Melt Transesterification of Dimethyl Terephthalate with Ethylene Glycol

The kinetics of a semibatch melt transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) is studied with zinc acetate as a catalyst. This paper quantifies the effect of various reactor operating conditions on the transesterification rate and the product composition distribution. Our experiments support the assumption that the methylesters in DMT and growing oligomer chains have the same reactivities for transesterification with EG and that the reactivity of hydroxyl groups in pure EG for esterification with DMT is twice that of the hydroxyl group in oligomers. With a molecular species model in which various oligomers are identified by the type of functional end groups, the progress of the transesterification and the oligomer concentration distribution were estimated and the agreement between the model predictions and the experimental data were excellent. It has also been shown that 30 wt. % of oligomers are produced for [EG]/[DMT] molar ratio of three, and up to 70 wt. % oligomers are produced at the [EG]/[DMT] molar ratio of one.

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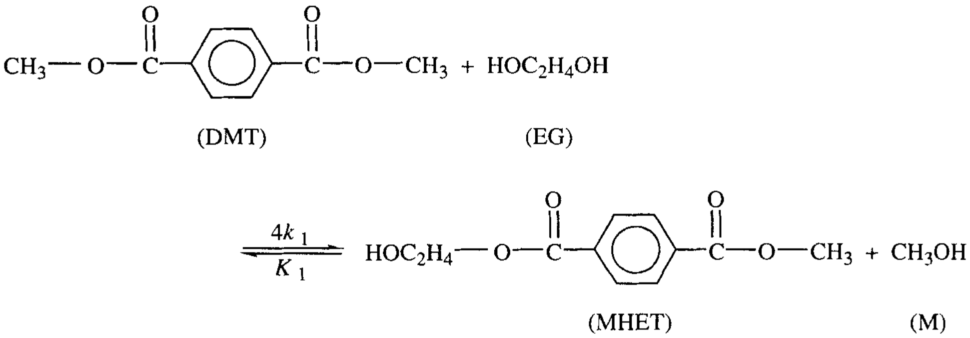
Introduction

The melt transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) is the first stage in the synthesis of polyethylene terephthalate (PET) which is one of the fastest growing thermoplastic polyesters. PET is manufactured by step growth melt polymerization process which consists of three reaction steps: 1) melt transesterification of DMT with EG; 2) prepolymerization at 250° ~ 300°C and ~4 kPa; 3) finishing polymerization at 280° ~ 300°C and <0.13 kPa. Due to the stringent industrial specifications that today's polymers must meet, the need for an improved quality control through more effective reactor operation is now increasingly important. Although PET can be synthesized by starting with terephthalic acid (TPA) and EG, particularly for fiber-grade PET, DMT is still the preferred raw material for PET and other thermoplastic polyesters such as polybutylene terephthalate (PBT). This paper deals with the kinetics of the melt transesterification of DMT with EG in a semibatch reactor through experimentation and theoretical modeling.

The main reactions (ester interchange and transesterification reactions) take place reversibly in a series-parallel fashion as shown below and lead to the bishydroxyethyl terephthalate (BHET), which is the monomer to be polymerized in the polycondensation stage.



(1)

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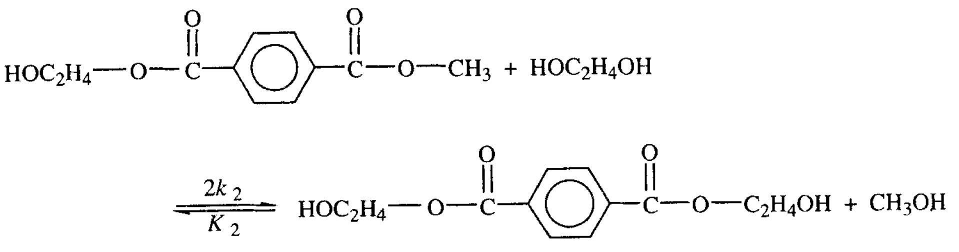
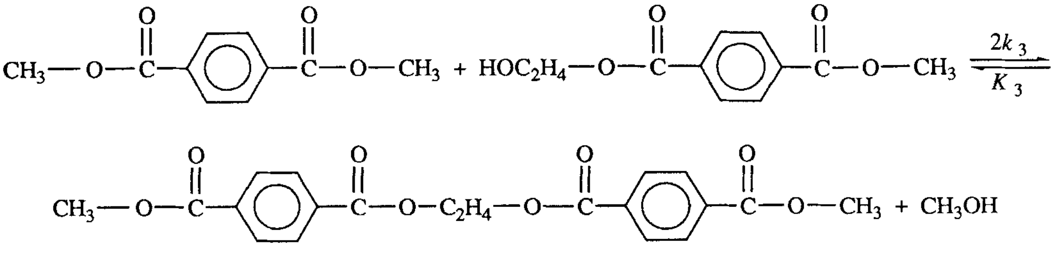

(BHET)

(2)

where MHET is the methyl hydroxyethyl terephthalate and M is the condensation byproduct, methanol. k_1 is the rate constant for the reaction of hydroxyethyl group of EG and the methylester group of DMT, and k_2 the rate constant for the reaction of hydroxyethyl group of EG and the methylester group of MHET. K_1 and K_2 are the equilibrium rate constants.

In addition to the above major reactions, a host of similar reactions also proceed and yield a mixture of oligomers. The following shows some examples of the reactions which may occur to produce two different types of dimers:

Transesterification reaction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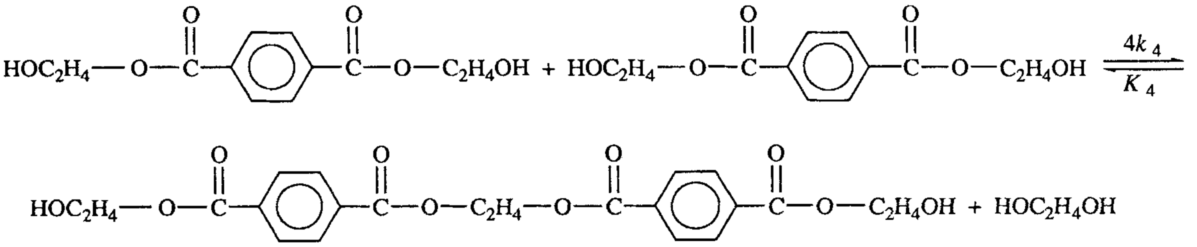
Polycondensation reaction


(4)

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where k_3 represents the rate constant for the reaction of methylester group of DMT and the hydroxyethyl group of MHET, and k_4 represents the rate constant between the hydroxyethyl groups of BHET. K_3 and K_4 are the corresponding equilibrium rate constants.

Many researchers have studied the kinetics of ester interchange reactions and polycondensation reactions. A recent review by Ravindranath and Mashelkar (1986a, b) should prove to be very instructive in understanding the reaction chemistry and some important aspects related to the process modeling and reactor design. Depending upon the type of catalyst and reaction conditions, many reported results on the kinetics of melt transesterification show some inconsistencies. Griehl and Schnock (1957) reported that the transesterification with zinc acetate catalyst was second order with respect to DMT and catalyst and that the reaction rates were independent of glycol concentration. Mihail et al. (1958) suggested the reaction order being fractional with zinc oxide catalyst in the concentration range of 0.14 ~ 0.28%. Sorokin and Chebotareva (1969) reported that the reaction was first order with respect to EG and catalyst (Zn stearate) concentrations and second order with respect to DMT concentration.Recent reports (Fontana, 1968; Tomita and Ida, 1973; Yamanis and Adelman, 1976; Datye and Raje, 1985) showed that the transesterification reaction was third order: i.e., first order with respect to DMT, EG, and catalyst, respectively. Tomita and Ida (1973) investigated the effect of various transesterification catalyst systems on the reaction rate and found that the linear dependence of the reaction rate on the catalyst concentration was valid only within some limited range of catalyst concentrations. Similar observation was also reported by Shah et al. (1984).

Another issue discussed by many workers in the past is related to the reactivities of functional end groups involved in the transesterification, e.g., hydroxyethyl group and methylester group. Peebles and Wagner (1959) reported that the reactivities of the hydroxyethyl groups were the same for both ethylene glycol and oligomers ($k_1 = k_3$) and that the reactivity of the methylester groups of DMT was three times larger than that of MHET

($k_1 = 3k_2$). Fontana (1968) suggested that the hydroxyl group of EG was twice as reactive as the hydroxyl group of the MHET ($k_1 = 2k_2$). According to the analysis of Yamanis and Adelman (1976) and Ravindranath and Mashelkar (1982), the methylester end groups of DMT and MHET are equally reactive, and oligomerization reactions do not proceed to any significant extent, i.e., $k_1 = k_2$ and $k_1 \gg k_3$. The uncertainties in the relative reactivities of the functional end group as reported in the literature make it difficult and complicated to interpret the transesterification kinetics.

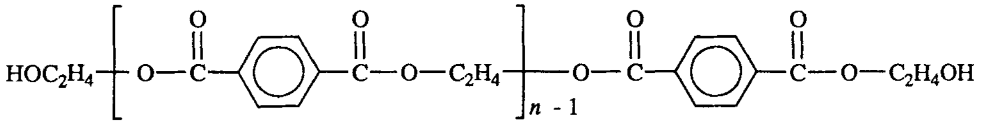
Since all the reactions in the transesterification stage are reversible, it is necessary to remove the condensation byproduct, methanol, continuously from the reaction mixture in order to obtain high conversion of methylester groups. The use of high reactor temperature lowers the equilibrium concentration of methanol in the liquid phase, and a continuous purge of the reaction mixture with inert gases such as nitrogen may drive out the vaporized methanol from the reactor to promote the forward reactions. Both of these actions may help the continuous removal of the condensate but make the efficient reflux of ethylene glycol, even DMT, more difficult. At ambient pressure, it is difficult to obtain complete conversion of methylester groups due to the phase equilibrium of methanol in the reactor. This suggests that the reverse reactions in both the ester interchange and the transesterification reactions must be considered in a realistic modeling work. Challa (1960) measured the equilibrium constant using fractional vacuum distillation and sublimation methods for the analysis of the equilibrium products from a closed reactor system. Using the equilibrium constants suggested by Challa, Ravindranath and Mashelkar (1981, 1982) developed the functional group models for semibatch and continuous transesterification reactors, and Kumar et al. (1984) developed optimal reactor operating schemes to obtain high methylester group conversion and low side-product concentrations in a semibatch reactor system. No experimental verification of the models was carried out in these works.

As described earlier, the main reaction products in the transesterification stage are BHET, MHET, unreacted DMT, and oligomers. This final reaction mixture will be fed into the continuous prepolymerization reactor operating at higher temperature and lower pressure. When the semibatch reactor is used, the reaction temperature and the pressure are varied to promote the polycondensation reaction. Lei and Choi (1988) have investigated the effect of incomplete transesterification of methylester groups on the performance of semibatch polycondensation process in detail and found that there exists some optimal methylester group conversion which yields high molecular weight in short reaction time in the prepolymerization stage. Therefore, it is critical to develop an accurate model for the melt transesterification of DMT with EG for the optimization of whole PET process. In this work, we develop a molecular species model for the semibatch transesterification process and compare the model simulations with our experimental data.

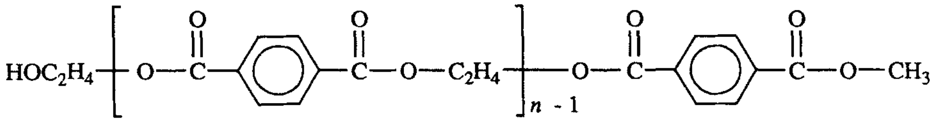
Model Development

A detailed molecular species model is developed to describe the various esterification reactions occurring in the melt transesterification stage. In our previous work (Choi, 1987), the complete removal of methanol from the reaction mixture was assumed, and therefore the reverse reactions were not considered in the kinetic scheme. In the present modeling work, these reactions are included. Since the rate of side-product formation (e.g., diethylene glycol) in the transesterification stage is quite low compared with that in the polymerization stages (Besnoin, 1988), side-product formation reactions are not considered. Following the definition of polymeric species by Lei and Choi (1988), one can define the following three oligomeric species:

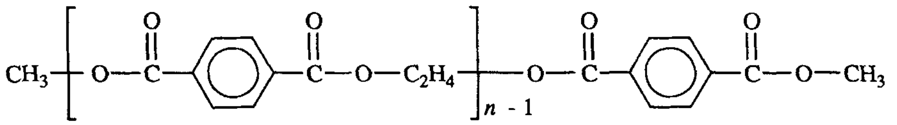
P_n:



Q_n:

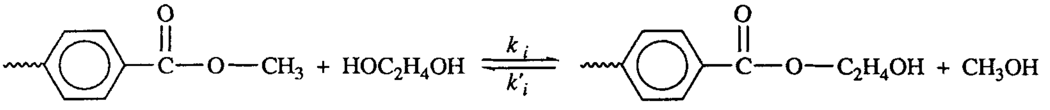


R_n:



From the HPLC analysis of the transesterification reaction products obtained in the present work, it was found that the content of the oligomers having more than four repeating units was negligible (Besnoin, 1988). In our model, oligomers (P_n, Q_n, R_n species) having up to seven repeating units are considered for the numerical solution of the component mass balance equations. Note that BHET, MHET, and DMT are the species P_1, Q_1 and R_1, respectively. The present catalyst system uses zinc acetate which is one of the most efficient transesterification catalysts used in many industrial processes.

Let us assume that the reactivities of methylester end groups in DMT and MHET are the same as reported by many workers and that the reactivities of the functional groups are independent of oligomer chain length. Then, the ester interchange reaction can be represented as:

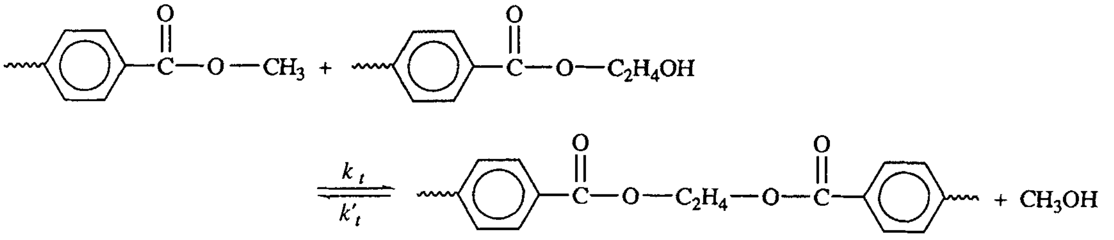

(5)

where k_i is the rate constant for the reaction of the methylester end group and the hydroxyethyl group of ethylene glycol, and k_i' is the rate constant for the reaction of methanol and the hydroxyethylester end group. In the molecular species model, the ester interchange reactions are represented as follows (for $1 \leq n \leq 7$):

$$Q_n + EG \rightleftharpoons P_n + M \tag{6}$$

$$R_n + EG \rightleftharpoons Q_n + M \tag{7}$$

Since the polycondensation rate is very low under the ester interchange and transesterification conditions (e.g., 101.3 kPa, 170 ~ 190°C), the polycondensation reactions can be ignored in our model. Thus, various oligomers are produced only by the following transesterification reactions:


(8)

where k_t is the rate constant for the reaction of the methylester end group and the hydroxyethyl end group, and k_t' is the rate constant for the reaction of methanol and the ester linkage in the oligomer. The above oligomerization reactions are expressed as following (for $2 \leq n + m \leq 7$):

$$P_n + Q_m \rightleftharpoons P_{n+m} + M \tag{9}$$

$$P_n + R_m \rightleftharpoons Q_{n+m} + M \tag{10}$$

$$Q_n + Q_m \rightleftharpoons Q_{n+m} + M \tag{11}$$

$$Q_n + R_m \rightleftharpoons R_{n+m} + M \tag{12}$$

Based on the reaction schemes shown above and the assumption of perfect mixing and constant melt density, one can derive the kinetic modeling equations for isothermal conditions. Since the reaction volume decreases with conversion due to the continuous removal of methanol from the reactor, it will be more convenient to use the material balance equations based on the number of moles of each species in the reactor. Assuming that the dependence of the reaction rate on the catalyst concentration is not known *a priori* for the time being, one can derive the rate expressions for various species as follows:

For Species P

$$\frac{dP_1}{dt} = \frac{1}{V} f([C^*]) \left\{ 2k_i Q_1 G - 2k_i' P_1 M - 2k_t P_1 \sum_{n=1}^{7} (Q_n + 2R_n) \right.$$
$$\left. + k_t' M \sum_{m=2}^{7} (2P_m + Q_m) \right\} \quad G = \text{Ethylene Glycol} \tag{13}$$

$$\frac{dP_n}{dt} = \frac{1}{V} f([C^*]) \left\{ 2k_i Q_n G - 2k_i' P_n M - 2k_t P_n \sum_{n=1}^{7} (Q_n + 2R_n) \right.$$
$$- 2(n-1) k_t' P_n M + 2k_t \sum_{r=1}^{n-1} P_r Q_{n-r}$$
$$\left. + k_t' M \sum_{m=n+1}^{7} (2P_m + Q_m) \right\} (2 \leq n \leq 6) \tag{14}$$

$$\frac{dP_7}{dt} = \frac{1}{V} f([C^*]) \left\{ 2k_i Q_7 G - 2k_i' P_7 M - 6(2k_t' P_7 M) \right.$$
$$\left. + 2k_t \sum_{r=1}^{6} P_r Q_{7-r} \right\} \tag{15}$$

For Species Q

$$\frac{dQ_1}{dt} = \frac{1}{V} f([C^*]) \left\{ 2k_i G(2R_1 - Q_1) + k_i' M(2P_1 - Q_1) \right.$$
$$- 2k_t Q_1 \sum_{n=1}^{7} (P_n + Q_n + R_n)$$
$$\left. + 2k_t' M \sum_{m=2}^{7} (P_m + Q_m + R_m) \right\} \tag{16}$$

$$\frac{dQ_n}{dt} = \frac{1}{V} f([C^*]) \left\{ 2k_i G(2R_n - Q_n) + k_i' M(2P_n - Q_n) \right.$$
$$- 2k_t Q_n \sum_{n=1}^{7} (P_n + Q_n + R_n) - 2(n-1) k_t' Q_n M$$
$$+ k_t \sum_{r=1}^{n-1} (4P_r R_{n-r} + Q_r Q_{n-r})$$
$$\left. + 2k_t' M \sum_{m=2}^{7} (P_m + Q_m + R_m) \right\} (2 \leq n \leq 6) \tag{17}$$

$$\frac{dQ_7}{dt} = \frac{1}{V} f([C^*]) \left\{ 2k_i G(2R_7 - Q_7) + k_i' M(2P_7 - Q_7) \right.$$
$$\left. - 6(2k_t' Q_7 M) + k_t \sum_{r=1}^{6} (4P_r R_{7-r} + Q_r Q_{7-r}) \right\} \tag{18}$$

For Species R

$$\frac{dR_1}{dt} = \frac{1}{V}f([C^*])\left\{-4k_iR_1G + k_i'Q_1M - 2k_tR_1\sum_{n=1}^{7}(2P_n + Q_n) + k_t'M\sum_{m=2}^{7}(Q_m + 2R_m)\right\} \quad (19)$$

$$\frac{dR_n}{dt} = \frac{1}{V}f([C^*])\left\{-4k_iR_nG + k_i'Q_nM - 2k_tR_n\sum_{n=1}^{7}(2P_n + Q_n) - 2(n-1)k_t'R_nM + 2k_t\sum_{r=1}^{n-1}Q_rR_{n-r} + k_t'M\sum_{m=2}^{7}(Q_m + 2R_m)\right\}(2 \le n \le 6) \quad (20)$$

$$\frac{dR_7}{dt} = \frac{1}{V}f([C^*])\left\{-4k_iR_7G + k_i'Q_7M - 6(2k_t'R_7M) + 2k_t\sum_{r=1}^{6}Q_rR_{7-r}\right\} \quad (21)$$

For Volatile Species

$$\frac{dM}{dt} = \frac{1}{V}f([C^*])\left\{2k_iG\sum_{n=1}^{7}(Q_n + 2R_n) - k_i'M\sum_{n=1}^{7}(2P_n + Q_n) - 2k_t'M\sum_{n=2}^{7}(n-1)(P_n + Q_n + R_n) + 2k_t\left[\sum_{n=1}^{6}P_n\sum_{m=1}^{7-n}(Q_m + 2R_m) + \sum_{n=1}^{6}Q_n\sum_{m=1}^{7-n}R_m + \sum_{n=1}^{3}Q_n\sum_{m=n}^{7-n}Q_m\right]\right\} \quad (22)$$

$$\frac{dG}{dt} = \frac{1}{V}f([C^*])\left\{-2k_iG\sum_{n=1}^{7}(Q_n + 2R_n) + k_i'M\sum_{n=1}^{7}(2P_n + Q_n)\right\} \quad (23)$$

where upper case symbols represent the number of moles of each species, V is the volume of reaction mixture, and $f([C^*])$ is the function of catalyst concentration.

For the calculation of the concentrations of volatile species (ethylene glycol and methanol) in the melt and in the vapor phase, a quasisteady-state assumption is used for the vapor-liquid equilibrium in small increments of time. The vapor phase is assumed to follow the ideal gas law

$$V^v\sum_i p_i = RT\sum_i n_i^v \quad (24)$$

and liquid phase to follow the Raoult's law (Ravindranath and Mashelkar, 1981)

$$p_i = p_i^{sat}x_i \quad (25)$$

where p_i and p_i^{sat} are the partial pressure and the saturated vapor pressure of volatile species i, n_i is the mole numbers of species i in the vapor phase, x_i is the mole fraction of species i in the liquid phase, V^v is the vapor phase volume, T is the reactor temperature, and R is the gas constant. Mass balance equations and the vapor-liquid equilibrium equations are combined and solved simultaneously to calculate the concentrations of volatile species in both the vapor phase and the liquid phase. The volume of the reaction melt is updated by subtracting the equivalent volume of the condensed methanol removed from the reactor.

To simulate the semibatch transesterification process, four rate constants (k_i, k_i', k_t, k_t') are used in our model. By measuring the amount of methanol generated in the semibatch transesterification process, it is possible to evaluate the initial rate of reaction r_0 which is equal to the initial rate of methanol generation:

$$r_0 = 4k_i\,[\mathrm{DMT}]_0\,[\mathrm{EG}]_0 f([C^*]_0) \quad (26)$$

where $[.]_0$ stands for the initial concentration of the given species, and the rate constant (k_i) is given in the Arrhenius form. For each transesterification experiment, the initial rate of methanol generation can be determined by extrapolating the rate curve to the origin (i.e., time = 0). Several experiments were first carried out to determine the dependence of the reaction rate on the catalyst concentration for various initial catalyst concentrations at the same temperature and EG to DMT molar ratio. The activation energy and frequency factor can also be determined by conducting the experiments at different temperatures with other reaction conditions held constant. Details of our experimental procedure will be presented in the next section. With the k_i value determined experimentally, the reactivity of the hydroxyethyl end groups on species P_n and Q_n is then assumed to be half of the reactivity of hydroxyethyl groups on EG, i.e., $k_t = 0.5\,k_i$. k_i and k_t are also assumed to have the same activation energy value (Ravindranath and Mashelkar, 1981). Finally, the values of k_i' and k_t' were determined using a standard optimal parameter estimation technique with the experimental conversion data and the weight fraction data, respectively. Table 1 lists the physical constants and the base operating conditions used in our simulations.

Experimental Studies

The melt transesterification experiments have been carried out using 100 mL stirred glass reactor fitted with a four-necked reactor head. The reactor is also fitted with a distillation system (column packed with glass beads, Liebig condenser, and graduated receiver). The remaining two parts are for a thermocouple and nitrogen purge/sampling. In order to prevent the condensation of methanol in the distillation column, the column temperature is maintained at 95 ~ 100°C. The top of the reactor is also heated and insulated to prevent the deposition of DMT and oligomers. The reactor is wrapped with a heating tape and insulated. The reactor temperature is controlled accurately (±1°C) by a PID temperature controller.

The reactor is first charged with the predetermined amount of DMT (0.3 mol) and 1.1 g less than EG needed, depending on the experiment we wish to perform. The mixture is heated to the desired reaction temperature while being stirred. Meanwhile, a catalyst solution ($\mathrm{Zn(OAc)_2 \cdot 2H_2O}$ in EG) is prepared: the correct amount of zinc acetate catalyst is diluted with hot EG in a 10-mL volumetric flask. After complete dissolution, the solution is cooled down and the meniscus is adjusted. 1 mL (1.11 g) of catalyst solution is then injected to the reactor with a 1,000-μL

Table 1. Numerical Values of Physical Constants and Base Reactor Operating Conditions

Physical Constants and Parameters	
$k_i = 5.28 \times 10^{16} \exp(-33{,}700/RT)$	$\frac{L^2}{\text{mol}^2\ \text{min}}$
$k_i' = 3.52 \times 10^{16} \exp(-31{,}500/RT)$	$\frac{L^2}{\text{mol}^2\ \text{min}}$
$k_t = 2.64 \times 10^{16} \exp(-33{,}700/RT)$	$\frac{L^2}{\text{mol}^2\ \text{min}}$
$k_t' = 7.63 \times 10^{15} \exp(-31{,}500/RT)$	$\frac{L^2}{\text{mol}^2\ \text{min}}$
$p_{EG}^{sat} = 0.133 \times 10^{(21.61 - 3729/T - 4.042\log_{10}T)}$	kPa
$p_M^{sat} = 4.044 \times 10^{-4}T^2 - 0.297T + 55.196(\text{K})$	kPa*
$V^v = 0.190$	L
$\rho = 1.11$	$\frac{kg}{L}$

Base Reactor Operating Conditions
Temperature: 180°C
Initial [EG]/[DMT] ratio: 2
Initial catalyst concentration: 2.0 × 10^{-3} mol/L (Zinc acetate)

*Polynomial correlation by curve-fitting the vapor pressure data listed in *Perry's Chemical Engineering's Handbook* at 138°C–214°C.

syringe when the reactants are at the desired reaction temperature.

For the measurement of reaction product (P_n, Q_n, R_n, and BHET, MHET, and DMT) concentrations, HPLC has been used. Our method is adapted from Zaborsky (1977) who used an HPLC to separate PET prepolymers. We adopted the same system of solvents used by Zaborsky (1977), but we modified the relative proportions in order to get an acceptable trade-off between the resolution and the time of analysis. P_n species are perfectly separated, whereas Q_n species are only partially separated. At very low sample concentration, however, better resolution can be obtained. Unfortunately, R_n species are not separated at all and are eluted as a single-fused peak.

A sample concentration of 0.1 to 0.15 mg/mL was used. The sample is dissolved in the eluent (chloroform/ethanol/methanol/*n*-propanol: 100/4.5/0.25/0.25 v/v). Using the standards that are available to us, we can identify the chromatographic peaks corresponding to DMT, MHET, and BHET. We can also assign unambiguously the oligomer peaks. Two criteria are the basis of our assertion: polarity and size of the molecules. Compounds are first separated according to their polarity which gives rise to three families of peaks corresponding to P_n, Q_n, and R_n species. The more polar family (P_n) has more affinity for the column and is eluted last. The less polar family (R_n) is eluted first. Compounds of a same family are then separated according to their size, the smaller being eluted last (Zaborsky, 1977). Then it is possible to evaluate the amount of each oligomer (except for those of the R_n family) using the response coefficients obtained (Besnoin, 1988).

Results and Discussion

In order to compare the model simulations with the experimental results, the results of the model simulations are presented in the form of the methanol yield as a function of reaction time and the concentration distribution of oligomeric species as a function of the methanol yield. Defined as the ratio of the amount of condensed methanol to the theoretical amount of methanol at complete conversion of methylester group, the methanol yield is the only reaction variable measurable on-line. The conversion of methylester end groups, however, will always be slightly higher than the yield of methanol, because the equilibrium amounts of methanol are trapped in both the liquid and the vapor phase of the reactor. The amount of methanol in the reactor is normally 2 ~ 5% of the total amount liberated and depends on the reaction temperature and the reactor volume. There is also a slight delay between the time of catalyst injection and the time when the first drop of condensed methanol is observed. This time lag is the time needed for the methanol to fill up the vapor space in the reactor and to go from the reactor to the receiver via a distillation column. Ethylene glycol was not detected in the condensate collected. Since some loss of ethylene glycol from the sample occurs during either the sampling or the storage of the samples before analysis, the oligomer concentrations are normalized with respect to the total amount of nonvolatile oligomeric species including DMT, MHET, and BHET. Thus, the oligomer concentrations in the reaction mixture are presented as the weight fraction in the mixture of nonvolatile compounds.

Effect of catalyst concentration

It has been shown that the transesterification reaction was a third-order reaction: first order in DMT, EG, and catalyst concentration, respectively (Fontana, 1968; Tomita and Ida, 1973; Datye and Raje, 1985). However, according to the experimental data of r_0 and $[C^*]_0$ obtained in the present study, it was found that the dependence of r_0 on $[C^*]_0$ is not linear over the entire range of catalyst concentration studied. Figure 1 shows the plot of r_0 vs. catalyst concentration. Note that the origin and the first two data points can be fitted with a straight line whereas the points corresponding to higher catalyst concentrations can be fitted with another straight line of different slope. The linear relationship between the reaction rate and the catalyst concentration at low catalyst concentration is not surprising. However, the deviation from the linearity at higher catalyst concentrations is apparent.

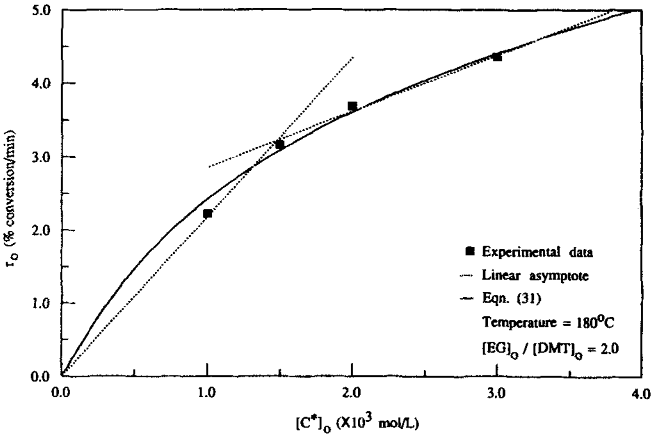
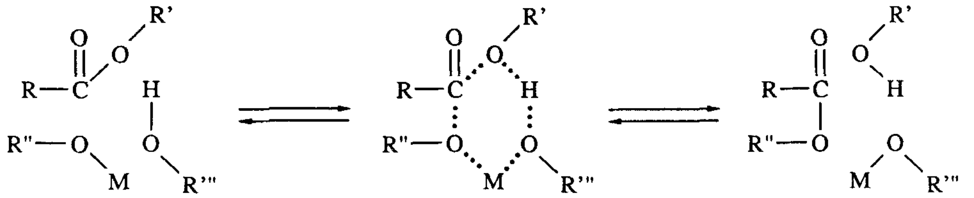


Figure 1. Effect of catalyst concentration on the initial rate of reaction: theory vs. experiment.

The catalytic mechanism of the transesterification of dimethyl terephthalate with ethylene glycol using metal acetate has been studied very scarcely. Fontana (1968) first proposed a mechanism of the reaction between the metal acetate catalyst and hydroxyl end groups leading to acetic acid and metal alcoholate which was thought to be the actual catalytic species. This mechanism supported by Walker (1983) is shown below:



It implies that the catalytic activity is a function of the ionic species bound to the metal ion, due to acid-base reactions involved. It has been reported later by Tomita and Ida (1975) that the reactivity of sodium salts increases with the basic character of the counter-ion, validating Fontana's proposition. However, they did not observe the same trend with zinc salts: the reactivity was found to be independent of the anionic entity. This means that the catalytic mechanisms for sodium and zinc are not the same. A recent mechanistic study justifies this difference (Otton et al., 1988). Tomita and Ida (1975), after Yoda (1970), showed that the catalytic activity of metal acetate catalysts was dependent strongly on the electronegativity of the metal ion. This suggests that the key point in the catalytic mechanism could be the interaction between the metal atom and the oxygen atom of the carbonyl group of the ester, as pointed out by Shah and coworkers (1984). Otton and coworkers (1988) proposed a mechanism based on this assumption after their experimental study of alcoholysis reaction with metal compounds: the metal complex is bound to the oxygen atom of the carbonyl group. However, the reaction medium exhibits a significant electroconductivity suggesting that ionic species are actually present in the mixture. Thus, we propose that the actual catalytic species is not the zinc complex itself, but the ion Zn^{2+}. This implies that a dissociation equilibrium takes place in the reaction melt.

Then, let us consider the dissociation of catalyst, $Zn(OAc)_2$:

$$Zn(OAc)_2 \underset{k/K}{\overset{k}{\rightleftharpoons}} Zn^{2+} + 2OAc^- \tag{27}$$

K is the dissociation constant given by

$$K = \frac{[Zn^{2+}][OAc^-]^2}{[Zn(OAc)_2]} \tag{28}$$

Let $[C^*]$ be the concentration of $Zn(OAc)_2$ before the dissociation, and x is the concentration of Zn^{2+} after the dissociation. Then, we have the following two relationships:

$$K = \frac{4x^3}{[C^*] - x} \tag{29}$$

or

$$[C^*] = x + \frac{4}{K}x^3 \tag{30}$$

The active species in the catalytic process is Zn^{2+}. Consequently, the rate constant is certainly linear in x (free Zn^{2+}) and not in $[C^*]$. However, for sufficiently low concentrations of the catalyst $x \gg (4/K)x^3$ and $[C^*] \approx x$. For higher concentrations, $x \ll (4/K)x^3$ and $[C^*]$ is proportional to x^3 or x is proportional to $\sqrt[3]{[C^*]}$.

Assuming that r_0 is proportional to x_0 (value of x at time $t = 0$) for any concentration, Eq. 30 can be rewritten as:

$$[C^*]_0 = Ar_0 + Br_0^3 \tag{31}$$

with the coefficients A and B be 3.00×10^{-4} min and 1.96×10^{-5} $L^2 \cdot min^3 \cdot mol^{-2}$ obtained by standard curve fitting technique. From this result, it is now possible to determine the numerical value of the dissociation constant K at 180°C. From Eqs. 30 and 31, we have

$$K = \frac{4A^3}{B} = 5.48 \times 10^{-6}\ mol^2/L^2$$

or

$$pK = 5.26$$

The solid line in Figure 1 shows the calculated initial reaction rate vs. the zinc acetate concentration predicted by Eq. 31. It is in very good agreement with the experimental data. From the duplicate experiment, we found $pK = 5.32$ which is very close to the other value. Then, an average value ($pK = 5.29$) can be used.

In order to get an explicit expression for the function of catalyst concentration, we inverted the function $[C^*](x)$ to $x([C^*])$ by solving Eq. 30. Let $a = (K/4)$ and $b = -(K[C^*])/4$. Then, since

$$\frac{b^2}{4} + \frac{a^3}{27} > 0 \tag{32}$$

there is only one real solution:

$$x = \sqrt[3]{-\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}} - \sqrt[3]{\frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}} \tag{33}$$

The function $f([C^*])$ now takes the form

$$f([C^*]) = x([C^*], K) \tag{34}$$

K is assigned the value determined by curve fitting. The effective catalyst concentration, $[C^*]$, changes with time due to the volume change of the reaction mixture.

Tomita and Ida (1973) showed the variation of k_i as a function of $[C^*]$ on a log-log plot. This graph consists of two straight lines. We measured the slopes of these straight lines and found that, at low catalyst concentration, the slope is 1 whereas it is close to 1/3 at higher catalyst concentration. This experimental observation is in perfect agreement with the theory we have proposed: at low catalyst concentration, k_i is proportional to $[C^*]$ whereas it is proportional to $\sqrt[3]{[C^*]}$ at higher catalyst concentration.

Now we propose the following reaction mechanism. It is similar to the one proposed recently by Otton and coworkers (1988) who used metal compounds. However, Zn^{2+}, not $Zn(OAc)_2$, is regarded as the catalyst species in our proposed mechanism shown schematically as follows:

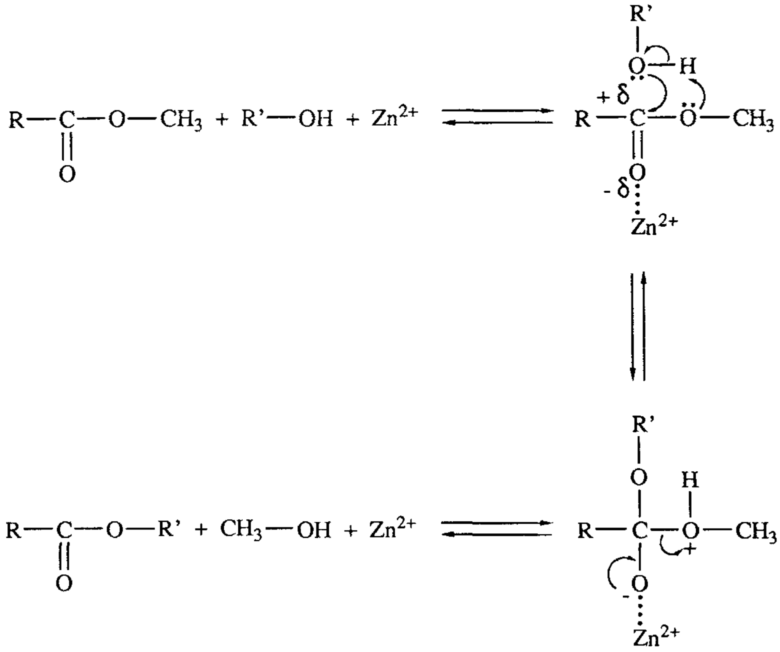
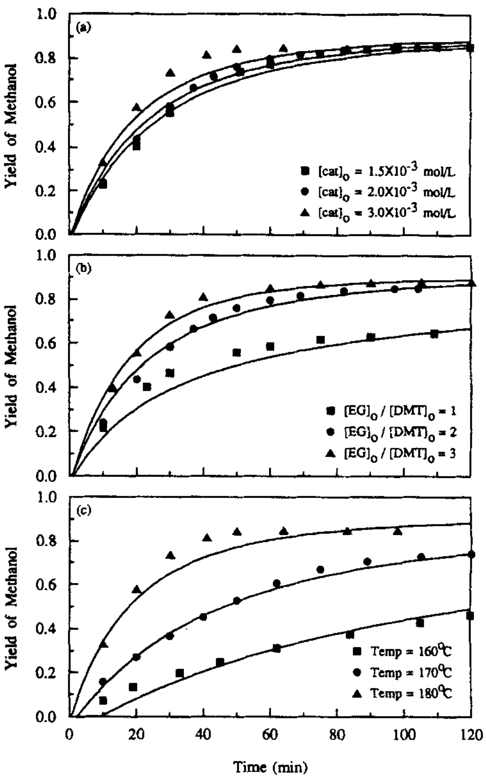


Figure 2a shows the yield of methanol as a function of time for three different catalyst concentrations. Here, the solid lines represent the model simulations. As expected, the higher the catalyst concentration, the faster we reach the equilibrium. However, the equilibrium yield is independent of the catalyst concentration. The fact that we observe an equilibrium conversion is an evidence of the presence of methanol in the reaction melt; otherwise, 100% conversion should be obtained in a finite time. Our model predictions agree with the experimental data very well; however, there are minor deviations during the initial 30–60 min of reaction at high catalyst concentration (e.g., 3×10^{-3} mol/L). It is possible that a small discrepancy between the model and the experimental data is caused by the assumption of the equal reactivities of the methylester groups in our model simulations. However, the discrepancy observed is not large enough to seriously question the validity of the assumption and therefore we shall follow the equal reactivity assumption in our model.

In Figure 3, the normalized weight fractions of various oligomeric species are shown for varying catalyst concentration as a function of the yield of methanol. The oligomer concentration distribution such as Figure 3 has never been reported in the open literature. Note first that the agreement between the model predictions and the experimental data is excellent. In the calculation of the product composition, no parameter was adjusted. It is also observed that the whole data and the simulation results for a given catalyst concentration collapse into a set of master curves. It means that the repartition of oligomeric species does not depend on the catalyst concentration but only on the conversion of methylester groups. It also indicates that the rate constants of reactions 6–7 and 9–12 are the same function of catalyst concentration (first-order dependence on $[Zn^{2+}]$). A different result would have been surprising because, all these reactions are the transesterification reactions involving similar species. Choi (1987) also derived similar master curves for the melt transesterification of DMT with EG in the absence of the reverse reactions.

Effect of oligomerization reaction

In our model simulation, the reactivity of hydroxyethyl group on ethylene glycol was assumed to be twice the reactivity of hydroxyethyl groups on P_n and Q_n species. To the best of our knowledge, no experimental confirmation has been reported. However, a model simulation at different ratios of transesterification rate constant to ester interchange rate constant will show the significance of the oligomerization reactions. The effects of this reactivity ratio on the yield of methanol and the normalized weight fractions of BHET and oligomers are shown in Figure 4. Note that k_t/k_i value of 0.5 gives the best fit of the experimental



(a) effect of catalyst concentr., $T = 180°C$, $[EG]_0/[DMT]_0 = 2$;
(b) effect of [EG]/[DMT] molar ratio, $T = 180°C$, $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L;
(c) effect of temperature, $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L, $[EG]_0/[DMT]_0 = 2$

Figure 2. Effects of operating conditions on the yield of methanol.

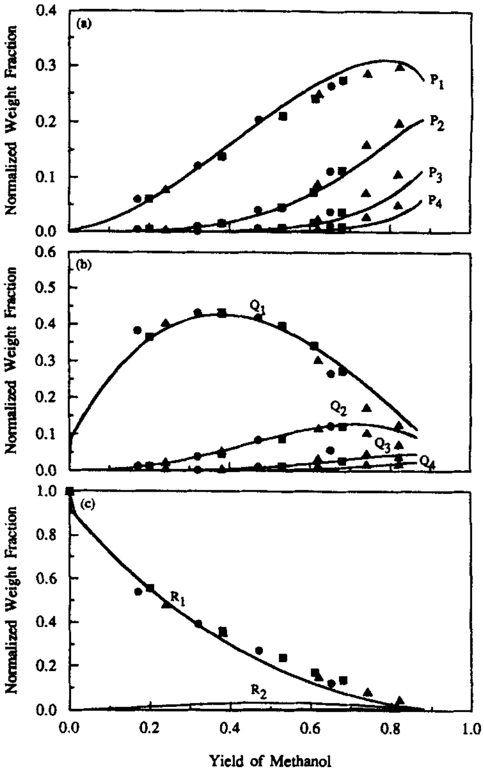


Figure 3. Effect of catalyst concentration on the normalized weight fraction of different species.

$T = 180°C$, $[EG]_0/[DMT]_0 = 2$; ■ $[C^*]_0 = 1.5 \times 10^{-3}$ mol/L; ● $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L; ▲ $[C^*]_0 = 3.0 \times 10^{-3}$ mol/L
(a) effect on species P, (b) effect on species Q, (c) effect on species R

data. A k_t/k_i value of 1.0 results in higher yield of methanol and larger amount of oligomers produced than that of the experimental data. As the value of k_t/k_i is reduced, less oligomerization reactions take place, and it is shown that for a ratio of 0.01 oligomerization reactions can be ignored. The yield of methanol increases as k_t/k_i value is increased, because the methylester groups on the oligomeric species are consumed more rapidly via the transesterification reaction. The importance of having the oligomerization reactions included in our model is that these oligomers reduce the equilibrium amount of BHET and bring out more oligomers in the reaction mixture. Figures 4b and c indicate that BHET accounts for only 29% and the oligomers account for up to 58% in the final reaction melt when the reactivity ratio is 0.5. These weight fractions have been confirmed by our HPLC analysis of the experimental samples. Since the yield of methanol is not very sensitive to the reactivity ratio as shown in Figure 4a, the oligomerization reactions could be easily ignored if one uses the model developed to estimate the conversion profiles only.

Effect of EG to DMT molar ratio

With the reaction temperature and catalyst concentration held constant at 180°C and 2×10^{-3} mol/L, respectively, we carried out experiments for varying EG to DMT molar ratio. The results are shown in Figure 2b and one can observe that the model predictions are very accurate. Since the hydroxyethyl group of ethylene glycol was assumed to be more reactive than that of oligomeric species, a large molar ratio will increase reaction rate. Also note that, the higher the molar ratio, the higher the equilibrium conversion as expected.

The normalized weight fraction of oligomeric species (P_n, Q_n, R_n) was determined experimentally and was also calculated using the model as shown in Figures 5 to 7. Both experimental and simulation data do not collapse into a set of master curves. But each species has its own curve of repartition. Figure 5 shows the repartition of P_n at three different EG to DMT molar ratio. Note that the calculated concentration profiles for P_1 (BHET) show a slight maximum and the peak shifts to the right as the ratio increases. The existence of the maximum concentration of P_1 indicates the transition of the reaction dominancy. When the oligomerization is dominant in the reaction, the consumption rate of P_1 by the transesterification reactions is faster than the production rate of P_1 by the ester interchange reactions. The transition makes more P_1 convert to oligomers, and therefore the weight fraction of P_1 decreases slightly at high conversion in a normalized plot. By converting the conversion scale to the time scale, one can easily find out that all these transitions occurred at the time when the concentrations of ethylene glycol reach their equilibrium values as shown in Figure 8.

Being the intermediates of the transesterification stage, Q_n species also show a maximum in its concentration profile as shown in Figure 6. Because of the difficulty of separating the R

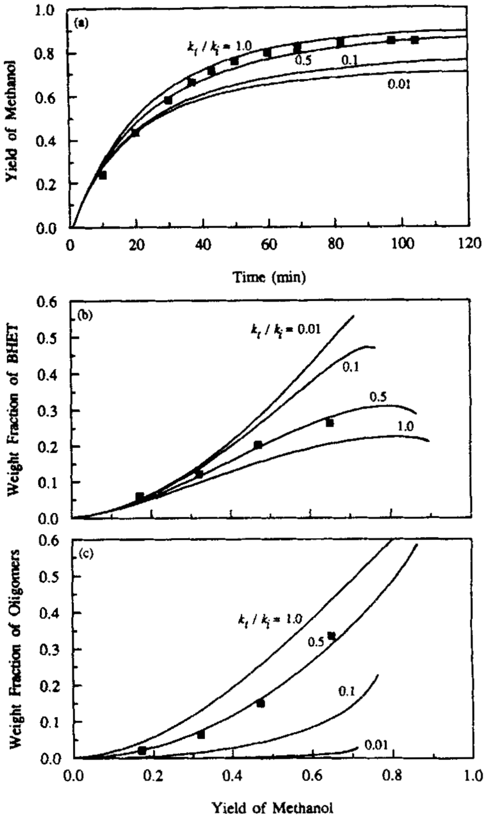


Figure 4. Effect of k_i/k_t values on the performance of the reactor.

$T = 180°C$; $[EG]_0/[DMT]_0 = 2$; $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L; ■ experimental data

(a) effect on the yield of methanol, (b) effect on the normalized weight fraction of BHET, (c) effect on the normalized weight fraction of oligomers

species in HPLC analysis, normalized weight fractions of total R_n species determined by experiment are plotted.

Figure 8 shows the effects of EG to DMT molar ratio on the weight fraction of DMT, MHET, BHET, ethylene glycol, methanol, and the oligomers with $n \geq 2$ in the reaction mixture. Note that more oligomerization occurs at low [EG]/[DMT] molar ratio. When the weight fraction of ethylene glycol reaches an equilibrium level, no net ester interchange reactions occur and the reaction is transesterification-dominant. All the methylester groups left in the reaction mixture at this moment will react with the hydroxyethyl group on BHET, MHET or oligomers to generate more oligomers. Therefore, the weight fraction profile of oligomers increases monotonically, and its slope is larger when the initial EG to DMT molar ratio is smaller, i.e., with more methylester groups left at this transition time. Figure 9 shows the effect of EG to DMT ratio on the molecular weight properties of the reaction mixture. With more oligomerization reactions occurring at low molar ratio, both the number average chain length ($\bar{X}_n$) and polydispersity ($\bar{X}_w/\bar{X}_n$) are larger than those at high molar ratio.

Effect of temperature

We ran our experiments at three different temperatures, 160, 170 and 180°C. The [EG]/[DMT] molar ratio was 2.0, and the catalyst concentration was 3.0×10^{-3} mol/L. Figure 2c shows

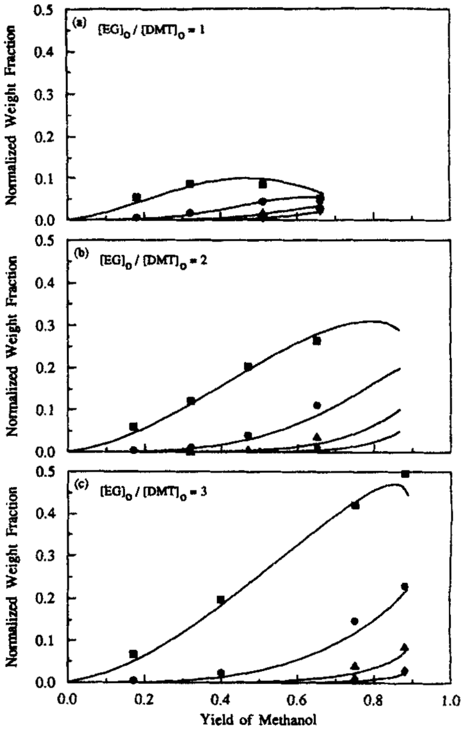


Figure 5. Effect of [EG]/[DMT] molar ratio on the normalized weight fraction of species *P*.

$T = 180°C$; $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L; ■ P_1; ● P_2; ▲ P_3; ◆ P_4
(a) $[EG]_0/[DMT]_0 = 1$; (b) $[EG]_0/[DMT]_0 = 2$; (c) $[EG]_0/[DMT]_0 = 3$

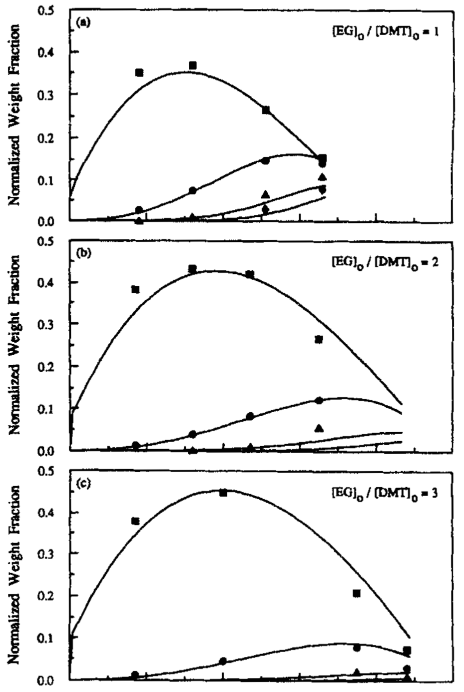


Figure 6. Effect of [EG]/[DMT] molar ratio on the normalized weight fraction of species *Q*.

$T = 180°C$; $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L; ■ Q_1; ● Q_2; ▲ Q_3; ◆ Q_4
(a) $[EG]_0/[DMT]_0 = 1$; (b) $[EG]_0/[DMT]_0 = 2$; (c) $[EG]_0/[DMT]_0 = 3$

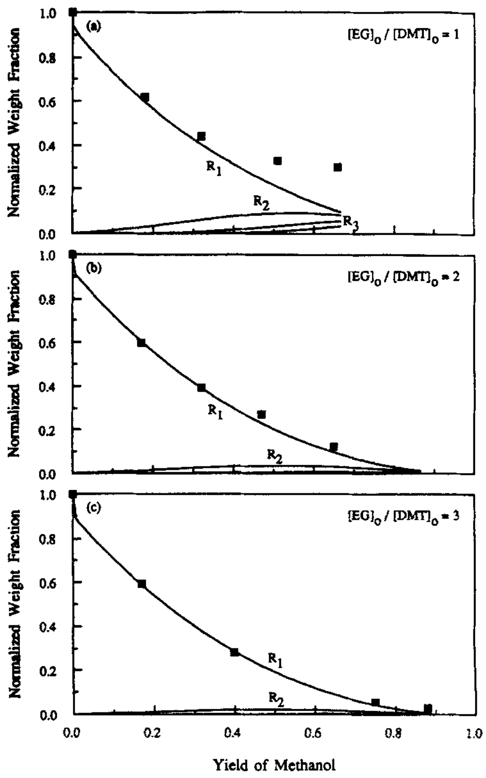


Figure 7. Effect of [EG]/[DMT] molar ratio on the normalized weight fraction of species *R*.

$T = 180°C$; $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L; ■ $R_1 + R_2 + R_3 + R_4$
(a) $[EG]_0/[DMT]_0 = 1$; (b) $[EG]_0/[DMT]_0 = 2$; (c) $[EG]_0/[DMT]_0 = 3$

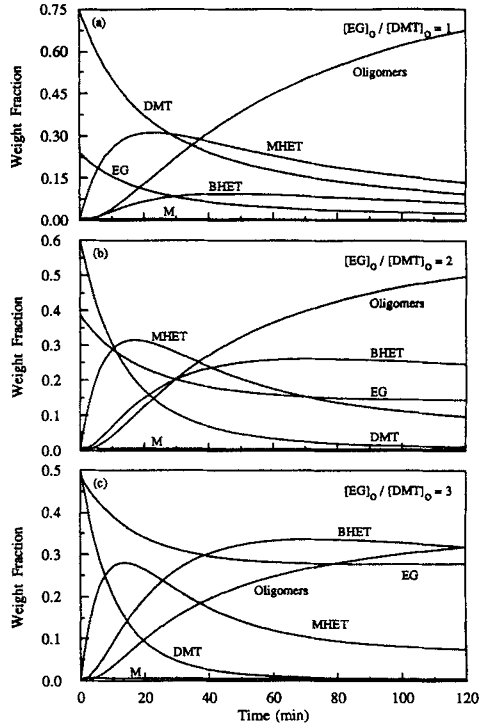


Figure 8. Effect of [EG]/[DMT] molar ratio on the weight fraction of monomer, oligomers, and volatile species.

$T = 180°C$; $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L
(a) $[EG]_0/[DMT]_0 = 1$; (b) $[EG]_0/[DMT]_0 = 2$; (c) $[EG]_0/[DMT]_0 = 3$

the effect of temperature on the yield of methanol. The model prediction is very good, albeit with slight deviations from the data at 180°C. The activation energy of k_i was found to be E = 141 kJ/mol from the standard Arrhenius plot. This value is quite different from those published in the open literature that range from 36 to 63 kJ/mol (Fontana, 1968; Tomita and Ida, 1973; Datye and Raje, 1985). This difference cannot be attributed to an error in the measurement of the initial rate. Moreover, our results are reproducible within 3% relative error. The activation energy of k_i' has also been determined to be 132 kJ/mol. Thus, the heat of reaction is 9.2 kJ/mol, which is close to the reported data of 5.9 kJ/mol (Challa, 1960).

Concluding Remarks

We have developed a molecular species model to describe the progress of transesterification of dimethyl terephthalate with ethylene glycol in a semibatch reactor with zinc acetate as a catalyst. With the vapor-liquid equilibrium of the volatile species and oligomerization reactions included, the model predicts satisfactorily the extent of the reaction and the composition distribution of the reaction melt. The nonlinear dependence of the reaction rate on the catalyst has been observed experimentally at high catalyst concentration. It is proposed that Zn^{2+} is the active catalytic species instead of the complex $Zn(OAc)_2$. The mechanism of dissociation equilibrium of the catalyst explains this phenomena well. This work is the first to show detailed oligomer concentration profiles for various reaction conditions through experimentation and verifying model simulations. It has also

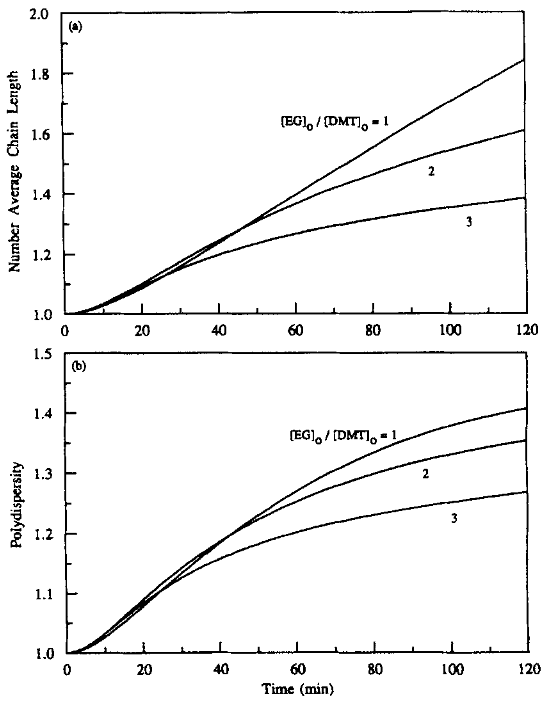


Figure 9. Effect of [EG]/[DMT] molar ratio on the number average chain length and polydispersity.

$T = 180°C$; $[C^*]_0 = 2.0 \times 10^{-3}$ mol/L
(a) effect on the number average chain length; (b) effect on polydispersity

been shown that 30 wt. % of oligomers can be produced in the final product even at very high [EG]/[DMT] molar ratio and up to 70 wt. % of oligomers are produced at low [EG]/[DMT] molar ratio. The information obtained in this work can be used to optimize the reactor operating conditions in the transesterification stage of the PET process. It should also be noted that the molecular species model presented in this paper can be easily modified for continuous transesterification process.

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Notation

k_j = rate constant of reaction j, $j = 1, 2, 3, 4$
K_j = equilibrium constant of reaction j, $j = 1, 2, 3, 4$
P_n = mole numbers of species P_n in the reaction melt, $n = 1, 2, \ldots, 7$
Q_n = mole numbers of species Q_n in the reaction melt, $n = 1, 2, \ldots, 7$
R_n = mole numbers of species R_n in the reaction melt, $n = 1, 2, \ldots, 7$
G = mole numbers of ethylene glycol in the reaction melt
M = mole numbers of methanol in the reaction melt
k_i = ester interchange rate constant
k_i' = reverse ester interchange rate constant
k_t = transesterification rate constant
k_t' = reverse transesterification rate constant
V = volume of the reaction mixture
$[C^*]$ = catalyst concentration
$[C^*]_0$ = initial catalyst concentration
$f([C^*])$ = function of catalyst concentration
p_i = partial pressure of volatile species i
p_i^{sat} = saturated vapor pressure of volatile species i
n_i = mole numbers of species i in the vapor phase
x_i = mole fraction of species i in the liquid phase
V^v = vapor phase volume
T = reaction temperature
R = gas constant
r_0 = initial rate of methanol generation
x = Zn^{2+} concentration
K = dissociation constant of catalyst

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