

SRC-TR-87-77

**CHEMICAL PROCESS SYSTEMS
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Ether) Glycol and 1,4-Butanediol Catalyzed
by Tetrabutyl Titanate

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CHEMICAL PROCESS SYSTEMS ENGINEERING LABORATORY

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**A CONSTITUENT LABORATORY OF
THE SYSTEMS RESEARCH CENTER**

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Kinetics of Transesterification of Dimethyl Terephthalate with Poly(tetramethylene Ether) Glycol and 1,4-Butanediol Catalyzed by Tetrabutyl Titanate

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Synopsis

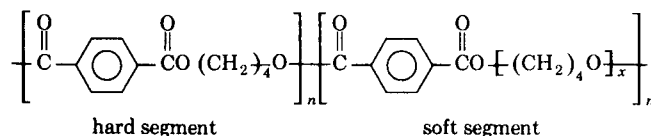
The kinetics of tetrabutyl titanate catalyzed transesterification of dimethyl terephthalate with poly(tetramethylene ether) glycol of various molecular weight has been studied in the presence and absence of 1,4-butanediol. Detailed analysis of experimental data with a proposed kinetic model indicates that the equal reactivity hypothesis for functional groups is valid within a wide range of experimental conditions studied. It is also found that the reactivity of hydroxyl groups of macrodiols such as poly(tetramethylene ether) glycol is independent of the chain length of the polymer. Effect of various reaction parameters on the transesterification rate and the resulting product composition is also discussed.

INTRODUCTION

In the ongoing search for high performance elastomers, thermoplastic polyether-ester (PEE) block copolymers have proven to be the excellent replacements for rubber in many engineering applications. The PEE is a random block copolymer prepared by step growth polymerization in two steps:

(1) the transesterification of dimethyl terephthalate (DMT) with the hydroxyl groups of both polyether glycols and low molecular weight diols such as 1,4-butanediol (BD);

(2) the low pressure melt polymerization at high temperature (250–350°C). The resulting polymers consist of crystalline polyester blocks (hard segments) and amorphous polyether blocks (soft segments). A typical structure of such thermoplastic elastomers when poly(tetramethylene ether) glycol is used is of the following form:

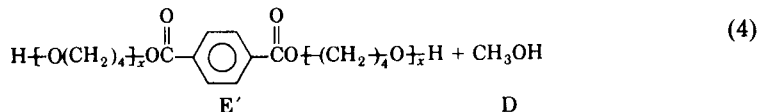
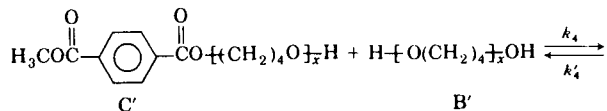
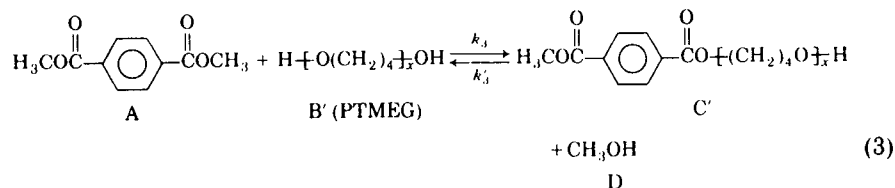
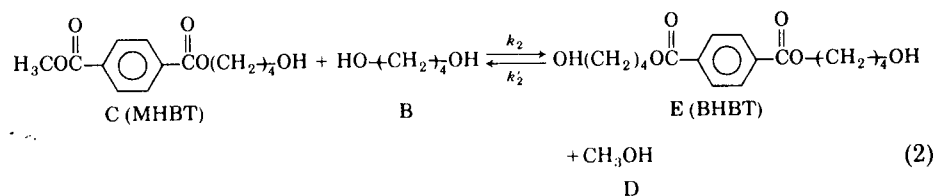
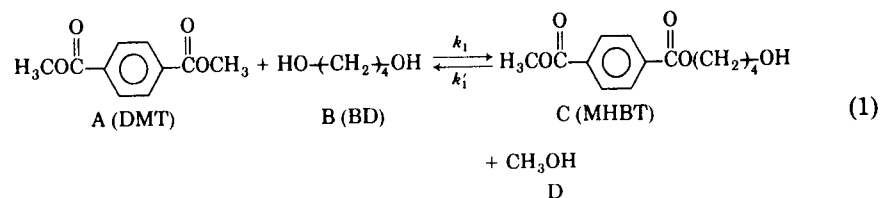


This unique structure offers excellent properties suitable for many applications.^{1,2,6,16} The properties of such copolymers depend strongly upon the nature of hard and soft segments, average block size, block size distribution, weight fraction of hard segments and soft segments, etc.¹⁻¹⁶ Therefore, it is of practical importance to understand the kinetics of both transesterification and polymerization for fine tuning of ultimate polymer properties to meet the needs required for specific applications of the polymer. Unfortunately,

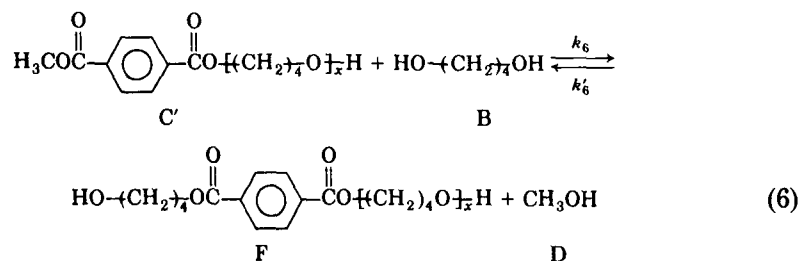
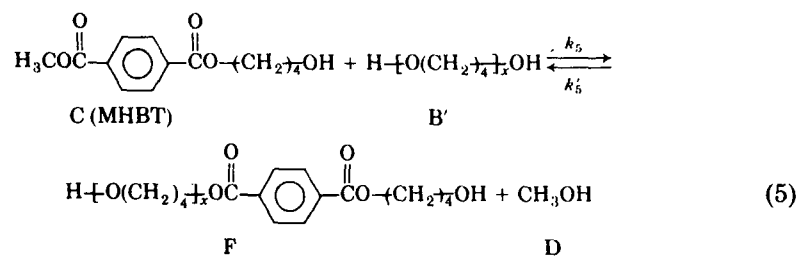
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however, there is a dearth of open literature on the reaction kinetics of both the transesterification of DMT with polyether glycols in the presence or absence of diols such as 1,4-butanediol and the melt polymerization. In this paper, we shall present a detailed analysis of the transesterification kinetics of DMT with poly(tetramethylene ether) glycol (PTMEG) which is commercially available in bulk quantity and BD catalyzed by tetrabutyl titanate. In our forthcoming paper, the kinetics of melt polymerization will be presented.

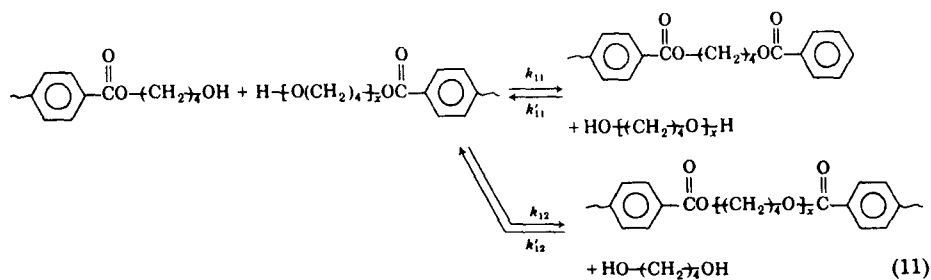
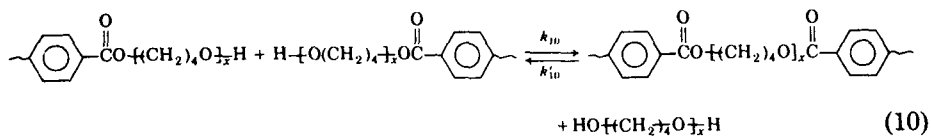
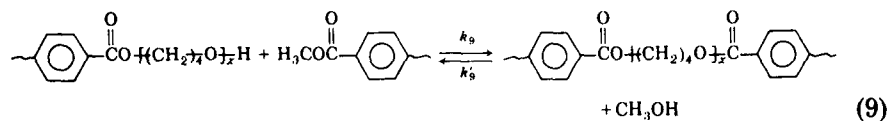
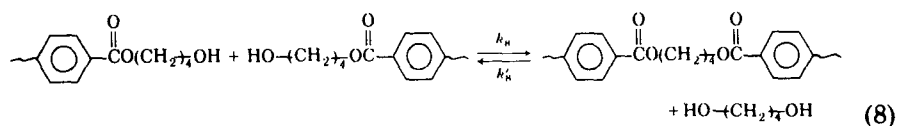
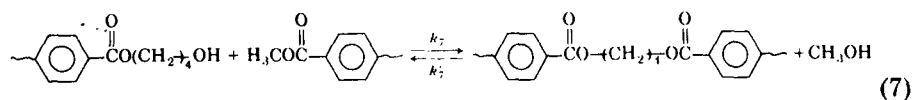
When DMT undergoes transesterification with PTMEG and BD in the presence of a metal catalyst, the following main reactions occur:



Here, MHBT and BHBT represent monohydroxybutyl terephthalate and bishydroxybutyl terephthalate, respectively. Note that C' and E' denote half-esterified DMT and fully esterified DMT with PTMEGs, respectively. Also cross reactions between the partially esterified intermediates can occur:



In addition to those reactions, the following oligomerization reactions may also be possible:



It was reported that in the transesterification of DMT with either ethylene glycol or BD, no significant oligomerization occurs up to about 80 ~ 90% conversion when excess diol is used.^{17,18} From this observation, eqs. (7)–(11) can be safely neglected [note that eqs. (7)–(11) are the major reactions in the low pressure melt *polymerization stage*]. As shown above, the transesterification reactions are essentially reversible; however, the forward reactions can be promoted by removing methanol efficiently from the reaction mixture. Methanol removal is facilitated by the relatively high transesterification temperature (~ 200°C) and vigorous agitation of the reaction medium.

It is well known that in the transesterification of DMT with ethylene glycol or BD, the reactive functional groups of various intermediates and reactants have equal reactivities.^{17–21} In this paper, we shall evaluate the applicability of the equal reactivity hypothesis to the transesterification of DMT with macrodiols such as PTMEG. Here, three different grades of PTMEGs (molecular weight: 650, 1000, 2000), which are used for the manufacture of commercial thermoplastic polyether–ester block copolymers will be used. The effect of various kinetic parameters on the transesterification rate and product composition distribution will also be analyzed.

EXPERIMENTAL

Transesterification of DMT with PTMEG

Predetermined amount of pure DMT (Aldrich Chemical) and PTMEG (TERACOL 2000, 1000, 650; DuPont) of a particular molecular weight was weighed and added to a 500 mL glass reaction flask. PTMEG is a waxy, white solid that melts to a clear, colorless liquid over a wide temperature range. Tetrabutyl titanate (Aldrich Chemical), the amount based on the DMT content in the reactor, was used without further purification and was injected into the reactor containing molten DMT and PTMEG. Upon addition of catalyst solution, methanol vapor evolved from the reactor almost immediately. To minimize the effect of oxidation, the reaction was carried out under nitrogen atmosphere. A Vigreux distillation column was attached to the reactor and maintained at 110–120°C to distill off the condensation byproduct (methanol). The methanol vapor was condensed and collected in a buret, and the rate of methanol evolution was used to estimate the conversion of methylester groups of the DMT. The standard reaction condition was as follows:

- Molecular weight of PTMEG = 1000;
- Temperature = 200°C;
- Catalyst concentration = 3.0×10^{-4} mol/mol DMT (or 0.94×10^{-4} mol/L);
- $[\text{PTMEG}]/[\text{DMT}] = 3.0$.

All experiments were duplicated to check the consistency of the experimental data and the reproducibility was excellent.

Transesterification of DMT with PTMEG and BD

DMT, PTMEG, and BD (Aldrich Chemical) were added to a 500-mL glass reaction flask in amounts that were in accordance with a specified initial

molar (or weight) percent of each reactant in the reaction mixture. The experimental procedure used for these experiments was almost identical to that described for the transesterification of DMT with PTMEG. Again, all the experimental runs were duplicated to check the consistency of the data.

RESULTS AND DISCUSSION

Transesterification of DMT with PTMEG

The four important reaction parameters in the transesterification of DMT with PTMEG are reaction temperature, catalyst concentration, molar ratio of PTMEG to DMT, and molecular weight of PTMEG. The first set of experiments was conducted at three different reaction temperatures (180, 200, 220°C) and the results are shown in Figure 1 in the form of a conversion of methyl ester groups of DMT vs. time curve. Compared with the transesterification rate of DMT with 1,4-butanediol,²⁰ the observed reaction rate with PTMEG in the present study is much slower than that with BD under similar reaction conditions. This is due to the relatively lower bulk concentration of hydroxyl groups in the reaction mixture when PTMEG is used than when 1,4-butanediol is used. Also note that the equilibrium conversion of methyl ester groups of DMT is only about 40% at 200°C. Again, this equilibrium conversion is much lower than the final conversion obtainable in the transesterification of DMT with BD (~90%). The activation energy of forward reaction [eq. (3)] estimated from the Arrhenius plot using the initial rates is 12.3 kcal/mol, which is about 35% higher than that for DMT-BD system (9.14 kcal/mol²⁰).

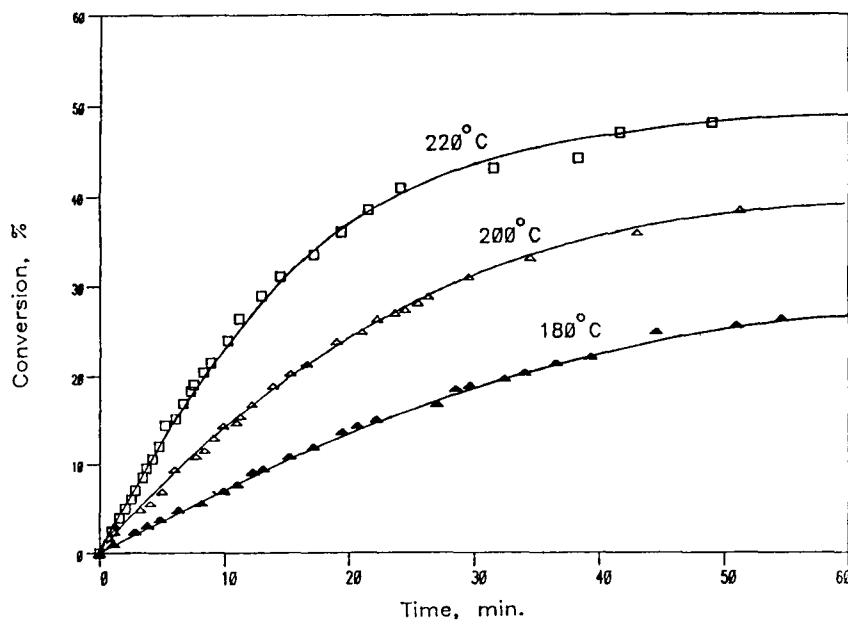


Fig. 1. Effect of reaction temperature on the transesterification of DMT with PTMEG (1000): $[C^*] = 0.94 \times 10^{-4}$ mol/L (or 3.0×10^{-4} mol/mol DMT); $[PTMEG]/[DMT] = 3.0$.

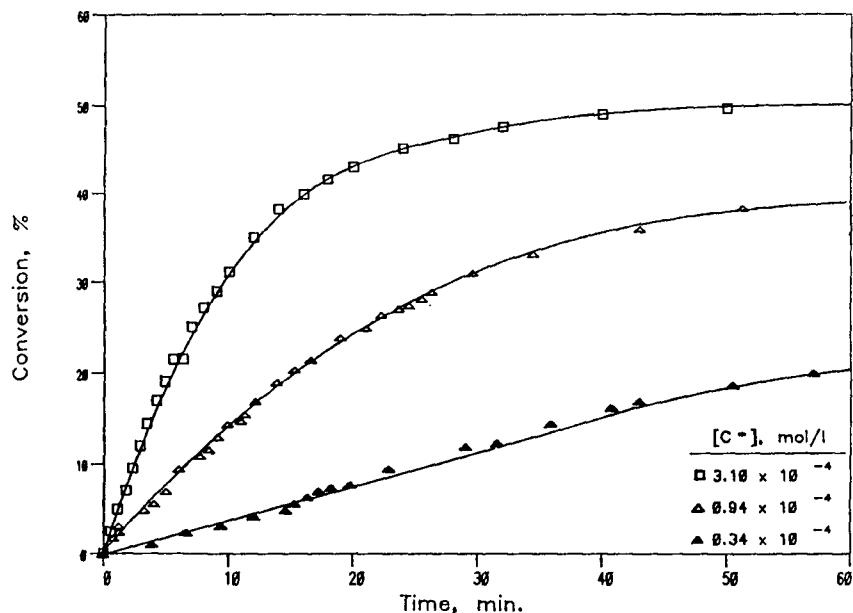


Fig. 2. Effect of catalyst concentration on the transesterification of DMT with PTMEG (1000): $T = 200^\circ\text{C}$, $[\text{PTMEG}]/[\text{DMT}] = 3.0$. $[C^*]$ (mol/L): (\square) 3.10×10^{-4} ; (Δ) 0.94×10^{-4} ; (\blacktriangle) 0.34×10^{-4} .

The effect of catalyst concentration ($[C^*]$) on the fractional conversion of methyl ester groups of DMT is illustrated in Figure 2. Note that the conversion levels off at about 50% for the highest catalyst concentration ($[C^*] = 3.1 \times 10^{-4}$ mol/L). It was observed during the experiments that when higher catalyst concentration was employed, undesirable entrainment of DMT to the distillation column and condenser occurred. The forward reaction of ester exchange [eq. (1)] has been found to be of the first order with respect to catalyst concentration as shown in Figure 3. Here, X_A denotes the fractional conversion of methyl ester groups of DMT and dX_A/dt is the initial reaction rate obtained from Figure 2.

The properties of PEE block copolymer are dependent on the molecular weight of PTMEG being used. Thus, it will be interesting to assess the reactivity of hydroxyl groups of PTMEG of various molecular weights. Figure 4 illustrates the effect of molecular weight of PTMEG on the conversion of methyl ester groups of DMT during the transesterification. Here, the PTMEGs being used have average molecular weights of 650, 1000, and 2000. In this experiment, the bulk concentration of catalyst and the molar ratio of PTMEG to DMT were held constant. The higher conversion of DMT with PTMEG of low molecular weight is noticeable. This is due to the high content of hydroxyl groups, represented by the high hydroxyl number, for low molecular weight PTMEGs as shown in Figure 5. Figure 5 also indicates that the rate of transesterification (i.e., dX_A/dt) is of the first order with respect to the concentration of hydroxyl groups of PTMEG and is independent of the chain length of PTMEG.

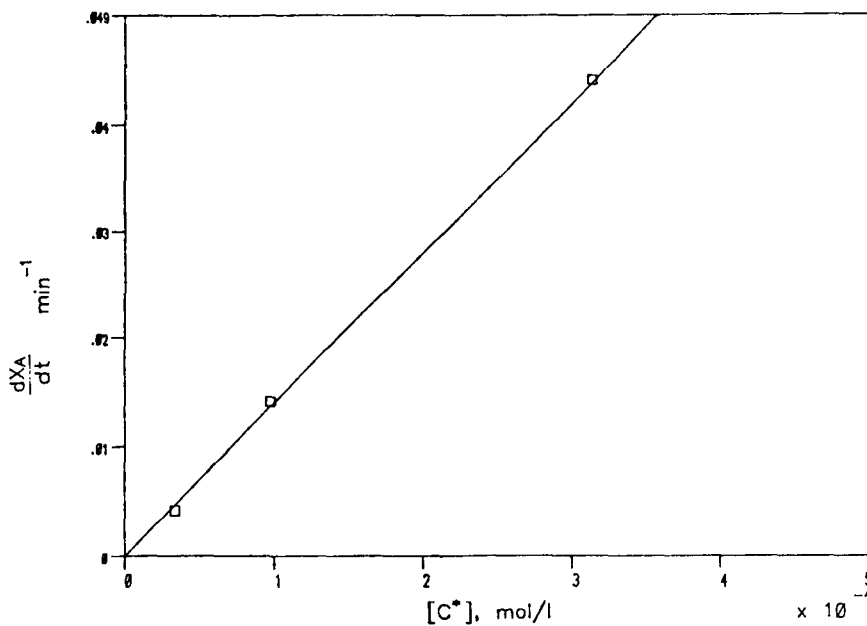


Fig. 3. Reaction rate vs. catalyst concentration for the transesterification of DMT with PTMEG (1000); $T = 200^{\circ}\text{C}$; $[\text{PTMEG}]/[\text{DMT}] = 3.0$.

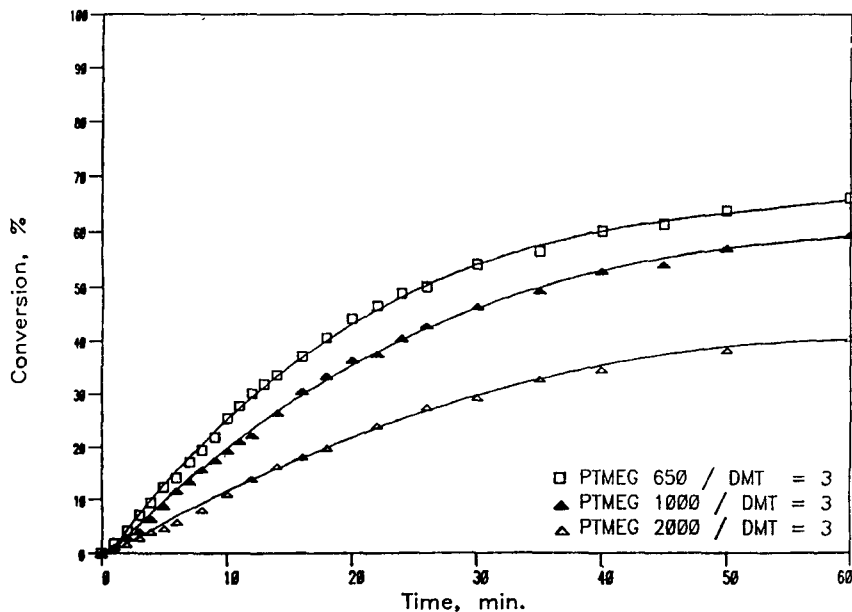


Fig. 4. Effect of molecular weight of PTMEG on the conversion of methyl ester groups: $T = 200^{\circ}\text{C}$; $[\text{C}^*] = 0.94 \times 10^{-4}$ mol/L; $[\text{PTMEG}]/[\text{DMT}] = 3.0$; (□) PTMEG 650/DMT; (▲) PTMEG 1000/DMT; (△) PTMEG 2000/DMT.

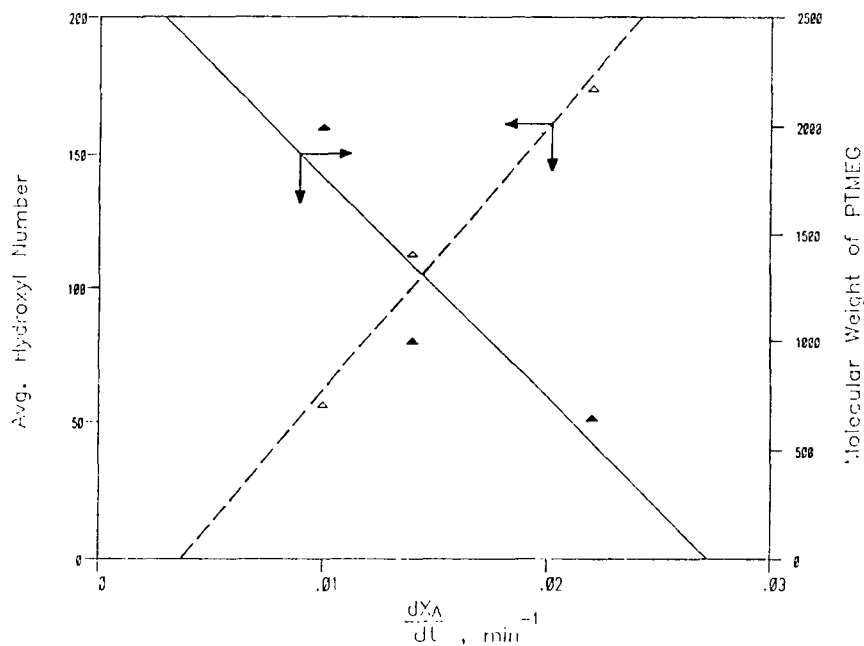


Fig. 5. Effect of molecular weight and hydroxyl number of PTMEG on the transesterification rate: $T = 200^{\circ}\text{C}$; $[C^*] = 0.94 \times 10^{-4}$ mol/L; $[\text{PTMEG}]/[\text{DMT}] = 3.0$; hydroxyl number from Ref. 22.

The effect of the molar ratio of $[\text{PTMEG}]$ to $[\text{DMT}]$ is illustrated in Figures 6(a), (b), and (c) for the three different PTMEGs of varying molecular weight. In conducting this experiment the bulk initial catalyst concentration was held constant at 0.94×10^{-4} mol/L. Within the range of concentration of PTMEG and DMT considered in our study, there is only a slight effect of $[\text{PTMEG}]/[\text{DMT}]$ ratio on the conversion of methyl ester groups of DMT. It is also observed that the transesterification reaction is of the first order with respect to methyl ester group concentration as shown in Figure 7. In carrying out the experiments for Figure 7, an excess amount of PTMEG was used to maintain relatively constant hydroxyl group concentration in the reaction mixture (i.e., $[\text{PTMEG}]/[\text{DMT}] = 4.0$). This figure also suggests that the reactivity of hydroxyl groups of PTMEG is independent of PTMEG chain length.

Transesterification of DMT with PTMEG and 1,4-Butanediol (BD)

In synthesizing the polyether ester block copolymer, DMT is first transesterified with PTMEG and BD in the presence of metal acetate catalyst. Physical, mechanical, and rheological properties of the resulting polymer are strongly dependent on the composition of the polymer, i.e., weight fraction of hard segments (crystalline polyester segments) and soft segments (amorphous elastomeric polyether segments), average block length of hard and soft segments, etc. For example, tear strength, hardness, and melting point increase with increasing content of tetramethylene terephthalate in the copolymer.^{1,2,11}

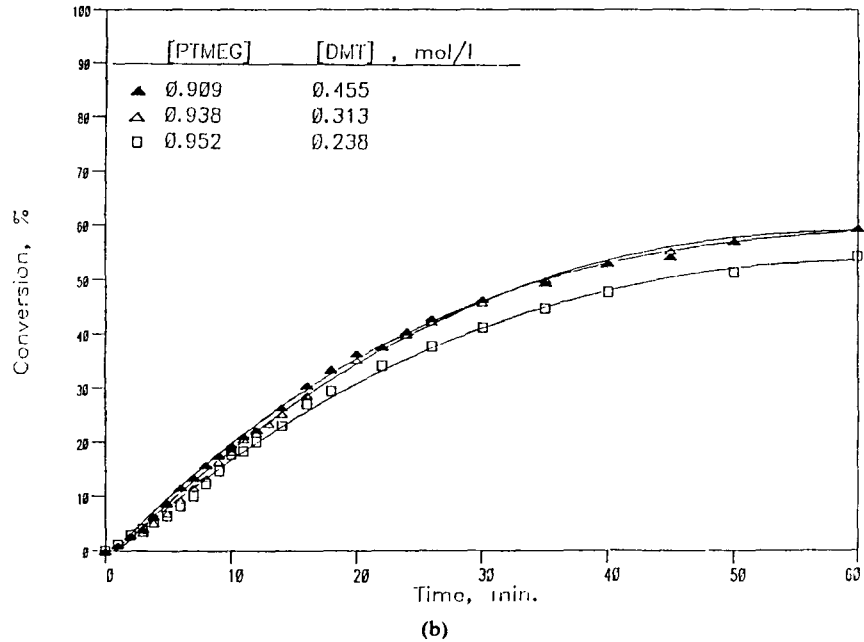
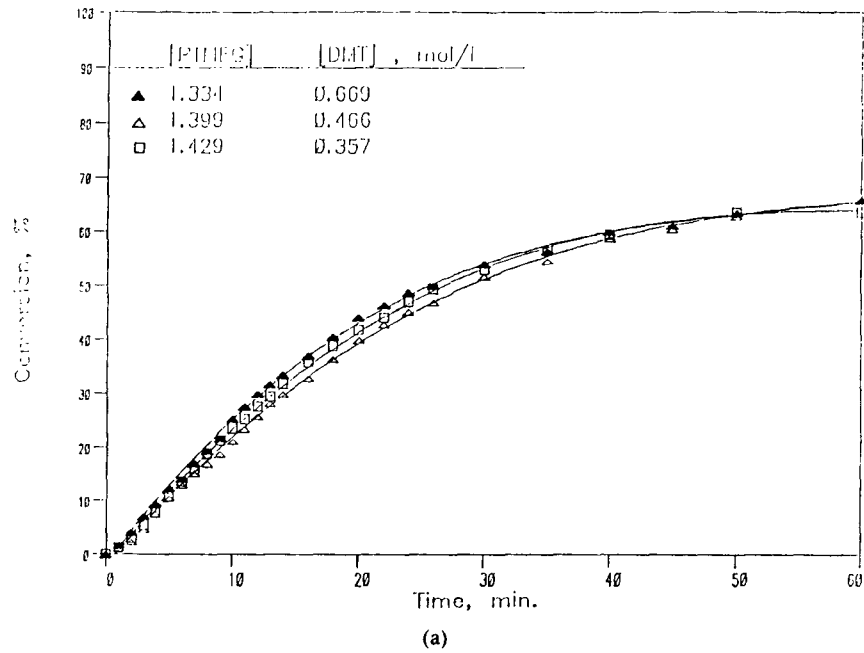


Fig. 6. Effect of [PTMEG]/[DMT] ratios on the conversion of methyl ester groups: $T = 200^\circ\text{C}$; $[C^*] = 0.94 \times 10^{-4}$ mol/L. (a) [PTMEG 650]/[DMT] (mol/L): (▲) 1.334/0.669; (△) 1.399/0.466; (□) 1.429/0.357. (b) [PTMEG 1000]/[DMT] (mol/L): (▲) 0.909/0.455; (△) 0.938/0.313; (□) 0.952/0.238. (c) [PTMEG 2000]/[DMT] (mol/L): (▲) 0.476/0.238; (△) 0.484/0.161; (□) 0.488/0.122.

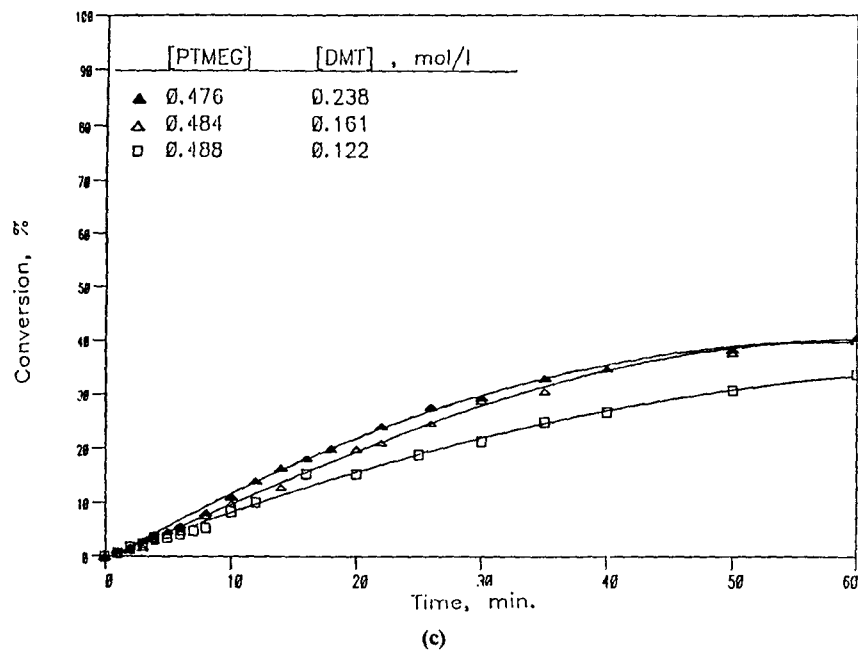
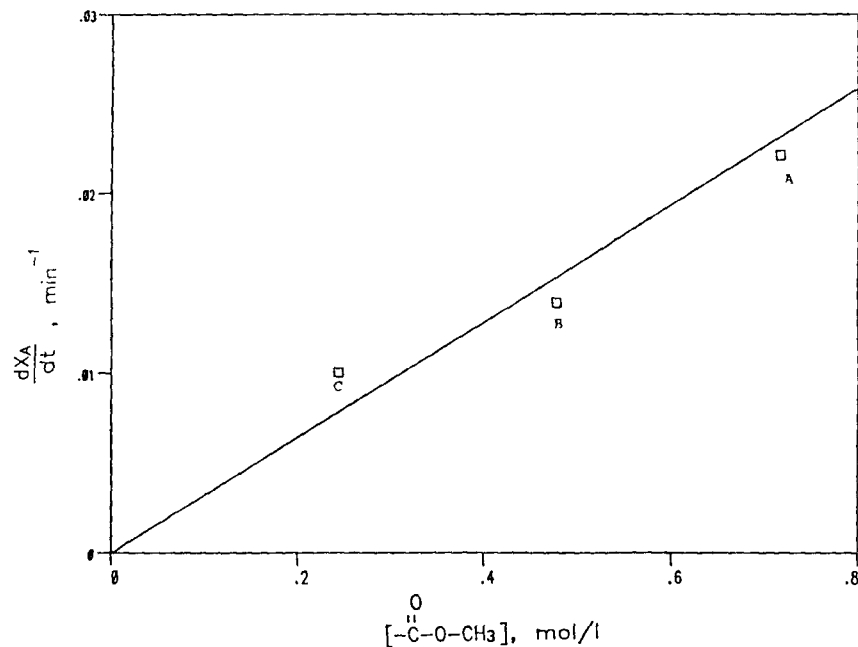


Fig. 6. (Continued from previous page)

Fig. 7. Reaction rate vs. methyl ester group concentration with excess amount of PTMEG: $T = 200^{\circ}\text{C}$; $[\text{PTMEG}]/[\text{DMT}] = 4.0$; $[C^*] = 0.94 \times 10^{-4} \text{ mol/L}$; PTMEG: (A) 650; (B) 1000; (C) 2000.

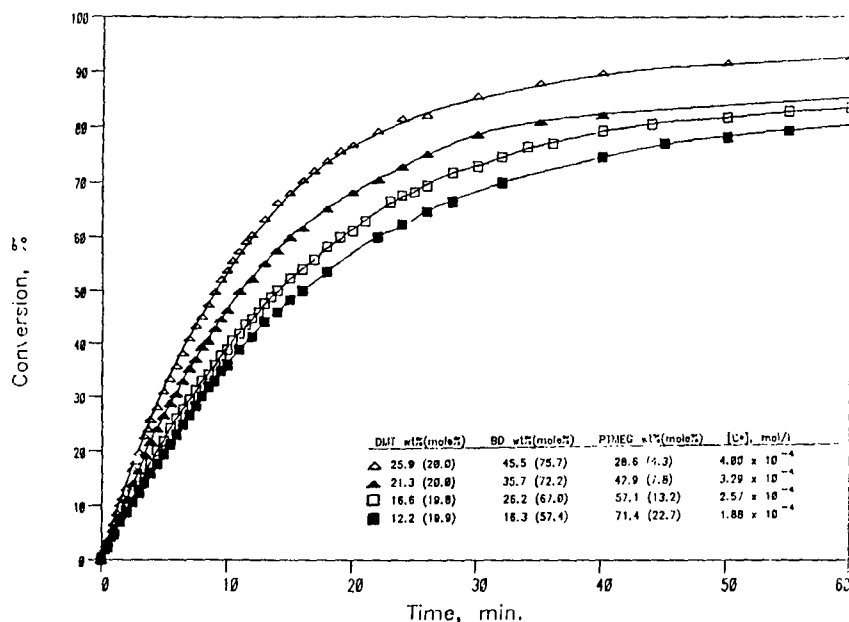


Fig. 8. Transesterification of DMT with PTMEG 1000 and 1,4-butanediol at 200°C: DMT/BD/PTMEG; [C*][wt% (mol %); mol/L]; (Δ) 25.9(20.0)/45.5(75.7)/28.6(4.3); 4.00×10^{-4} ; (\blacktriangle) 21.3(20.0)/35.7(75.2)/42.9(7.8); 3.29×10^{-4} ; (\square) 16.6(19.8)/26.2(67.0)/57.1(13.2); 2.57×10^{-4} ; (\blacksquare) 12.2(19.9)/16.3(57.4)/71.4(22.7); 1.88×10^{-4} .

With mole fraction of DMT held constant, mole fraction of BD and PTMEG was varied, and the resulting conversion profiles are shown in Figure 8. Note that the overall kinetic curves follow those of the DMT-BD transesterification due to the high reactivity of methyl ester groups of DMT with BD. Increasing the content of PTMEG decreases the reaction rate. It is also observed that the use of PTMEG of different molecular weight has a negligible effect on the conversion of DMT.

Estimation of Kinetic Parameters

If methanol is efficiently removed from the reaction mixture by distillation with negligible oligomerization and side reactions, only eqs. (1) and (2) become important in the transesterification of DMT with BD. The esterification reactions may be further simplified as being irreversible reactions and can be written in the form



where A is the DMT, B the 1,4-butanediol, C the monohydroxybutyl terephthalate, D the methanol, and E the bishydroxybutyl terephthalate.

Two rate constants, k_1 and k_2 , have been determined in our previous report,²⁰ and they are

$$k_1 = 6.22 \times 10^{11} \exp(-9,140/RT), \text{ mL}^2/\text{mol}^2 \text{ min}$$

$$k_2 = 3.18 \times 10^{11} \exp(-9,140/RT), \text{ mL}^2/\text{mol}^2 \text{ min}$$

here the activation energies are in cal/mol.

Now, let us consider the transesterification of DMT with PTMEG with tetrabutyltitanate as a catalyst. Under the same assumptions described above, only reactions (3) and (4) are important in the DMT-PTMEG transesterification system. These reactions can be rewritten as



where B' is the PTMEG, C' the half-transesterified DMT, and E' the fully transesterified DMT. The rate equations for reactions (14) and (15) are

$$r_3 = \frac{1}{V} \frac{d\xi_3}{dt} = k_3 \frac{1}{V^3} n^* n_A n_{B'} \quad (16)$$

$$r_4 = \frac{1}{V} \frac{d\xi_4}{dt} = k_4 \frac{1}{V^3} n^* n_{B'} n_{C'} \quad (17)$$

where ξ_3 and ξ_4 denote the extent of reaction for reactions (14) and (15), respectively. n^* is the number of moles of catalyst, n_i the number of moles of species i in the reaction mixture, and V the volume of reaction mixture. In the transesterification of DMT with PTMEG, the rate of change in the number of moles of A and C' takes the form

$$\frac{dn_A}{dt} = -k_3 \frac{1}{V^2} n^* n_A n_{B'} \quad (18)$$

$$\frac{dn_{C'}}{dt} = k_3 \frac{1}{V^2} n^* n_A n_{B'} - k_4 \frac{1}{V^2} n^* n_{B'} n_{C'} \quad (19)$$

Note that the effective catalyst concentration (n^*/V), and the bulk concentration of other components vary during the reaction due to the decrease in the volume of reaction mixture with continuous removal of methanol from the reactor. Assuming equal reactivity of the methyl ester groups in A and C' (i.e., $k_3 = 2k_4$), the following relation between $n_{C'}$ and n_A is obtained:

$$n_{C'} = 2n_A \left[\left(\frac{n_{A0}}{n_A} \right)^{1/2} - 1 \right] \quad (20)$$

From the stoichiometry, we obtain

$$n_{B'} = n_{B0'} - n_D \quad (21)$$

$$n_{C'} = 2(n_{A0} - n_A) - n_D \quad (22)$$

$$n_E = n_A - n_{A0} + n_D \quad (23)$$

where n_{A0} and $n_{B0'}$ represent initial number of moles of A and B', respectively.

From Eqs. (20) and (22), the following is obtained:

$$n_A = \frac{(2n_{A0} - n_D)^2}{4n_{A0}} \quad (24)$$

Hence, the amount of each species in the reaction mixture is expressed in terms of initial composition and the mass of methanol collected via distillation (n_D). Then, the rate of transesterification is estimated from the rate of methanol evolution as follows:

$$\frac{dn_D}{dt} = k_3 \frac{n^*}{V^2} (n_A n_{B'} + \frac{1}{2} n_{B'} n_{C'}) \quad (25)$$

where the reactor volume V is given by

$$V = V_0 - \frac{n_D}{\rho_D} \quad (26)$$

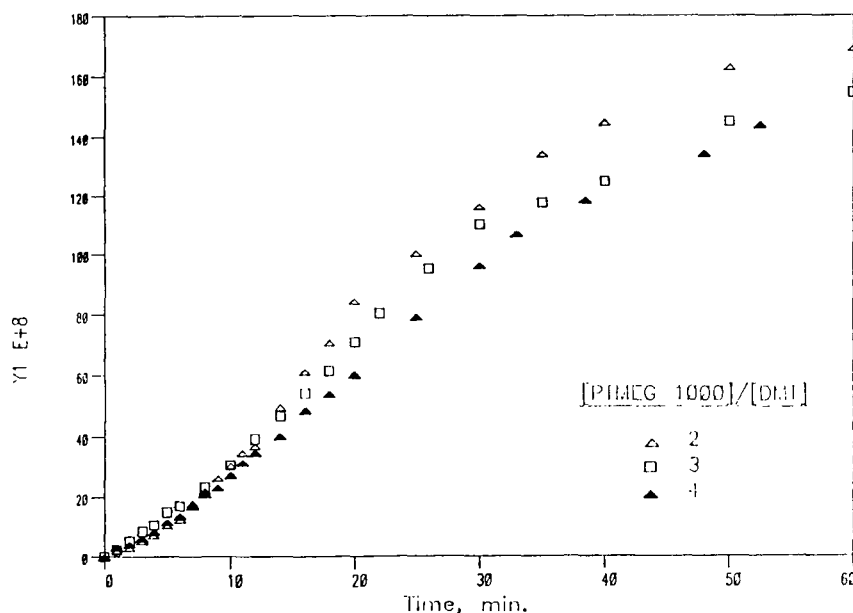


Fig. 9. Test of equal reactivity hypothesis with molecular species model [eq. (27)], $[C^*]/[DMT] = 3.0 \times 10^{-4}$ mol/mol. $[PTMEG 1000]/[DMT]$: (Δ) 2; (\square) 3; (\blacktriangle) 4.

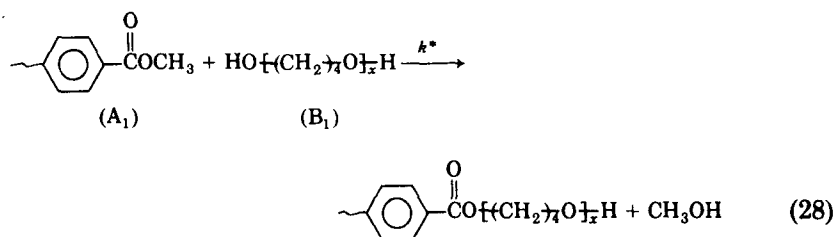
Here, V_0 and ρ_D denote initial reactor volume and the molar density of methanol, respectively. Upon integration of eq. (25), the following equation is obtained:

$$Y_1 = \int_0^{V_D} \frac{\rho_D (V_0 - V_D)^2 dV_D}{n^* \{ \Phi (n_{B_0'} - \rho_D V_D) + \frac{1}{2} (n_{B_0'} - \rho_D V_D) [2(n_{A_0} - \Phi) - \rho_D V_D] \}} = k_3 t \quad (27)$$

where $\Phi \triangleq (2n_{A_0} - \rho_D V_D)^2 / 4n_{A_0}$.

Experimental kinetic data for the DMT-PTMEG system with PTMEG of molecular weight 1000 have been tested with eq. (27) and the results are illustrated in Figure 9. Note that a linearity is good up to about 40-45% conversion [cf. Fig. 6(b)], and the experimental data tend to deviate from the model afterward.

In the approach above, the reactants (DMT and PTMEG) have been considered as the molecular species; however, the transesterification is a reaction between the functional groups of DMT and PTMEG (i.e., methyl ester groups and hydroxyl groups). Thus one may view the reaction as follows:



The corresponding rate equation is

$$\frac{d\xi^*}{dt} = k^* \frac{n^*}{V^2} (n_{A_1,0} - \xi^*) (n_{B_1,0} - \xi^*) \quad (29)$$

where ξ^* is the extent of reaction, $n_{A_1,0}$ and $n_{B_1,0}$ the initial number of moles of the methyl ester group and hydroxyl group, respectively. With the fractional conversion of the methyl ester groups (A_1) defined as

$$X_{A_1} = (n_{A_1,0} - n_{A_1}) / n_{A_1,0} \quad (30)$$

the above rate equation may be rewritten as

$$\frac{dX_{A_1}}{dt} = k^* \frac{n^* n_{B_1} (1 - X_{A_1}) [1 - (n_{A_1,0} / n_{B_1,0}) X_{A_1}]}{(V_0 - n_{A_1,0} X_{A_1} / \rho_D)^2} \quad (31)$$

Integrating eq. (31) yields

$$\frac{V_0^2}{n_{B0} n^*} \left[\begin{aligned} & \frac{1}{1-\gamma} \ln \left(\frac{1-\gamma X_{A1}}{1-X_{A1}} \right) - \frac{2n_{A0'}}{\rho_D V_0 (1-\gamma)} \\ & \times \left[-\ln(1-X_{A1}) + \frac{1}{\gamma} \ln(1-\gamma X_{A1}) \right] \\ & + \left(\frac{n_{A0'}}{\rho_D V_0} \right)^2 \left\{ \frac{1}{(1-\gamma)(1-X_{A1})} - \frac{1}{1-\gamma} + \frac{1}{(1-\gamma)^2} \right. \\ & \quad \left. \left[-\frac{1}{\gamma} \ln(1-\gamma X_{A1}) + (2-\gamma) \ln(1-X_{A1}) \right] \right\} \end{aligned} \right] = k^* t \quad (32)$$

where

$$\gamma \triangleq n_{A1,0}/n_{B,0}$$

Figure 10 shows the result of eq. (32) applied to experimental data. Note that some deviation from the linearity occurs near the equilibrium conversion. The tests were also conducted for the experimental data obtained using PTMEG of different molecular weights (i.e., 650 and 2000), and similar results were observed. The rate constants k^* , estimated from Figure 10, are shown in Table I. The average values of k^* are 1.35×10^8 , 1.97×10^8 , and 2.43×10^8

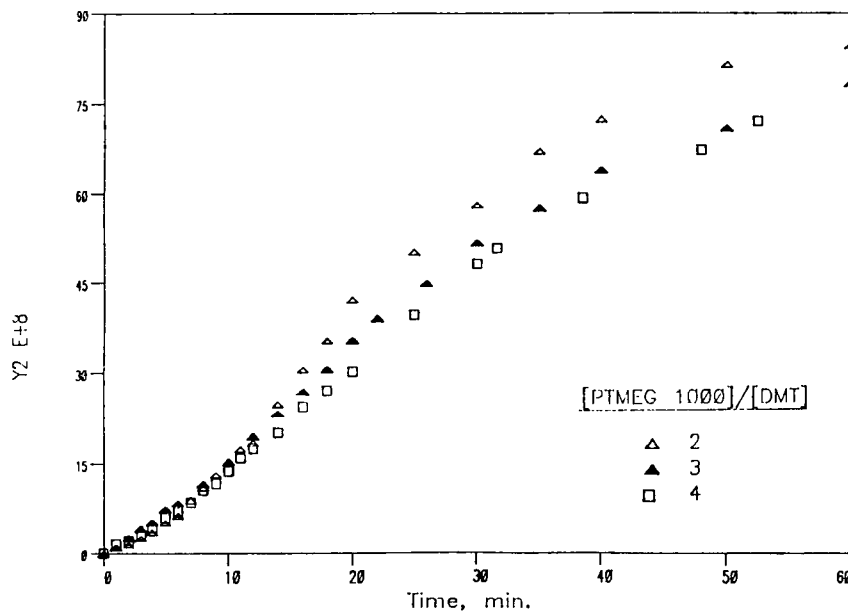


Fig. 10. Test of functional group model [eq. (32)]. [PTMEG 1000]/[DMT]: (Δ) 2; (▲) 3; (□) 4.

TABLE I
Rate Constants Estimated by Various Methods

Mol. wt. of PTMEG	[PTMEG]/[DMT]	Molecular species model		Functional group model	Simplex search	
		k_3 ($\times 10^8$)	k_4	k^a ($\times 10^8$)	k_3 ($\times 10^8$)	k_4 ($\times 10^8$)
650	2.0	2.70	1.35	1.35	2.83	1.36
	3.0	2.70	1.35	1.40		
	4.0	2.70	1.35	1.30		
	Avg. 2.70		1.35	1.35		
1,000	2.0	4.30	2.15	2.20	3.90	1.95
	3.0	3.70	1.85	1.90		
	4.0	3.50	1.75	1.80		
	Avg. 3.83		1.92	1.97		
2,000	2.0	5.30	2.65	2.80	4.86	2.44
	3.0	4.75	2.38	2.50		
	4.0	4.00	2.00	2.00		
	Avg. 4.68		2.34	2.43		

^a k 's in mL²/mol² min.

mL²/mol² min for PTMEGs of molecular weights 650, 1000, and 2000, respectively.

In the molecular species model described above, reactivities of all methyl ester group of DMT and half-esterified DMT are assumed equal. In what follows, the two rate constants (k_3 and k_4) for the transesterification of DMT with PTMEG will be determined without invoking the equal reactivity hypothesis.

From eqs. (16) and (17), the rate of volume change of the methanol collected is

$$\frac{dV_D}{dt} = \frac{k_3 n^* n_A n_{B'} + k_4 n^* n_{B'} n_C}{\rho_D (V_0 - n_D/\rho_D)^2} \quad (33)$$

where V_D denotes the volume of methanol evolved. Using the extent of reaction for reactions (14) and (15), one obtains the following rate expressions:

$$\frac{d\xi_3}{dt} = k_3 \frac{n^*}{\beta} (n_{A0} - \xi_3)(n_{B0'} - \xi_3 - \xi_4) \quad (34)$$

$$\frac{d\xi_4}{dt} = k_4 \frac{n^*}{\beta} (n_{B0'} - \xi_3 - \xi_4)(\xi_3 - \xi_4) \quad (35)$$

$$\frac{dV_D}{dt} = \frac{n^*}{\rho_D \beta} [k_3 (n_{A0} - \xi_3)(n_{B0'} - \xi_3 - \xi_4) + k_4 (n_{B0'} - \xi_3 - \xi_4)(\xi_3 - \xi_4)] \quad (36)$$

where

$$\beta \triangleq \left(V_0 - \frac{\xi_3 + \xi_4}{\rho_D} \right)^2 \quad (37)$$

During the early reaction period (i.e. $t \approx 0$), we may assume that the second reaction [eq. (15)] does not proceed to a considerable extent. Then, eq. (36) may be simplified to

$$\left. \frac{dV_D}{dt} \right|_{t \rightarrow 0} = \frac{k_3 n^* n_{A0} n_{B0'}}{\rho_D V_0^2} \quad (38)$$

Thus, one can estimate k_3 by extrapolating V_D vs. time curve to $t = 0$. With this k_3 value, the second rate constant k_4 has been estimated for various reaction conditions using modified multivariable simplex search technique in which the following objective function was minimized:

$$S = \sum_t (V_D - V_{D, \text{exp}})^2 \quad (39)$$

where $V_{D, \text{exp}}$ denotes the experimentally measured volume of methanol at time t . The details of computational procedure can be found in Ref. 21. The results of this parameter search study are listed in the last two columns of Table I. Note that the reaction rate constants obtained by this optimal search technique agree extremely well with those obtained by other methods in which equal reactivity hypothesis was employed.

The composition of the transesterification mixture for DMT and PTMEG is computed by solving the rate equations [(34)–(36)] with kinetic constants estimated in the previous sections. Figure 11 illustrates the product composition distribution curves for different [PTMEG]/[DMT] ratios during the course of transesterification of DMT with PTMEG. Note that the content of fully esterified DMT (denoted by E') becomes smaller with an increase in [PTMEG]/[DMT] ratio. This simulation result also indicates that the combined mole fraction of half-esterified DMT (C') and fully-esterified DMT (E') is less than 0.5 after 1 h of reaction period. This implies that longer reaction time is required to achieve high content of esterified DMT needed for the polymerization.

Product distribution of the DMT–PTMEG–BD transesterification system is also computed based on the rate constants obtained for DMT–BD and DMT–PTMEG systems, respectively. Since the equal reactivity hypothesis is applicable for both DMT–BD and DMT–PTMEG systems, it is most likely that the hypothesis also holds for the cross reactions (5) and (6). In such case, the reaction rate is only a function of the species reacting with the methyl ester group; therefore we assume $k_5 \approx k_4$ and $k_6 \approx k_2$. The simplified form of

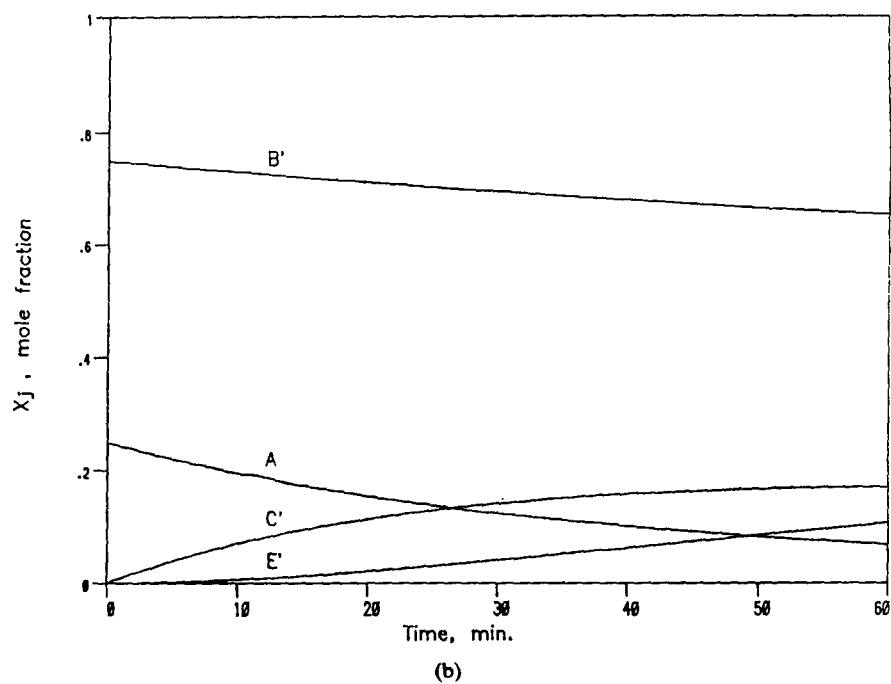
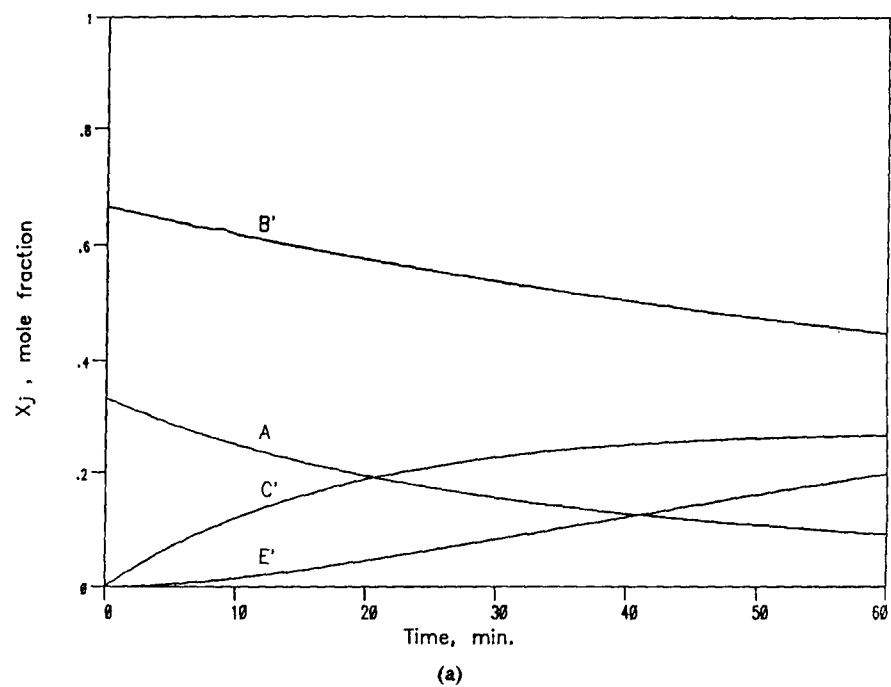
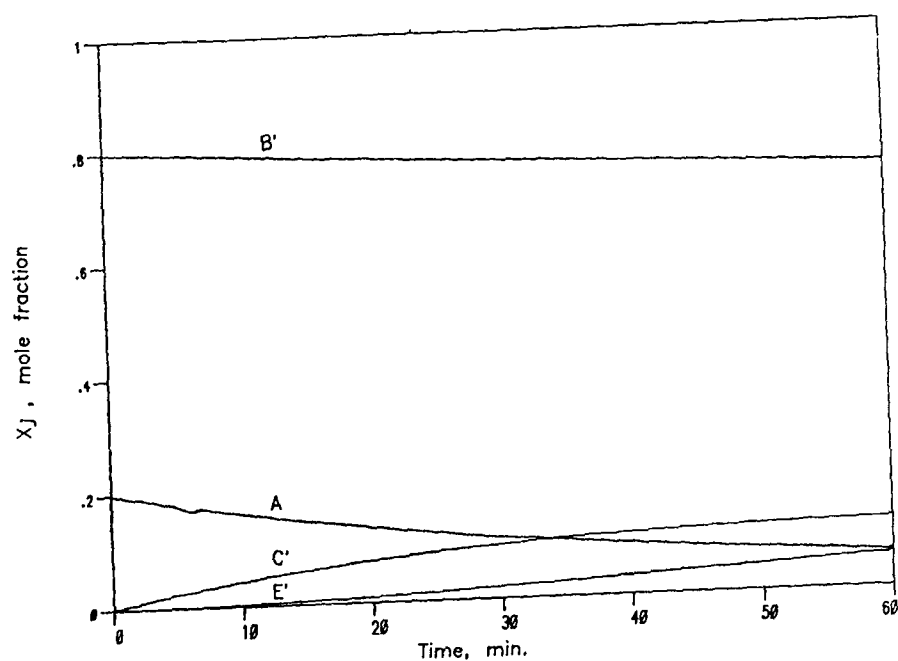


Fig. 11. Effect of [PTMEG 1000]/[DMT] on the product composition $T = 200^\circ\text{C}$; $[\text{C}^*]/[\text{DMT}] = 3.0 \times 10^{-4}$ mol/mol. [PTMEG]/[DMT]: (a) 2.0; (b) 3.0; (c) 4.0.



(c)

Fig. 11. (Continued from previous page)

reactions (1)–(6) is given as



Here, ξ_j denotes the extent of reaction for the j th reaction. For this reaction

system, the following rate equations are obtained:

$$\frac{d\xi_1}{dt} = \frac{V}{\lambda} k_1 n^* (n_{A0} - \xi_1 - \xi_3)(n_{B0} - \xi_1 - \xi_2 - \xi_6) \quad (41a)$$

$$\frac{d\xi_2}{dt} = \frac{V}{\lambda} k_2 n^* (n_{B0} - \xi_1 - \xi_2 - \xi_6)(\xi_1 - \xi_2 - \xi_5) \quad (41b)$$

$$\frac{d\xi_3}{dt} = \frac{V}{\lambda} k_3 n^* (n_{A0} - \xi_1 - \xi_3)(n_{B0'} - \xi_3 - \xi_4 - \xi_5) \quad (41c)$$

$$\frac{d\xi_4}{dt} = \frac{V}{\lambda} k_4 n^* (n_{B0'} - \xi_3 - \xi_4 - \xi_5)(\xi_3 - \xi_4 - \xi_6) \quad (41d)$$

$$\frac{d\xi_5}{dt} = \frac{V}{\lambda} k_4 n^* (n_{B0'} - \xi_3 - \xi_4 - \xi_5)(\xi_1 - \xi_2 - \xi_5) \quad (41e)$$

$$\frac{d\xi_6}{dt} = \frac{V}{\lambda} k_4 n^* (n_{B0} - \xi_1 - \xi_2 - \xi_6)(\xi_3 - \xi_4 - \xi_6) \quad (41f)$$

The rate of reactor volume change is given by

$$\begin{aligned} \frac{dV_D}{dt} = \frac{V}{\rho_D \lambda} & \left[k_1 n^* (n_{A0} - \xi_1 - \xi_3)(n_{B0} - \xi_1 - \xi_2 - \xi_6) \right. \\ & + k_2 n^* (n_{B0} - \xi_1 - \xi_2 - \xi_6)(\xi_1 - \xi_2 - \xi_5) \\ & + k_3 n^* (n_{A0} - \xi_1 - \xi_3)(n_{B0'} - \xi_3 - \xi_4 - \xi_5) \\ & + k_4 n^* (n_{B0'} - \xi_3 - \xi_4 - \xi_5)(\xi_3 - \xi_4 - \xi_6) \\ & + k_4 n^* (n_{B0'} - \xi_3 - \xi_4 - \xi_5)(\xi_1 - \xi_2 - \xi_5) \\ & \left. + k_2 n^* (n_{B0} - \xi_1 - \xi_2 - \xi_6)(\xi_3 - \xi_4 - \xi_6) \right] \quad (42) \end{aligned}$$

where

$$\lambda \triangleq \left[V_0 \frac{\sum_{j=1}^6 \xi_j}{\rho_D} \right]^3$$

and at $t = 0$, $\xi_j = 0$, and $V_D = 0$. n^* denotes the initial number of moles of catalyst in the reactor.

The product composition is obtained by simultaneously solving the differential equations above with the fourth-order Runge-Kutta algorithm. Figure 12 shows the comparison of methanol evolution rate during the reaction observed experimentally and predicted by the model using kinetic parameters estimated in the previous section. Note that the agreement is quite satisfactory. Typical product distribution curve for the transesterification of DMT with PTMEG and BD is illustrated in Figure 13. Here, symbols A-F denote the

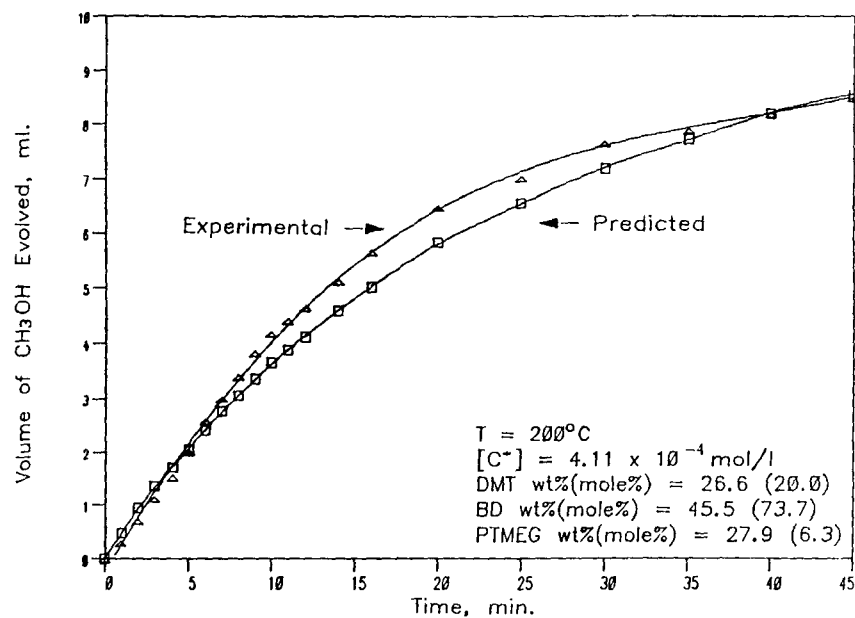


Fig. 12. Volume of methanol evolved during the transesterification of DMT with BD and PTMEG.

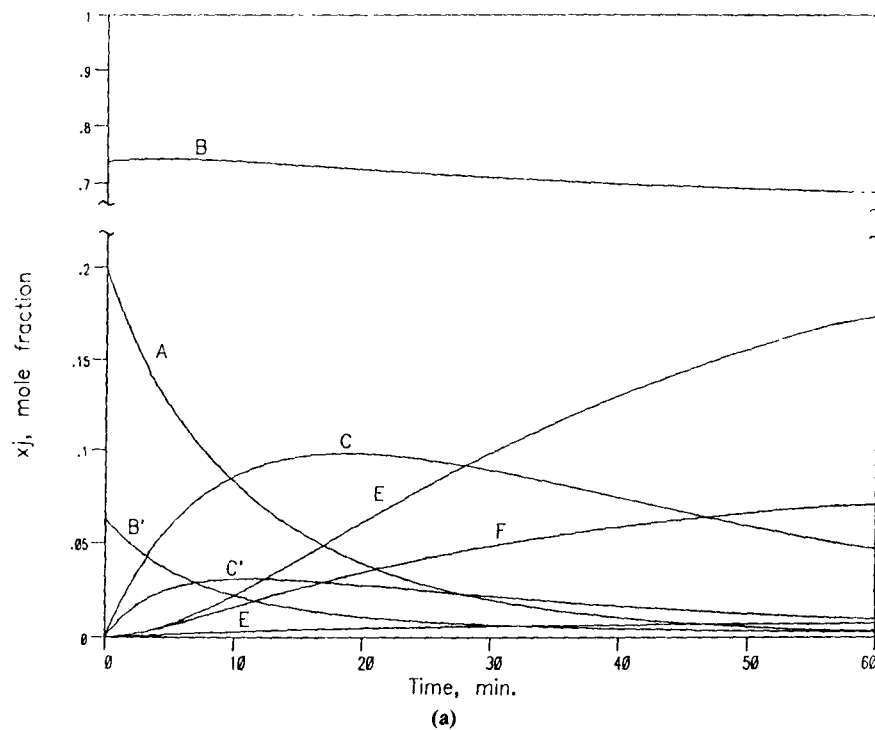


Fig. 13. Composition of transesterification mixture (a) PTMEG 650 wt% (mol %) = 26.6 (20.0), BD wt% (mol %) = 45.5 (73.7), DMT wt% (mol %) = 27.9 (6.3), $[C^*] = 4.11 \times 10^{-4} \text{ mol/l}$. (b) PTMEG 650 wt% (mol %) = 14.0 (20.0), BD wt% (mol %) = 16.2 (50.1), DMT wt% (mol %) = 69.8 (29.90), $[C^*] = 2.16 \times 10^{-4} \text{ mol/L}$.

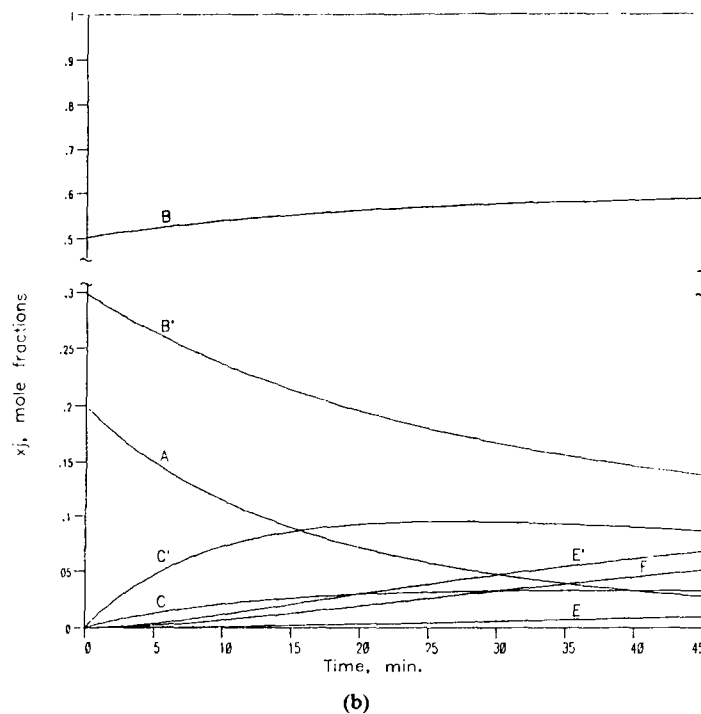


Fig. 13. (Continued from previous page)

species in eqs. (40). When the weight fraction of initial PTMEG charge is low [e.g., 30%, Fig. 13(a)], the major product species in the reactor are mono- and bis(hydroxy)butyl terephthalate (C and E) and component F which is produced by cross reactions [eqs. (5) and (6)]. The content of C' and E' is negligibly small. However, when the PTMEG loading is increased to 75 wt%, the mole fraction of both E' and F is also increased. The simulation result shown in Figure 13 suggests that a large fraction of polyester segment will be present in the polymers during the polymerization stage if the transesterification product as illustrated in Figure 13 is used as a monomer mixture. In other words, homopolymerization of PTMEG-transesterified DMT is less favored than that of BD-transesterified DMT. Simulation of the transesterification for PTMEGs of molecular weight 1000 and 2000 also shows quite similar product distribution profiles.²¹

CONCLUDING REMARKS

The kinetics of semibatch transesterification of dimethyl terephthalate (DMT) with poly(tetramethylene ether) glycol (PTMEG) and 1,4-butanediol (BD) was studied with tetrabutyl titanate as a catalyst. It has been found that the hydroxyl groups of PTMEG are equally reactive regardless of the polymer chain length within the range of experimental conditions employed. The equilibrium conversion of methyl ester groups of DMT at standard reaction conditions (200°C, [Cat] = 0.94×10^{-4} mol/L, [PTMEG]/[DMT] = 3) is about 40–45%, which is much lower than that of DMT transesterifica-

tion with 1,4-butanediol under similar reaction conditions. Three different methods were used to estimate the transesterification rate constants for the DMT-PTMEG system and the equal reactivity hypothesis was found to be valid. Complete product distribution curves were also computed for both DMT-PTMEG and DMT-PTMEG-BD transesterification systems with kinetic constants determined from this study. The simulation result indicates that the product distribution is quite strongly dependent on the initial weight percent of PTMEG charged to the transesterification reactor.

The authors are indebted to the Computer Science Center at the University of Maryland for computing time and to the National Science Foundation (Grant CBT-8504874) for the support of this research. We also thank the DuPont Co. for the generous donation of poly(tetramethylene ether) glycol (Teracol) for this study.

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Received March 5, 1986

Accepted April 16, 1986