Study of the significance of oligomerization in the reaction of dimethyl terephthalate with ethylene glycol by using methanol data

M. J. Barandiaran and J. M. Asúa*
Grupo de Ingenieria Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain
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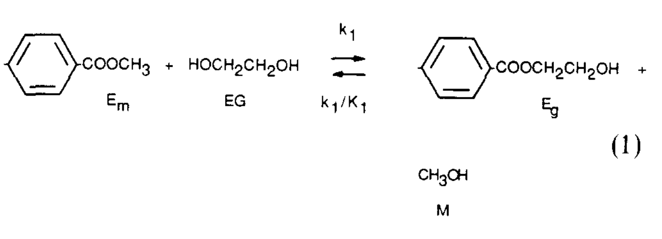
The importance of oligomerization during the reaction between dimethyl terephthalate and ethylene glycol was analysed by using as the only observed variable the methanol withdrawn from the reactor. Data obtained under a wide range of experimental conditions were used. Models including oligomerization reactions were used to fit experimental data and their performance compared by means of the χ^2 test with a model including only the ester interchange reaction. Contrary to what previous authors have reported, it is concluded that more observed variables are needed to elucidate the significance of oligomerization reactions.

(Keywords: oligomerization; dimethyl terephthalate; ethylene glycol; methanol data)

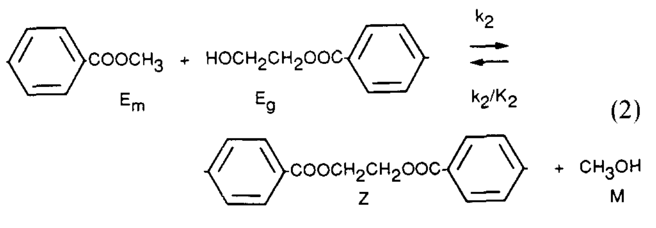
INTRODUCTION

Poly(ethylene terephthalate) (PET) is produced by polycondensation of bis(hydroxyethyl) terephthalate (BHET) or its oligomers. BHET may be synthesized both by the reaction of dimethyl terephthalate (DMT) and ethylene glycol (EG) and by the direct esterification of EG and terephthalic acid. Although direct esterification has recently gained importance, the DMT method remains the main process to obtain BHET.

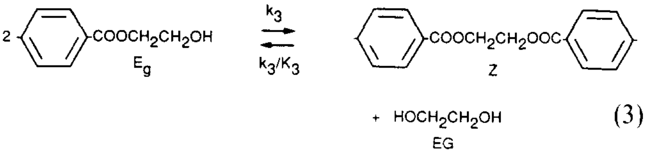
In the transesterification process, the extent of reaction has traditionally been followed by measuring the methanol withdrawn from the reactor. It has been shown[1] that a model based on the ester interchange reaction accounts for the methanol data obtained under a wide range of experimental conditions. Additionally, some attempts at using methanol data to elucidate the existence of oligomerization have been reported[2-4]. Oligomerization is produced through the following reactions:



(1)



(2)



(3)

To fit his methanol data, Fontana[2] developed a model based on reactions (1) and (2). He considered that the reactivity of -OH and groups of EG was twice that of -OH end groups of E_g, and assumed that this ratio was independent of temperature. This allowed the author to define an average reactivity of -OH end groups, which he used in parameter estimation. Yamanis and Adelman[3] pointed out that Fontana[2] forced the system to have a given degree of oligomerization by assuming a reactivity ratio $k_2/k_1 = 0.5$. Therefore, they extended Fontana's approach to the case with reactivity ratio an adjustable parameter. Yamanis and Adelman[3] fitted the non-isothermal methanol data of Fontana[2] by using the differential method of data analysis. They found that the data were well fitted by a reactivity ratio between 0.125 and 1. Since high values of reactivity ratio meant significant oligomerization and low values did not, the previously mentioned results did not allow any conclusion to be reached about the importance of oligomerization. Although, most of the data from Fontana[2] were non-isothermal, one experiment was almost isothermic (variations of 13°C were reported in the so-called isothermic experiment). Yamanis and Adelman[3] used the integral method of data analysis to fit that experiment, reporting that a very low value of reactivity ratio (≈ 0.01) was needed. Therefore, they concluded that oligomerization was negligible. The authors used the same approach to analyse the data of Peebles and Wagner[4] and Tomita and Ida[5], considering that those data were obtained under isothermal conditions. Although only one reaction from Tomita and Ida[5] was well fitted, Yamanis and

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* To whom correspondence should be addressed

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Adelman[3] claimed that for conversions of DMT of $<88\%$ and EG/DMT ratio $\geqslant 2$, oligomerization did not proceed to a significant extent. Ravindranath and Mashelkar[6] showed that some mistakes were made by Yamanis and Adelman[3] in the use of data from Tomita and Ida[5]. However, the conclusion reached by Yamanis and Adelman[3] did not change significantly.

To use the elegant approach proposed by Fontana[2] and Yamanis and Adelman[3], isothermal data are needed because the definition of the average reactivity of -OH end groups implies that quotient k_2/k_1 should be independent of temperature. Except for the trivial case of equal activation energies, this condition is only fulfilled under isothermal conditions. However, because of the experimental method used in these experiments (heating the DMT in the reactor until its melting point, ≈140°C, then adding the EG and the catalyst and heating again until the temperature reaches its final value, ≈190°C) the reactions were done in a very non-isothermal way. The non-isothermic character of the process has been clearly shown in cases where the internal reactor temperature was measured and reported[1,2].

The aim of the present work is to determine whether the importance of oligomerization can be elucidated by using as the only observed variable the methanol withdrawn from the reactor. To achieve this goal, the methanol data of Barandiaran and Asua[1] have been fitted by models including either reactions (1) and (2) or reactions (1)–(3). An algorithm for parameter estimation in differential equations based on the Gauss–Newton method[7] improved with the Marquardt extension[8] was used. These models and the one including only reaction (1), previously reported by Barandiaran and Asúa[1], were discriminated by means of the χ^2 test[9].

MODEL DESCRIPTION

To avoid repetition, only the model including the three reactions will be presented. From this model, the model considering ester interchange and transesterification reactions may easily 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:

$$\mathrm{E_m + EG} \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} \mathrm{E}_g + \mathrm{M} \tag{4}$$

$$\mathrm{E_m + E_g} \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} \mathrm{Z + M} \tag{5}$$

$$\mathrm{2E_g} \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} \mathrm{Z + EG} \tag{6}$$

Let us assume that the dependences with respect to the concentrations of ester groups, EG and catalyst found when methanol data were adjusted by a model including only the ester interchange reaction[1] hold when more reactions are included in the model. Therefore, first-order dependence with respect to ester groups, order 0.6 dependence for EG in the ester interchange reaction but first-order dependence in the polycondensation reaction, and hyperbolic dependence of reaction rate on catalyst concentration are included in the following material balances:

$$\frac{1}{V}\frac{\mathrm{d}e_\mathrm{m}}{\mathrm{d}t} = \left[-k_1\frac{e_\mathrm{m}}{V}\left(\frac{2g}{V}\right)^{0.6} + \frac{k_1}{K_1}\frac{e_\mathrm{g}}{V}\frac{m}{V} - k_2\frac{e_\mathrm{m}}{V}\frac{e_\mathrm{g}}{V} + \frac{k_2}{K_2}\frac{2z}{V}\frac{m}{V}\right] \times \left[\frac{C/V}{1+k(C/V)}\right] \tag{7}$$

$$\frac{1}{V}\frac{\mathrm{d}g}{\mathrm{d}t} = \left[-k_1\frac{e_\mathrm{m}}{V}\left(\frac{2g}{V}\right)^{0.6} + \frac{k_1}{K_1}\frac{e_\mathrm{g}}{V}\frac{m}{V} + k_3\left(\frac{e_\mathrm{g}}{V}\right)^2 - \frac{k_3}{K_3}\frac{2z}{V}\frac{2g}{V}\right] \times \left[\frac{C/V}{1+k(C/V)}\right] \tag{8}$$

where V is the reactor volume, e_m, e_g and z are equivalents of methyl ester, hydroxyethyl ester end groups and ethylene diester groups between two aromatic rings, respectively, m and g are moles of methanol and ethylene glycol in the reaction mixture and C is the number of moles of catalyst.

The parameters e_m, e_g and z may be calculated from the material balance of functional groups:

$$e_\mathrm{m} = e_{\mathrm{m}0} - m_\mathrm{T} \tag{9}$$

$$e_\mathrm{g} = 2(g_0 - g) - m_\mathrm{T} \tag{10}$$

$$z = m_\mathrm{T} - (g_0 - g) \tag{11}$$

where m_T is the total number of moles of methanol produced:

$$m_\mathrm{T} = m + m_\mathrm{R} \tag{12}$$

m_R being the methanol withdrawn from the reactor.

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

$$P_\mathrm{T} = P_\mathrm{M} + P_\mathrm{G} \tag{13}$$

where P_T is the reactor pressure and P_M and P_G the partial pressures of methanol and ethylene glycol, respectively. These partial pressures were calculated through the Flory–Huggins relationship[10].

PARAMETER ESTIMATION AND MODEL DISCRIMINATION

Parameters were estimated for the two models by means of a modified Gauss–Newton method for differential equations proposed by Hwang and Seinfeld[7]. Convergence was enhanced through a Marquardt like approach[8].

Reparametrization was performed by writing the rate constants in an equivalent mathematical form as follows:

$$k_{i0}\exp[-E_i/RT] = k'_{i0}\exp[(-E_i/R)(1/T - 1/T^*)] \tag{14}$$

where T^* is the mean temperature of all experiments.

Model based on the ester interchange reaction

Parameter estimation of the model including only the ester interchange reaction was presented in a previous paper[1]. The following values of the estimated parameters were obtained:

$$k_1 = (28.68 \pm 1.13) \times \exp\{-[14\,650 \pm 236)/R](1/T - 1/460)\} \quad (\mathrm{l}^{1.6}\,\mathrm{mol}^{-1.6}\,\mathrm{min}^{-1}) \quad (15)$$

$$k_1/K_1 = (82.24 \pm 5.66) \times \exp\{-[15\,705 \pm 300)/R](1/T - 1/460)\} \quad (\mathrm{l}^{2}\,\mathrm{mol}^{-2}\,\mathrm{min}^{-1}) \quad (16)$$

Model based on ester interchange and transesterification reactions

First, parameters were estimated by using the equilibrium constant given by Challa [11]. *Figure 1* shows that poor agreement between model prediction and experimental values was obtained. Therefore, equilibrium constants were included in the set of parameters to be estimated, giving the following results:

$$k_1 = (37.01 \pm 2.57) \times \exp\{-[(16\,500 \pm 390)/R](1/T - 1/460)\} \quad (\mathrm{l}^{1.6}\,\mathrm{mol}^{-1.6}\,\mathrm{min}^{-1}) \quad (17)$$

$$k_2 = (5.43 \pm 0.41) \times \exp\{-[11\,880 \pm 460)/R](1/T - 1/460)\} \quad (\mathrm{l}^{2}\,\mathrm{mol}^{-2}\,\mathrm{min}^{-1}) \quad (18)$$

$$k = 420 \quad (\mathrm{l\,mol}^{-1}) \quad (19)$$

$$K_1 = 15 \times 10^{-5}\exp(6000/RT) \quad (\mathrm{mol}^{0.4}\,\mathrm{l}^{-0.4}) \quad (20)$$

$$K_2 = 0.25 \quad (\mathrm{mol}^{0.4}\,\mathrm{l}^{-0.4}) \quad (21)$$

Figures 2 and *3* show that good agreement between model predictions and experimental data was achieved with the parameters given by equations (17)–(21). Note that the rate constant values indicate significant oligomerization.

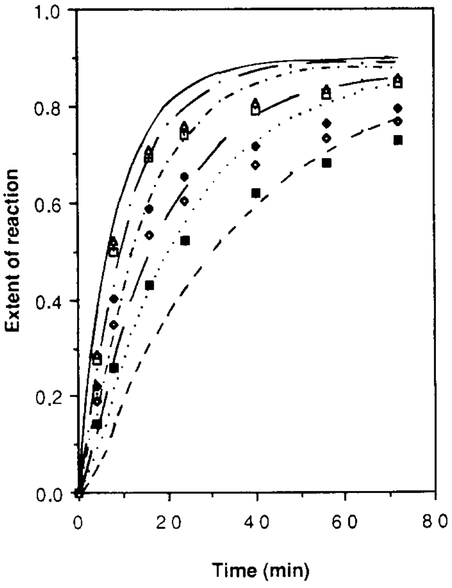

Figure 1 Comparison between experimental results obtained at different catalyst concentration and predictions of a model including ester interchange and transesterification reactions, with reversible reactions and Challa's equilibrium constants. Data are from Reference 1. Catalyst content (mol): ■, ––––––, 0.8 × 10^{-4}; ◇, ·········, 1.2 × 10^{-4}; ◆, ———, 1.6 × 10^{-4}; □, –·–·–·–, 2.4 × 10^{-4}; +, —·—·—, 4.0 × 10^{-4}; △, ————, 6.0 × 10^{-4}

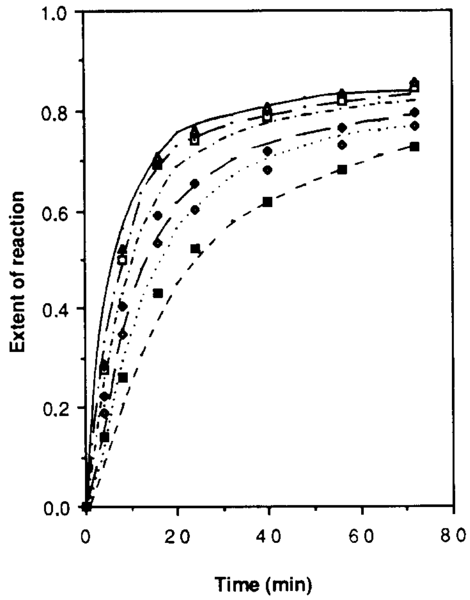

Figure 2 Fit of experimental results by the model including ester interchange and transesterification reactions, with reversible reactions and estimated equilibrium constants. Final reaction temperature was 190°C. Data are from Reference 1. Symbols are explained in *Figure 1*

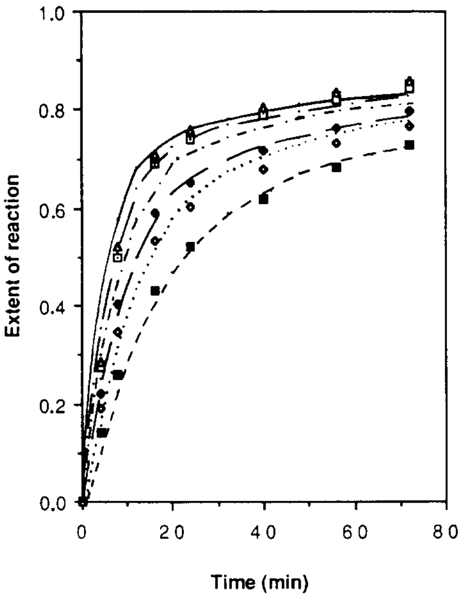

Figure 3 Fit of experimental results by the model including ester interchange and transesterification reactions, with reversible reactions and estimated equilibrium constants. Final reaction temperature was 195°C. Data are from Reference 1. Symbols are explained in *Figure 1*

Model based on ester interchange, transesterification and polycondensation reactions

Parameters were estimated by keeping $k = 420\,\mathrm{l\,mol}^{-1}$. The following values of the parameters were obtained:

$$k_1 = (36.79 \pm 1.30) \times \exp[-((15\,100 \pm 370)/R)(1/T - 1/460)] \quad (\mathrm{l}^{1.6}\,\mathrm{mol}^{-1.6}\,\mathrm{min}^{-1}) \quad (22)$$

$$k_2 = (4.98 \pm 0.37) \times \exp[-((13\,000 \pm 265)/R)(1/T - 1/460)] \quad (\mathrm{l}^{2}\,\mathrm{mol}^{-2}\,\mathrm{min}^{-1}) \quad (23)$$

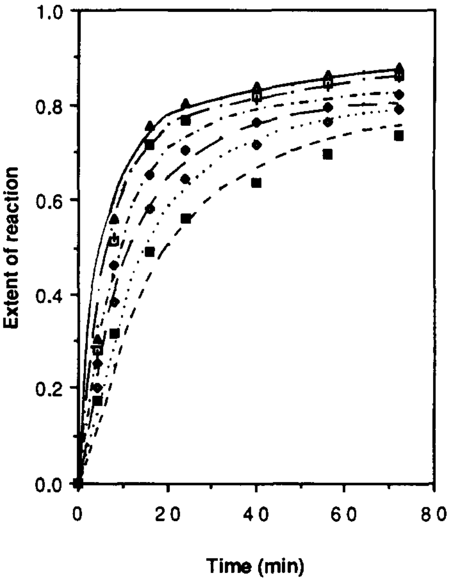

Figure 4 Comparison between experimental results and predictions of a model based on ester interchange, transesterification and polycondensation reactions. Final reaction temperature was 190°C. Data are from Reference 1. Symbols are explained in *Figure 1*

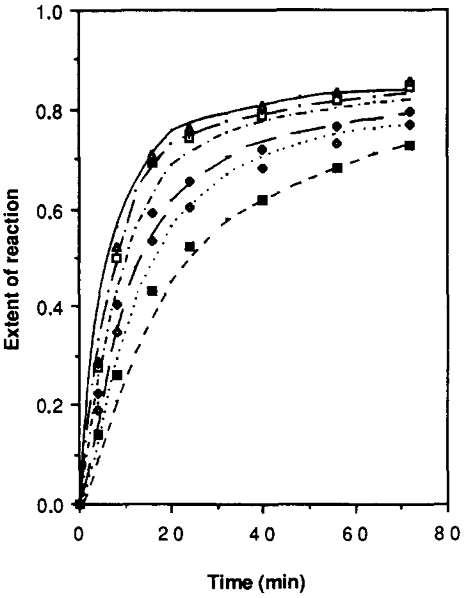

Figure 5 Fit of experimental results by the model including ester interchange, transesterification and polycondensation reactions. Final reaction temperature was 195°C. Data are from Reference 1. Symbols are explained in *Figure 1*

$$k_3 = (0.09 \pm 0.01) \times \exp[-((10\,800 \pm 420)/R)(1/T - 1/460)] \quad (\mathrm{l^2\,mol^{-2}\,min^{-1}}) \qquad (24)$$

$$K_1 = 15 \times 10^{-5} \exp(6000/RT) \quad (\mathrm{mol^{0.4}\,l^{-0.4}}) \qquad (25)$$

$$K_2 = 0.25 \qquad (26)$$

$$K_3 = 0.40 \qquad (27)$$

Figures 4 and *5* show that, as for the model based on reactions 1 and 2, experimental data are well fitted by the model including the three reactions.

Table 1 Data for the χ^2 test of discrimination between models

Model	Parameters	d_f	s^2
Reaction 1	3	429	12.339×10^{-4}
Reactions 1 and 2	4	428	7.874×10^{-4}
Reactions 1–3	6	426	8.528×10^{-4}

Model discrimination

To determine which of the models described best fitted the methanol data, a χ^2 test of discrimination between models was used. *Table 1* presents the data needed to perform the discrimination. Considering the three models, the calculated value of χ^2 was 26.02 which is greater than that obtained from the χ^2 distribution with a confidence interval of 95%: χ^2 (2, 0.95) = 5.99[12]. This means that the error distributions were not homogeneous and the model with the greatest sum of error squares should be rejected. Therefore, the model including only reaction 1 was rejected and the χ^2 test was applied to the other two models. In this case, the calculated value of χ^2 was 0.654, lower than that obtained from the distribution[12]: χ^2 (1, 0.95) = 3.84. Therefore, on a statistical basis, no significant differences between the models were found and, hence, the models based on two and three reactions cannot be discriminated. Note that this result is based on extensive experimental data obtained under a wide range of experimental conditions.

CONCLUSIONS

It has been shown that models including two and three reactions fitted the methanol data better than the model including only the interchange reaction. Additionally, equilibrium constants slightly different from those reported by Challa[1] were obtained with models including two and three reactions. Nevertheless, it may be argued that the better fit was due to the larger number of parameters involved in those models. Therefore, with only methanol data, there was no strong basis to conclude that oligomerization proceeded to a significant extent during the reaction of DMT and EG. However, it is evident that, contrary to what has been reported by previous authors[3,4], there were no grounds for neglecting the importance of transesterification and polycondensation reactions. As a consequence, the importance of oligomerization reactions cannot be evaluated by using as the only observed variable the methanol withdrawn from the reactor. To do this, more information, i.e. the number of groups Z, needs to be available.

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NOMENCLATURE

C	Number of moles of catalyst
d_f	Degrees of freedom
E_i	Activation energy (cal mol^{-1})
e_m, e_g	Number of equivalents of methyl and glycol ester end groups
g	Number of moles of ethylene glycol
g_0	Initial number of moles of ethylene glycol
k	Kinetic constant in equation (7) (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
m_R	Number of moles of methanol removed from the reactor
m_T	Total number of moles of methanol produced
P_M, P_G	Partial pressure of methanol and ethylene glycol, respectively
P_T	Reactor total pressure
R	Gas constant (cal mol^{-1} K^{-1})
s^2	Experimental error variance
T	Temperature (K)
V	Volume of reaction mixture (l)
z	Number of equivalents of diester groups