratio of DMT and EG decreased.

CONCLUSIONS

The extent of oligomerization during the reaction of dimethyl terephthalate and ethylene glycol was determined experimentally by measuring the number of ethylene diester groups by *FT*i.r. Kinetic analysis of the system was carried out by using the methanol withdrawn from the reactor and the ethylene diester groups as observable variables. Two models were considered in the kinetic analysis. In the first, the ester interchange reaction and the transesterification reaction were included. In the second, the ester interchange reaction, the transesterification reaction and the polycondensation reaction were included. The rate constants of the two models were estimated by means of a modified Gauss–Newton method for parameter estimation in differential equations. Both models were found to give a good fit to the experimental data. In addition, model discrimination was not possible because, on a statistical basis, there were no significant differences between the models. The effect of both reaction temperature and the ratio of DMT and EG in the feed on the chain length distribution was simulated by using the model including the three reactions and the values of the parameters estimated in the kinetic analysis. It was found that, contrary to what

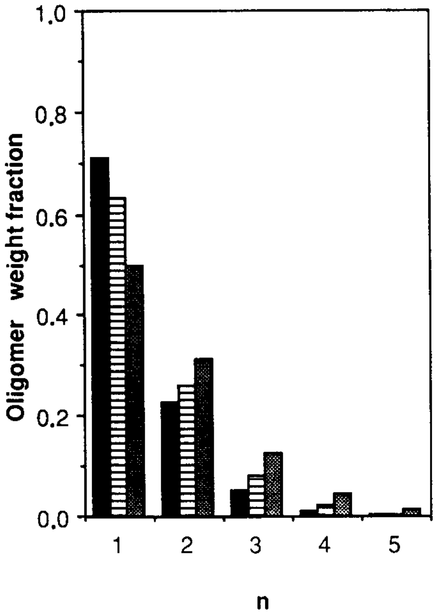

Figure 9 Effect of temperature on chain length distribution for DMT/EG = 1/1.8: ■, 180°C; ⊟, 190°C; ▨, 210°C

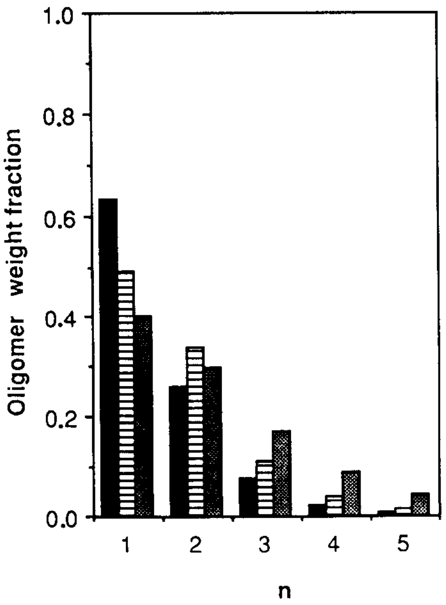

Figure 10 Effect of temperature on chain length distribution for DMT/EG = 1/1.6: ■, 180°C; ⊟, 190°C; ▨, 210°C

has previously been reported based on methanol data[2–4], significant oligomerization occur during the reaction of dimethyl terephthalate with ethylene glycol. In addition, the degree of polymerization was found to increase when the reaction temperature increased and the ratio DMT/EG decreased.

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NOMENCLATURE

C	Number of moles of catalyst
D_n	Number of moles of species with length n and two methyl ester end groups
d_f	Degrees of freedom
E_m, E_g	Number of groups of methyl ester and hydroxyethyl ester end groups, respectively
e_{m0}	Initial number of moles of methyl ester end groups
e_m, e_g	Number of moles of methyl ester and hydroxyethyl ester end groups, respectively
g_0	Initial number of moles of ethylene glycol
g	Number of moles of ethylene glycol
H_n	Number of moles of species with length n and one methyl ester and one hydroxyethyl ester end group
k	Kinetic constant in equations (14) and (15) ($l\,mol^{-1}$)
k_1	Fractionary order rate constant ($l^{1.6}\,mol^{-1.6}\,min^{-1}$)
k_2, k_3	Third order rate constants ($l^2\,mol^{-2}\,min^{-1}$)
K_1	Equilibrium constant ($mol^{0.4}\,l^{-0.4}$)
K_2, K_3	Equilibrium constants
m	Number of moles of methanol in the reactor
N	Maximum oligomer length
P_M, P_G	Partial pressure of methanol and ethylene glycol, respectively
P_n	Number of moles of species with length n and two hydroxyethyl ester end groups
P_T	Reactor total pressure
R	Gas constant ($cal\,mol^{-1}\,K^{-1}$)
s^2	Experimental error variance
T	Temperature (K)
T_{COO}	Total number of –COO groups
T_f	Final temperature (K)
V	Volume of reaction mixture (l)
z	Number of moles of ethylene diester groups
z^*	Number of ethylene diester groups per molecule of oligomer