

# Kinetics of Transesterification of Dimethylene Terephthalate with Ethylene Glycol\*

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## Synopsis

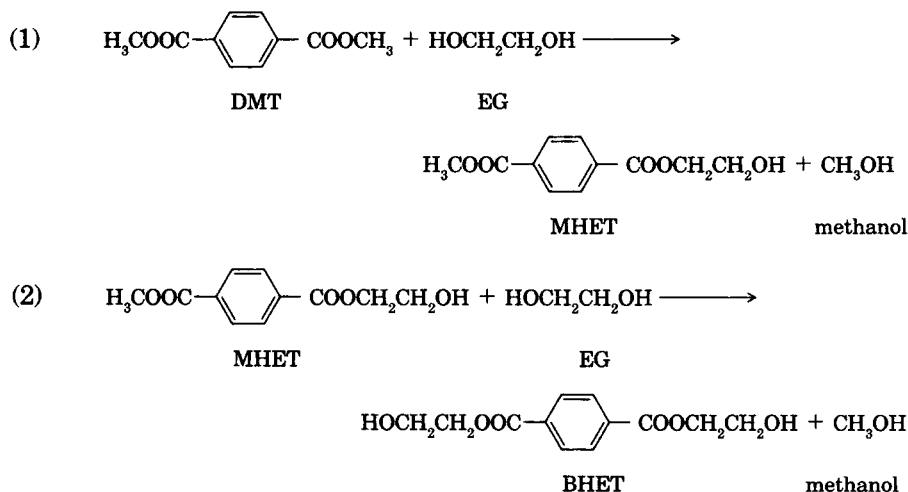
There is a disagreement about the order of reaction of transesterification of DMT with EG. The reactivity of the two ester groups is not compared yet. The transesterification of DMT and MHET is studied to establish the kinetics of the process. Attempts are made to treat the kinetic data on a mathematical model for third-order reaction.

## INTRODUCTION

The transesterification reaction is an essential part of the manufacturing process of polyethylene terephthalate. The success of this reaction depends mainly on the reaction conditions chosen. The degree of purity of raw materials and technical arrangement of the ester interchange equipment also play a part.

The transesterification reaction is strongly dependent on a catalyst; without addition of a catalyst it proceeds very slowly. The kinetics of the catalytic transesterification has received the attention of several investigators. Griehl and Schnock<sup>1</sup> concluded that the reaction is of second order (including catalyst) whereas Fontana<sup>2</sup> concluded it to be of third order. Peebles and Wagner<sup>3</sup> could not conclusively determine the order of reaction.

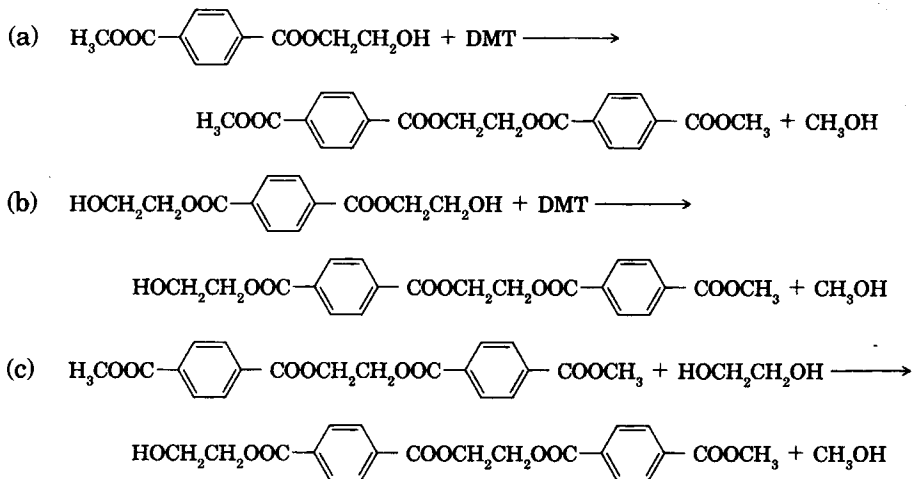
The aim of the present work is to examine the kinetics of transesterification in more detail to establish the order of reaction. For this purpose only the two prominent reactions may be considered.



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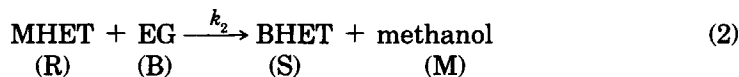
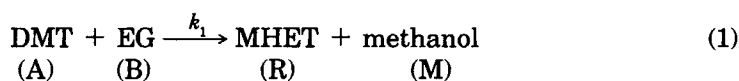
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The experimental conditions for the present study chosen involve the use of excess of ethylene glycol (EG) and the continuous removal of liberated methanol. Under these conditions, the following reactions can be conveniently neglected:

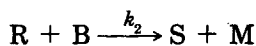
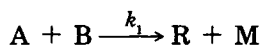


### Mathematical Treatment

The following abbreviations are used: A = dimethyl terephthalate (DMT); B = ethylene glycol (EG); R = methyl, hydroxyethyl terephthalate (MHET); M = methanol (M); S = bishydroxyethyl terephthalate (BHET); C = catalyst; V = Reaction volume (mL);  $k_1$  = third-order rate constant for reaction (1) mL<sup>2</sup>/mol<sup>2</sup> min;  $k_2$  = Third order rate constant for reaction (2) mL<sup>2</sup>/mol<sup>2</sup> min;  $N_i$  = moles of species  $i$ ;  $N_{i0}$  = moles of species  $i$  at zero time;  $t$  = time (min);  $x$  = conversion. The reaction system can be represented as



Thus,



Assuming that the reactions are of first order with respect to each reactant, viz., DMT, MHET, EG, and the catalyst, the mathematical treatment may be given as follows: Rate of disappearance of A

$$-\frac{1}{V} \frac{dN_A}{dt} = k_1 \left( \frac{N_A}{V} \right) \left( \frac{N_B}{V} \right) \left( \frac{N_C}{V} \right) \quad (3)$$

and rate of formation of R

$$-\frac{1}{V} \frac{dN_R}{dt} = \left[ -k_1 \left( \frac{N_A}{V} \right) \left( \frac{N_B}{V} \right) + k_2 \left( \frac{N_R}{V} \right) \left( \frac{N_B}{V} \right) \right] \left( \frac{N_C}{V} \right) \quad (4)$$

Reactivity of methylester group in DMT and MHET has been assumed to be the same. Therefore,  $k_1 = 2k_2$ . Hence eq. (4) becomes

$$\frac{1}{V} \frac{dN_R}{dt} = k_1 \left( \frac{N_C}{V} \right) \left( \frac{N_B}{V} \right) \left[ \frac{N_A}{V} - 0.5 \left( \frac{N_R}{V} \right) \right] \quad (5)$$

Dividing (5) by (3), we obtain

$$\frac{dN_R}{dN_A} = -1 + 0.5 \left( \frac{N_R}{N_A} \right) \quad (6)$$

Solving this differential equation with initial condition at  $t = 0$ ,  $N_A = N_{A0}$ ,  $N_B = N_{B0}$ , and  $N_R = 0$ , we obtain

$$N_R = \frac{N_A}{0.5} \left[ \left( \frac{N_{A0}}{N_A} \right)^{0.5} - 1 \right]$$

or

$$N_R = 2N_A \left[ \left( \frac{N_{A0}}{N_A} \right)^{0.5} - 1 \right] \quad (7)$$

The mole balance for ethylene glycol is

$$N_{B0} = N_B + N_R + 2N_S \quad (8)$$

Also,

$$N_{B0} = N_B + N_M \quad (9)$$

The mole balance for DMT is

$$N_{A0} = N_A + N_R + N_S \quad (10)$$

Simplifying, we obtain

$$N_B = N_{B0} - N_M \quad (11)$$

$$N_R = -2(N_A - N_{A0}) - N_M \quad (12)$$

$$N_S = N_A - N_{A0} + N_M \quad (13)$$

Comparing (7) and (12), we obtain

$$2(N_{A0} - N_A) - N_M = -2N_A + 2N_A^{0.5}N_{A0}^{0.5}$$

Therefore,

$$N_A^{0.5} = \left( \frac{2N_{A0} - N_M}{2N_{A0}^{0.5}} \right) \quad (14)$$

or

$$N_A = \frac{(2N_{A0} - N_M)^2}{4N_{A0}}$$

Now the rate of methanol formation

$$-\frac{1}{V} \frac{dN_M}{dt} = -k_1 \frac{N_C}{V} \left[ \left( \frac{N_A}{V} \right) \left( \frac{N_B}{V} \right) + 0.5 \left( \frac{N_R}{V} \right) \left( \frac{N_B}{V} \right) \right]$$

Let the apparent rate constant  $k_a = k_1 N_C$ . Therefore,

$$\frac{dN_M}{dt} = \frac{k_a N_B (N_A + 0.5 N_R)}{V^2}$$

Therefore,

$$\frac{dN_M}{N_B (N_A + 0.5 N_R) / V^2} = k_a dt$$

Let

$$N_B (N_A + 0.5 N_R) / V^2 = y_{N_M}$$

$$V = V_0(1 - \epsilon x) \quad \text{and} \quad \epsilon = \frac{V_0 - V_{\text{final}}}{V_0}$$

Therefore,

$$\frac{dN_M}{y_{N_M}} = k_a dt$$

Integrating, we obtain

$$\int_0^{N_M} \frac{dN_M}{y_{N_M}} = k_a t$$

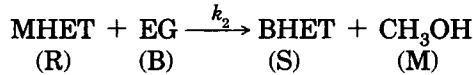
Let  $lhs = Y_{NM}$ . Thus  $Y_{NM} = k_a t$ .

If the mathematical model holds good then plot of  $Y_{NM}$  vs.  $t$  will be a straight line passing through the origin and with slope equal to the apparent rate constant  $k_a$ .

From the knowledge of  $k_a$ , the true rate constant  $k_1$  can be calculated by

$$k_1 = \frac{k_a}{N_C} \frac{mL^2}{\text{mol}^2 \text{ min}}$$

There is no evidence in literature to assume that the reactivity of methyl ester group in DMT and MHET is same. Therefore, the transesterification of MHET may also be treated as follows:



$$-\frac{1}{V} \frac{dN_R}{dt} = k_2 \frac{N_R}{V} \frac{N_B}{V} \frac{N_C}{V} \tag{15}$$

Conversion

$$\begin{aligned} x &= \frac{N_{R0} - N_R}{N_{R0}} = \frac{N_M}{N_{R0}} \\ N_R &= N_{R0} (1 - x) \end{aligned} \tag{16}$$

Also

$$\begin{aligned} N_B &= N_{B0} - N_M \\ &= N_{B0} - N_{R0} x \\ &= N_{R0} \left( \frac{N_{B0}}{N_{R0}} - x \right) \end{aligned}$$

Taking  $N_{B0} = N_{R0}$ , we obtain

$$N_B = N_{R0}(1 - x) \tag{17}$$

Substituting (16) and (17) in (15), we obtain

$$N_{R0} \frac{dx}{dt} = \frac{k_2 N_{R0}(1 - x) N_{R0}(1 - x) N_C}{V^2}$$

Therefore,

$$\frac{dx}{dt} = \frac{k_2 N_{R0} N_C (1 - x)^2}{V_0^2 (1 - \epsilon x)^2}$$

TABLE I  
Kinetic Data on Transesterification of DMT at 170°C<sup>a</sup>

Time (min)	$N_M$	$N_B$	$x$	$V$	$N_A$	$N_R$	$y_{NM} \times 10^5$	$(1/y_{NM}) \times 10^{-5}$	$Y_{NM} \times 10^{-4}$
0	0.0000	0.8950	0.000	117.7	0.311	0.000	2.01	0.498	0.00
15	0.2000	0.6950	0.320	109.1	0.143	0.136	1.23	0.813	1.32
30	0.3025	0.5925	0.486	104.6	0.082	0.155	0.86	1.163	2.30
45	0.3875	0.5075	0.623	100.9	0.044	0.146	0.58	1.712	3.56
60	0.4600	0.4350	0.740	97.7	0.021	0.120	0.37	2.717	5.06

<sup>a</sup> DMT = 60.322 g = 0.311 mol; EG = 55.5 g = 0.895 mol; zinc acetate catalyst = 0.0145 g = 6.621  $\times 10^{-5}$  mol;  $\epsilon = 0.23$ .

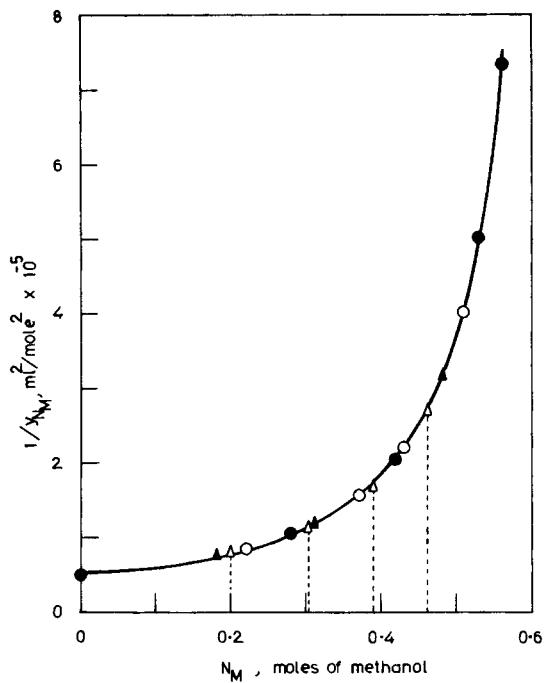


Fig. 1. Relationship between  $1/y_{N_M}$  and  $N_M$  for the transesterification of DMT: (●) 190°C; (○) 185°C; (▲) 175°C; (△) 170°C.

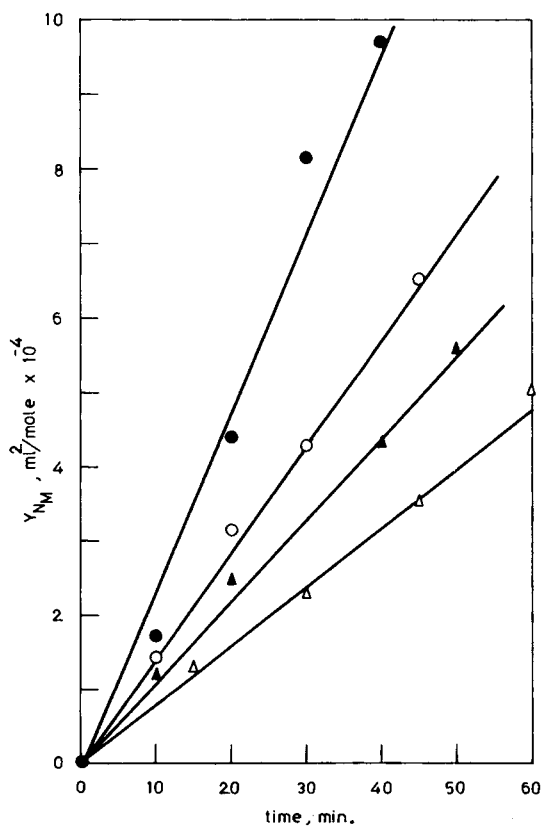


Fig. 2. Relationship between  $Y_{N_M}$  and time for the transesterification of DMT: (●) 190°C; (○) 185°C; (▲) 175°C; (△) 170°C.

TABLE II  
Kinetic Data on Transesterification of MHET at 170°C<sup>a</sup>

Time (min)	$N_M$	$x$	$Y_x$
0	0	0.0000	0.00
15	0.0475	0.2375	0.30
30	0.0875	0.4375	0.72
45	0.1025	0.5125	0.95
60	0.1200	0.6000	1.33

<sup>a</sup> MHET = 44.5 g = 0.2 mol; EG = 12.4 g = 0.2 mol; zinc acetate catalyst = 0.0140 g =  $6.393 \times 10^{-5}$  mol;  $\epsilon = 0.155$ .

Let apparent rate constant

$$k'_a = \frac{k_2 N_{R0} N_C}{V_0^2}$$

Then

$$\frac{(1 - \epsilon x)^2}{(1 - x)^2} dx = k'_a dt$$

Integrating, we obtain

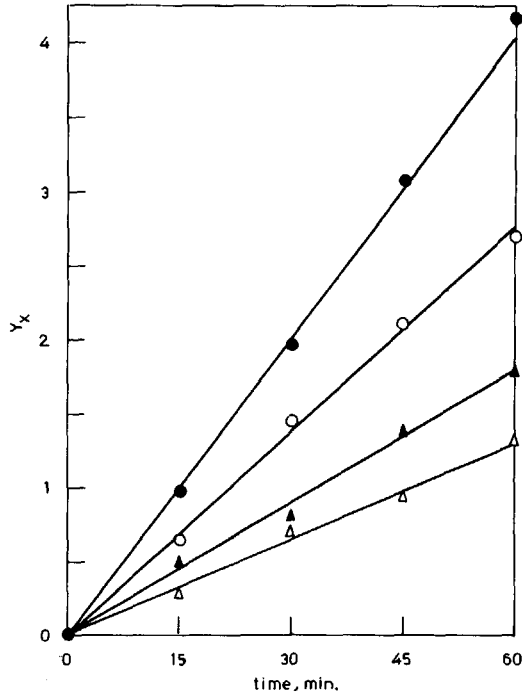


Fig. 3. Relationship between  $Y_x$  and time for the transesterification of MHET: (●) 190°C; (○) 185°C; (▲) 175°C; (△) 170°C.



TABLE III  
Kinetic Data on Transesterification of DMT at 175°C\*

Time (min)	$N_M$	$N_B$	$x$	$V$	$N_A$	$N_R$	$y_{NM} \times 10^5$	$(1/y_{NM}) \times 10^{-5}$	$Y_{NM} \times 10^{-4}$
0	0	0.8950	0.000	117.7	0.311	0.000	2.01	0.498	0.00
10	0.1800	0.7150	0.270	109.9	0.157	0.128	1.31	0.764	1.23
20	0.3125	0.5825	0.502	104.2	0.077	0.155	0.83	1.205	2.48
40	0.4300	0.4650	0.691	98.9	0.030	0.133	0.46	2.193	4.32
50	0.4800	0.4150	0.770	96.7	0.016	0.110	0.32	3.175	5.60

\* DMT = 60.322 g = 0.311 mol; EG = 55.5 g = 0.895 mol; zinc acetate catalyst = 0.0154 g =  $7.032 \times 10^{-5}$  mol;  $\epsilon = 0.23$ .

TABLE IV  
Kinetic Data on Transesterification of MHET at 175°C<sup>a</sup>

Time (min)	$N_M$	$x$	$Y_x$
0	0.0000	0.0000	0.00
15	0.0700	0.3500	0.51
30	0.0950	0.4750	0.82
45	0.1225	0.6125	1.39
60	0.1350	0.6750	1.80

<sup>a</sup> MHET = 44.8 g = 0.2 mol; EG = 12.4 g = 0.2 mol; zinc acetate catalyst = 0.0137 g =  $6.256 \times 10^{-5}$  mol;  $\epsilon = 0.155$ .

$$\int_0^x \frac{(1 - 2\epsilon x + \epsilon^2 x^2)}{(1 - x)^2} dx = k'_a \int_0^t dt \quad (18)$$

Hence

$$\frac{(1 - \epsilon)^2 x}{(1 - x)} + \epsilon^2 x^2 - 2\epsilon(1 - \epsilon) \ln(1 - x) = k'_a t$$

Let lhs =  $Y_x$ . Then, if the mathematical model holds good, the plot of  $Y_x$  vs.  $t$  should be a straight line passing through origin with slope equal to apparent rate constant  $k'_a$ . From the knowledge of  $k'_a$ , the true rate constant  $k_2$  can be calculated as

$$k_2 = \frac{k'_a V_0^2}{N_{R0} N_C} \frac{\text{mL}^2}{\text{mol}^2 \text{min}}$$

Experimental work was undertaken to test these models.

### EXPERIMENTAL

**Materials:** DMT (polymerization grade); EG (polymerization grade); zinc acetate; MHET (prepared by the SPRC process<sup>4</sup>). All experiments were carried out in a Corning three-necked flask.

The reaction vessel was charged with 60 g DMT and 50 g EG. The vessel was heated in an oil bath to melt the charge and bring the temperature. The thermometers were located in reaction mixture and in the bath. The catalyst was dissolved separately in 5 g EG, and the reaction was started by adding this mixture to the charge maintained at the desired temperature.

A packed column was provided to separate methanol and ethylene glycol, and the system was lagged up to the condenser. Chilled water was circulated through condenser, and the methanol collector was kept in an ice bath.

The same experimental set up was used for the experiments with MHET charge, wherein 44.8 g MHET and 12.4 g EG were used.

No reaction occurred prior to the catalyst addition and methanol was almost explosively evolved upon the addition of catalyst; because of this, the zero time was the time of addition of catalyst.

TABLE V  
Kinetic Data on Transesterification of DMT at 185°C<sup>a</sup>

Time (min)	$N_M$	$N_B$	$x$	$V$	$N_A$	$N_R$	$y_{NM} \times 10^5$	$(1/y_{NM}) \times 10^{-5}$	$Y_{NM} \times 10^{-4}$
0	0.00	0.895	0.00	118.2	0.313	0.000	2.01	0.496	0.00
10	0.22	0.675	0.35	108.6	0.132	0.143	1.16	0.858	1.43
20	0.37	0.525	0.59	102.1	0.052	0.151	0.64	1.563	3.17
30	0.43	0.465	0.69	99.0	0.031	0.129	0.45	2.208	4.28
45	0.51	0.388	0.81	95.7	0.011	0.096	0.25	4.000	6.52

<sup>a</sup> DMT = 60.76 g = 0.313 mol; EG = 55.5 g = 0.895 mol; zinc acetate catalyst = 0.0147 g =  $6.71 \times 10^{-5}$  mol;  $\epsilon = 0.231$ .

TABLE VI  
Kinetic Data on Transesterification of MHET at 185°C<sup>a</sup>

Time (min)	$N_M$	$x$	$Y_x$
0	0.0000	0.0000	0.00
15	0.0825	0.4125	0.65
30	0.1250	0.6250	1.46
45	0.1425	0.7125	2.11
60	0.1525	0.7625	2.69

<sup>a</sup> MHET = 44.8 g = 0.2 mol; EG = 12.4 g = 0.2 mol; zinc acetate catalyst = 0.0166 g =  $7.56 \times 10^{-5}$  mol;  $\epsilon = 0.155$ .

The reactants were stirred at sufficiently high speed to eliminate mass transfer constraints.

### RESULTS

Data on analysis of a typical run is shown in Table I. The relationship between  $1/y_{N_M}$  and  $N_M$  is shown in Figure 1. The area under the curve from  $N_M = 0$  to  $N_M = N_M$  gives the value of  $Y_{N_M}$  as shown in Table I.

$Y_{N_M}$  is correlated with time in Figure 2 and the slope of this plot gives the apparent rate constant  $k_a$ . The slope of this plot is 791.11 (mL<sup>2</sup>/mol min):

$$k_1 = -791.11/6.621 \times 10^{-5} = 11.95 \times 10^6 \text{ mL}^2/\text{mol}^2 \text{ min}$$

Similarly Table II contains the data on analysis of a typical run carried out with MHET at 170°C. The relationship between  $Y_x$  and time is shown in Figure 3. The slope of this plot gives the apparent rate constant  $k'_a$ . The slope of this plot is 0.0218 min<sup>-1</sup>:

$$\begin{aligned} k_2 &= 0.0218 \times V_0^2/N_C \times N_{R0} = 0.0218 \times 56.036^2/(0.0140/219) \times 0.2 \\ &= 5.35 \times 10^6 \text{ mL}^2/\text{mol}^2 \text{ min} \end{aligned}$$

The data for other runs are given in Tables III–VIII. Summary of the values of  $k_1$  and  $k_2$  obtained at various temperatures is given in Table IX.

Activation energy for the two reactions is obtained from Arrhenius plots (Fig. 4). From Figure 4 the activation energy for reaction (1) is 14.34 kcal/mol and that for reaction (2) is 14.69 kcal/mol.

Thus experiments with zinc acetate catalyst gave the third-order rate constant. The rate constants are given by the equations (least-squares fit)

$$\ln k_1 = -7216/T + 32.625$$

where  $T$  is the temperature (K) and

$$\ln k_2 = -7392/T + 32.245$$

### DISCUSSION

The results clearly demonstrate that the reaction is of the first order with respect to each reactant, i.e., the total order of reaction is 3. Thus all

TABLE VII  
Kinetic Data on Transesterification of DMT at 190°C<sup>a</sup>

Time (min)	$N_M$	$N_B$	$x$	$V$	$N_A$	$N_R$	$\gamma_{NM} \times 10^5$	$(1/\gamma_{NM}) \times 10^{-5}$	$Y_{NM} \times 10^{-4}$
0	0.00	0.895	0.00	118.2	0.313	0.000	2.01	0.49	0.00
10	0.28	0.615	0.45	106.0	0.096	0.155	0.95	1.05	1.73
20	0.42	0.475	0.67	99.9	0.034	0.138	0.49	2.04	4.40
30	0.53	0.368	0.84	95.3	0.008	0.089	0.20	5.02	8.14
40	0.56	0.340	0.88	94.1	0.004	0.063	0.14	7.34	9.70

<sup>a</sup> DMT = 60.76 g = 0.313 mol; EG = 55.5 g = 0.895 mol; zinc acetate catalyst = 0.0209 g = 9.543 × 10<sup>-5</sup> mol;  $\epsilon = 0.231$ .

TABLE VIII  
Kinetic Data on Transesterification of MHET at 190°C<sup>a</sup>

Time (min)	$N_M$	$x$	$Y_x$
0	0.0000	0.0000	0.00
15	0.1050	0.5250	0.99
30	0.1400	0.7000	1.99
45	0.1575	0.7875	3.07
60	0.1675	0.8375	4.17

<sup>a</sup> MHET = 44.8 g = 0.2 mol; EG = 12.4 g = 0.2 mol; zinc acetate catalyst = 0.0199 g =  $9.087 \times 10^{-5}$  mol;  $\epsilon = 0.155$ .

TABLE IX  
Rate Constants for Transesterification of DMT and MHET

Temp. (°C)	$k_1 \times 10^{-6}$	$k_2 \times 10^{-6}$
170	11.95	5.35
175	15.64	7.53
185	21.28	9.57
190	24.88	11.76

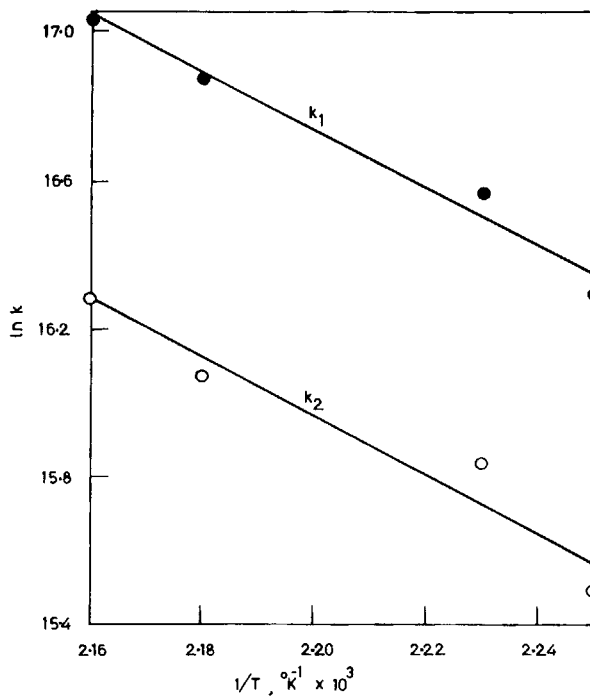


Fig. 4. Relationship between  $\ln k$  and  $1/T$ .

the data fit very well with the mathematical models developed on this assumption.

The transesterification of the two ester groups in DMT takes place in the same fashion giving almost expected rate constants and activation energy for the reaction. However, the rate constant values for the transesterification of MHET are always slightly less than the expected values from  $k_1$  (i.e.,  $k_1/2$ ). It is difficult to reject this observation as an experimental error. It will be interesting to find out whether the reactivity of the second ester group is in fact reduced by the introduction of glycol residue in place of the methanol residue.

### CONCLUSION

The kinetics of transesterification of DMT and MHET with EG is studied at 170–190°C. The rate constants for the two reactions are determined, and the activation energy for the reaction is estimated. It is concluded that the transesterification reaction is of third order with respect to DMT, EG, and the catalyst. Both the ester groups appear to have almost similar reactivity.

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