Kinetic and Catalytic Aspects in Melt Transesterification of Dimethyl Terephthalate with Ethylene Glycol in the Presence of Different Catalytic Systems

M. DI SERIO,[1] R. TESSER,[2] F. TRULLI,[1] and E. SANTACESARIA[1],*

[1]Dipartimento di Chimica dell'Università degli Studi "Federico II," Via Mezzocannone 4 (80130) Napoli, Italy, and [2]Montefibre S.p.A., Acerra, Napoli, Italy
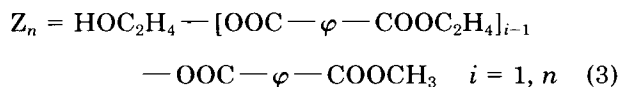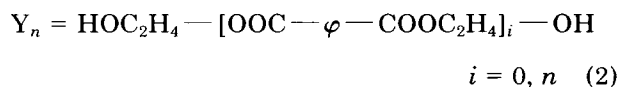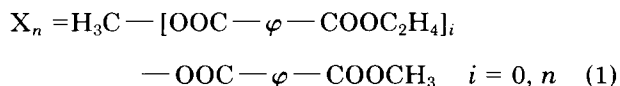
SYNOPSIS

The kinetics of transesterification of dimethyl terephthalate with ethylene glycol performed in the presence of catalysts such as: Pb, Zn, Mg, Co, and Mn acetates and a mixture of Mg, Mn, and Zn acetates has been studied in semibatch conditions. The catalytic behavior of Sb_2O_3 has been proven, too. The performance of the different catalytic systems has been investigated following both the amount of methanol released during time and the evolution with time of the concentration of any kind of oligomer formed as consequence of the reaction. The oligomers obtained were separated, identified, and quantitatively determined by HPLC analysis. In this way, information have been achieved on both the activities and selectivities of the different catalysts. The experimental data have been interpreted through a classic kinetic model based on a complex reaction scheme. Despite the complexity of the model, only two kinetic parameters and two equilibrium constants are necessary to simulate the kinetic behavior of all the oligomers. A kinetic constant (K_1) is related to the reaction of a methyl group with a hydroxyl of ethylene glycol, while the other (K_2) corresponds to the reaction of a methyl group with a terminal hydroxyl of a growing chain. The Mn, Pb, and Zn acetates have shown comparable high catalytic activities; however, the Mn selectivity to give oligomers with hydroxyl-hydroxyl terminal groups is better and similar to that shown by Co and Mg acetate, at a lower activity. Sb_2O_3 has a very low activity in transesterification but this activity could be important to eliminate the residual terminal methyl group during the polycondensation step. The catalytic activity of the mixture of Mg, Mn, and Zn acetate was greater than that shown by each component the mixture, while its selectivity was comparable with that of Mn and Mg acetate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The melt transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) is the first stage of the production of polyethyleneterephthalate (PET).

Besnoin et al.[1] and Santacesaria et al.[2] have recently shown by HPLC analysis that this reaction occurs with the formation of many oligomers characterized by the terminal groups of the chains, which can be hydroxyl-hydroxyl, methyl-hydroxyl or methyl-methyl such as in the following scheme:

$$X_n = H_3C - [OOC - \varphi - COOC_2H_4]_i$$
$$- OOC - \varphi - COOCH_3 \quad i = 0, n \quad (1)$$

$$Y_n = HOC_2H_4 - [OOC - \varphi - COOC_2H_4]_i - OH$$
$$i = 0, n \quad (2)$$

$$Z_n = HOC_2H_4 - [OOC - \varphi - COOC_2H_4]_{i-1}$$
$$- OOC - \varphi - COOCH_3 \quad i = 1, n \quad (3)$$

where X_0 corresponds to DMT; Y_0 to EG; Z_1 to methyl hydroxyethylterephthalate (MHET); Y_1 to bishydroxyethylterephtalate BHET, etc. The value of n depends on the operative conditions: for example, for a transesterification performed in a pilot

---

* To whom correspondence should be addressed.

plant it is about 10, as we ascertained by HPLC analysis.

It is evident that type X oligomers are not active in the polycondensation reaction steps during PET production, while type Y oligomers have a double activity in respect to the oligomer Z in the same reaction. Therefore, transesterification catalysts should have not only good activity but also good selectivity to produce oligomers of the type Y, for instance, the catalyst must promote the reaction of a methyl group with a hydroxyl of ethylene glycol rather than the reaction of a methyl group with a hydroxyl in a chain.

Hence, in order to compare the performance of several catalysts, it is necessary to evaluate not only the amount of methanol released as function of time as usually reported in literature[3-5] but also to analyze samples of the reaction mixture withdrawn at different reaction times by the HPLC technique.[1,2]

In a previous work,[2] the behavior of zinc acetate as melt transesterification catalyst has been studied and both the activity and selectivity to produce type Y oligomers have been determined. In the same article, a mathematical model able to simulate the evolution with time of the concentration of all species during the reaction has been developed and described.

This model was based on the classic definition of the complex reaction scheme characterized from the combination of many simultaneous and consecutive reactions. At any subsequent reaction sequence, reactants, products, and reactions involving them strongly increase. For example, by truncating the reaction scheme at the fourth stage the model consists of 58 reactions and 24 oligomeric species. Despite the large number of oligomers and occurring reactions, only two kinetic parameters occur to describe the system. The first kinetic constant (K_1) is related to the reaction of a methyl group with a hydroxyl of ethylene glycol, while the second (K_2) corresponds to the reaction of methyl groups with a hydroxyl terminating a chain. The related selectivity of these two reactions can simply be expressed as:

$$S_1 = K_1/(K_1 + K_2)   S_2 = K_2/(K_1 + K_2)   (4)$$

A brief description of the mathematical model used is reported in the present article, while more details can be found in the mentioned article.[2]

In the present work, the behavior of different catalyst such as Pb, Co, Mg, and Mn acetate, and of the mixtures of Mg, Mn, and Zn acetate has been investigated and compared with the behavior of zinc acetate catalyst.[2] The performance of Sb_2O_3 in the

transesterification reaction has been studied, too, confirming the low activity[4,5] of this catalyst already observed in literature.[4,5] However, this activity can be useful in the polymerization step to eliminate the residual methyl groups.

EXPERIMENTAL SECTION

Methods, Techniques, and Reagents

Kinetic runs have been carried out in a 500 mL jacketed glass reactor fitted with a distillation system able to remove the released methanol as soon as possible.

Normally, 100 g of DMT were put in the reactor and heated at the reaction temperature, then an appropriate amount of EG was added keeping the ratio EG/DMT = 2. Finally, the catalyst previously dissolved in about 15 mL EG was added.

Samples of the reaction mixture were withdrawn at different reaction times and submitted to HPLC analysis. At the corresponding times, the collected methanol volume was carefully read.

A list of the performed kinetic runs is reported in Table I, together with the catalyst employed and the operative conditions applied.

The HPLC analysis was carried out with a JASCO/PV 980 apparatus, and a UV JASCO 975 detector operating at 254 nm, using a Sperisorb S5W column of Labservice Analytica (25 cm length, 0.46 cm i.d., silica 5 μm). The mobile phase fed to the column was a mixture of hexane and dioxane changing composition with time according to a scheduled program.

More information on both the reactor and the employed analytical method are reported in a previous article.[2] All the reagents were furnished from Aldrich Co. at the highest purity available.

Kinetic Model

Adopting the general formulas (1)–(3) reported in the introduction, we can draw a reaction scheme as reported in Figure 1.

This reaction scheme, reported as an example, is truncated at the third stage of the reaction sequence and contains 15 reactions involving 12 different oligomers. Observing the scheme of Figure 1, it can be observed that the same oligomers are involved in many reactions; therefore, in order to exactly follow the evolution with time of all the oligomers, it is useful to make the stoichiometric matrix a_{ij} and define the rate of formation of i species as:

Table I **List of the Catalytic Systems Used with the Corresponding Operative Conditions and the Kinetic and Equilibrium Parameters Obtained from Mathematical Regression Analysis**
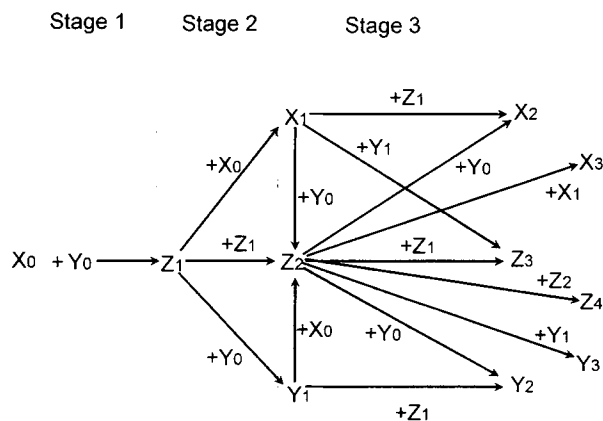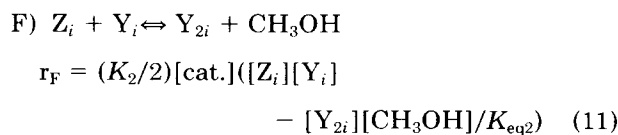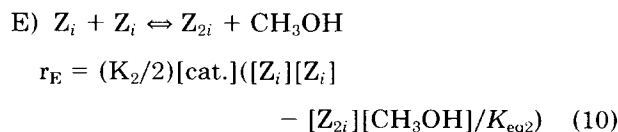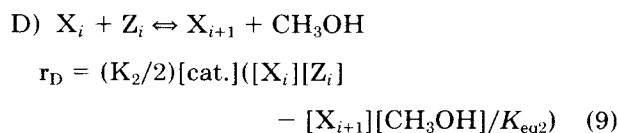
Metal	[Metal] $\mathrm{mol/L} \times 10^3$	Temp. °C	K_1 $\mathrm{L^2\ mol^{-2}\ min^{-1}}$	K_2 $\mathrm{L^2\ mol^{-2}\ min}$	K_{eq1}	K_{eq2}
Pb^{2+}	3.63	180	5.1	5.6	0.28	0.21
Zn^{2+}	1.87	180	5.0	4.0	0.28	0.21
Mn^{2+}	3.63	180	8.3	2.1	0.28	0.21
Co^{2+}	3.50	180	3.9	0.9	0.28	0.21
Mg^{2+}	3.67	180	4.2	1.2	0.28	0.21
Mg/Mn/Zn (Mix)	1.37	175	10.4	2.4	0.32	0.24
Mg/Mn/Zn (Mix)	1.38	185	16.6	4.2	0.27	0.19
Sb^{3+}	3.50	195	0.23	0.12	0.24	0.16

$$dC_i/dt = \sum_{j=1,m} \alpha_{ij} r_j \quad i = 1, n \qquad (5)$$

by truncating the reaction sequence at the fourth stage, because it has been showed that this level of accuracy is enough to describe the laboratory kinetic runs,[2] $m = 58$ (number of reactions) and $n = 24$ (number of oligomers). The details of a more complete kinetic scheme are reported in detail in a previous article.[2]

It is now necessary to give a kinetic expression for all the r_j with $j = 1,58$.

In a previous article,[2] it has been showed that: (i) the reactivity of a hydroxyl group of ethylene glycol can be different from the reactivity of a hydroxyl group in a chain; (ii) reactivity is not affected by the chain length; (iii) chains containing different terminal groups are less active by a factor one-half than those having terminal groups of the same type; (iv) the kinetic law is of second-order with respect to the reagents. On the basis of these observations, we can write the following six kinetic equations, r_{A-F}:

Stage 1   Stage 2   Stage 3
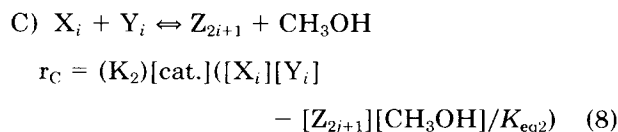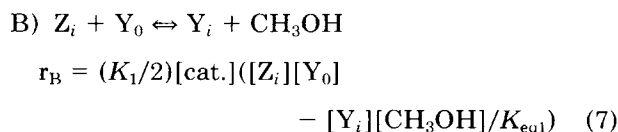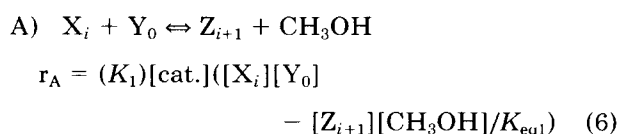
Figure 1 Reaction scheme truncated at the third stage.

A) $X_i + Y_0 \Leftrightarrow Z_{i+1} + CH_3OH$

$r_A = (K_1)[cat.]([X_i][Y_0]$

$- [Z_{i+1}][CH_3OH]/K_{eq1})$ (6)

B) $Z_i + Y_0 \Leftrightarrow Y_i + CH_3OH$

$r_B = (K_1/2)[cat.]([Z_i][Y_0]$

$- [Y_i][CH_3OH]/K_{eq1})$ (7)

C) $X_i + Y_i \Leftrightarrow Z_{2i+1} + CH_3OH$

$r_C = (K_2)[cat.]([X_i][Y_i]$

$- [Z_{2j+1}][CH_3OH]/K_{eq2})$ (8)

D) $X_i + Z_i \Leftrightarrow X_{i+1} + CH_3OH$

$r_D = (K_2/2)[cat.]([X_i][Z_i]$

$- [X_{i+1}][CH_3OH]/K_{eq2})$ (9)

E) $Z_i + Z_i \Leftrightarrow Z_{2i} + CH_3OH$

$r_E = (K_2/2)[cat.]([Z_i][Z_i]$

$- [Z_{2i}][CH_3OH]/K_{eq2})$ (10)

F) $Z_i + Y_i \Leftrightarrow Y_{2i} + CH_3OH$

$r_F = (K_2/2)[cat.]([Z_i][Y_i]$

$- [Y_{2i}][CH_3OH]/K_{eq2})$ (11)

As it can be seen, only two kinetic constants (K_1 and K_2) and two corresponding equilibrium constants (K_{eq1} and K_{eq2}) appear in the kinetic expressions, r_{A-F}. As already mentioned, the kinetic constant K_1 is related to the reaction of a methyl group with the EG hydroxyl, while K_2 is related to the reaction of a methyl group with a hydroxyl terminating an oligomeric chain.

Introducing the kinetic expressions r_A, r_B, r_C, r_D, r_E, and r_F, in eq. (5), we obtain 24 differential equations: when integrated, they can describe the evolution with time of all the different oligomeric species. It is possible
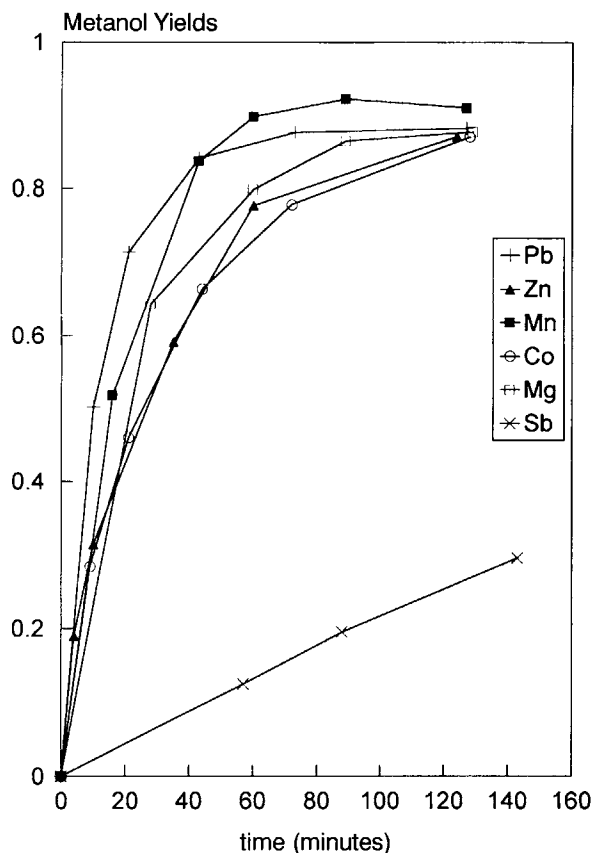
Figure 2   Methanol yields at different times for some runs reported in Table I.

to calculate the quantity of the released methanol from the mass balance considering the amount of the residual methyl group in the reaction mixture.

The methanol partition between the liquid and the vapor phase has been considered to have an ideal behavior; therefore, the methanol concentration in the reaction mixture has been calculated through the Raoult law:

$$x_M \approx 1/P° \qquad (12)$$

where, $P°$ can be calculated applying the Antoine relation:

$$P° = \exp[18.5878 - 3626.55/(T - 34.29)]/760. \quad (13)$$

RESULTS AND DISCUSSION

Figure 2 reports the methanol yields obtained at different times for some runs of Table I. As it can be seen, Mn, Pb, and Zn acetate (to be considered that zinc has been used at a lower concentration) have

roughly the same activity, the activities of Co and Mg acetate are lower, while Sb_2O_3 is the worst catalyst. These results agree with those reported by Tomita et al.[3,4] for runs performed considering only the volume of collected methanol during time.

The analysis of the curves of methanol yields does not give any information about the evolution of the oligomeric composition and catalyst selectivity. These aspects can be investigated only by submitting the samples withdrawn at different reaction times to HPLC analysis.

In Figure 3–6 the results of the HPLC analysis are reported, as examples, for some runs of Table I. Examining these types of results it can be recognized that some of the examined catalysts are more selective to give Y oligomers at the end of the reaction. This selectivity has quantitatively been defined after the
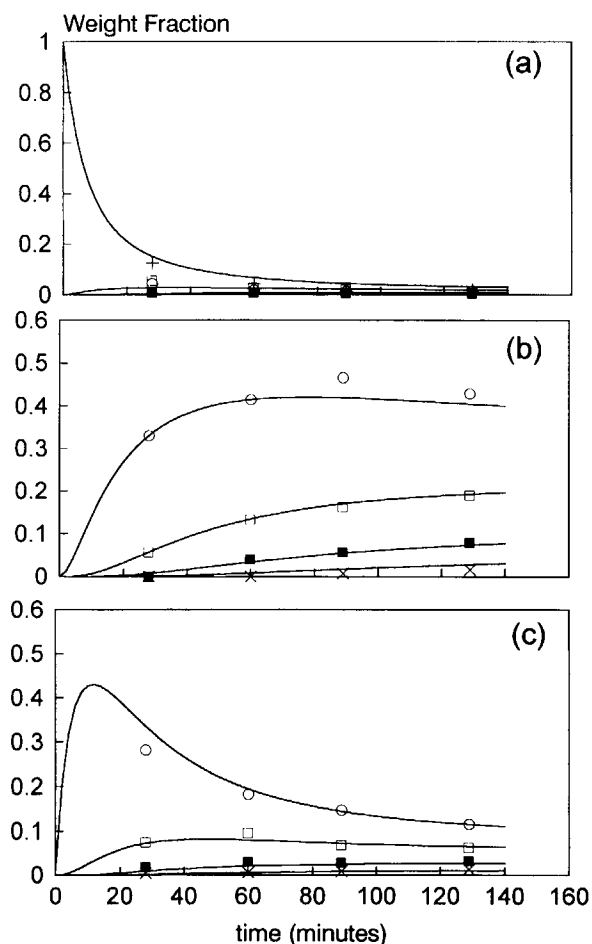

Figure 3   Example of the agreement obtained between the experimental and calculated oligomers distribution of type X (a), Y (b), and Z (c), respectively, for the kinetic run of Table I related to Mg acetate. Lines are calculated, symbols are experimental data and correspond to the different oligomers: (+) 0, (O) 1, (□)2, (■) 3, (X) 4.
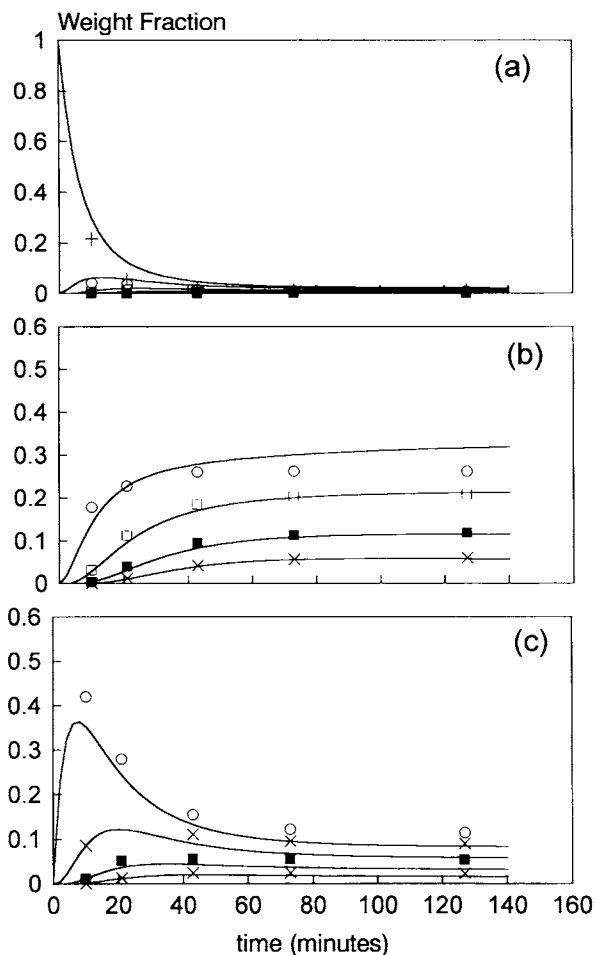
Figure 4 Example of the agreement obtained between the experimental and calculated oligomers distribution of type X (a), Y (b), and Z (c), respectively, for the kinetic run of Table I related to Pb acetate. Lines are calculated, symbols are experimental data and correspond to the different oligomers: (+) 0, (O) 1, (□)2, (■) 3, (X) 4.

simulation of the kinetic runs also by the ratio S_1 = $K_1/(K_1 + K_2)$. As matter of fact, Figure 7 reports both the total weight fraction of Y species and the value of S_1 ratio; as it can be seen, the selectivity of Mn, Mg, and Co acetate to give Y type oligomers is greater that one of Zn and Pb acetate. Therefore, Zn and Pb acetate promote much more the reaction of the hydroxyls of the chains than Mn, Mg, and Co acetate.

The experimental data related to the runs reported in Table I have been submitted to mathematical regression analysis[6] applying the described kinetic model and using as objective function the sum of the square of the difference between experimental and calculated reagents and products concentrations. The values of the constants K_1 and K_2 obtained by regression analysis are also reported in Table I.

The agreements obtained in the description of the oligomer distributions are quite satisfactory, as it can be appreciated in Figure 3–6, where symbols are experimental and lines calculated data.

It is possible to conclude, first of all, that the proposed kinetic model is able to describe the kinetic runs in detail.. The sum of the kinetic constants (K_1 + K_2) indicates the overall activity of the catalyst, while, S_1 ratio provides the catalyst selectivity.

As it has been seen, different catalysts have different activities and/or selectivities. This different performance is obviously consequence of the reaction mechanism. Two controversial mechanisms, an ionic[7] and a coordinate one,[8,9] are reported in the literature. In both cases, metals act as Lewis acid on the oxygen of the carbonyl group of the ester,
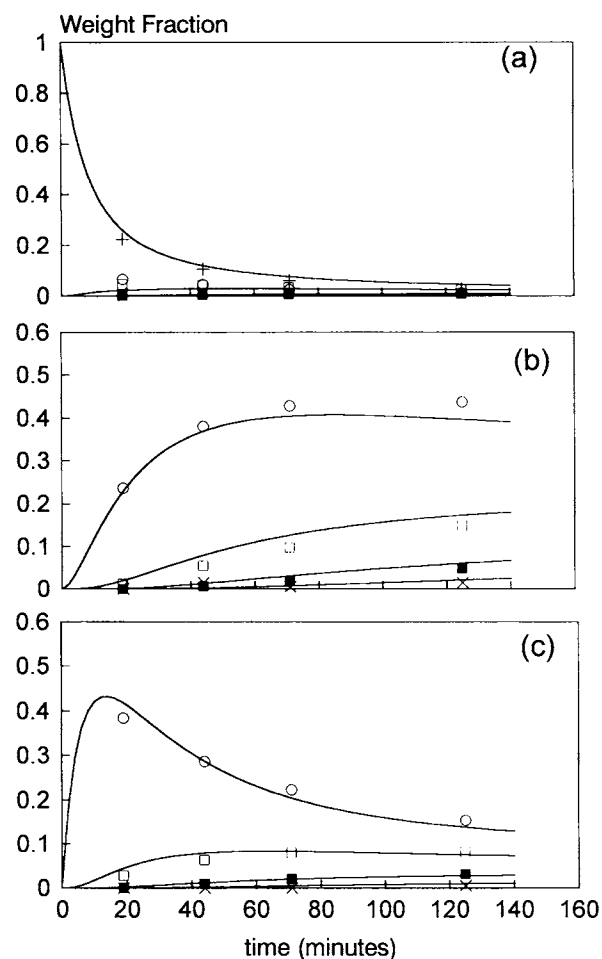

Figure 5 Example of the agreement obtained between the experimental and calculated oligomers distribution of type X (a), Y (b), and Z (c), respectively, for the kinetic run of Table I related to Mg, Mn, and Zn acetate mixture at 175°C . Lines are calculated, symbols are experimental data and correspond to the different oligomers: (+) 0, (O) 1, (□)2, (■) 3, (X) 4.
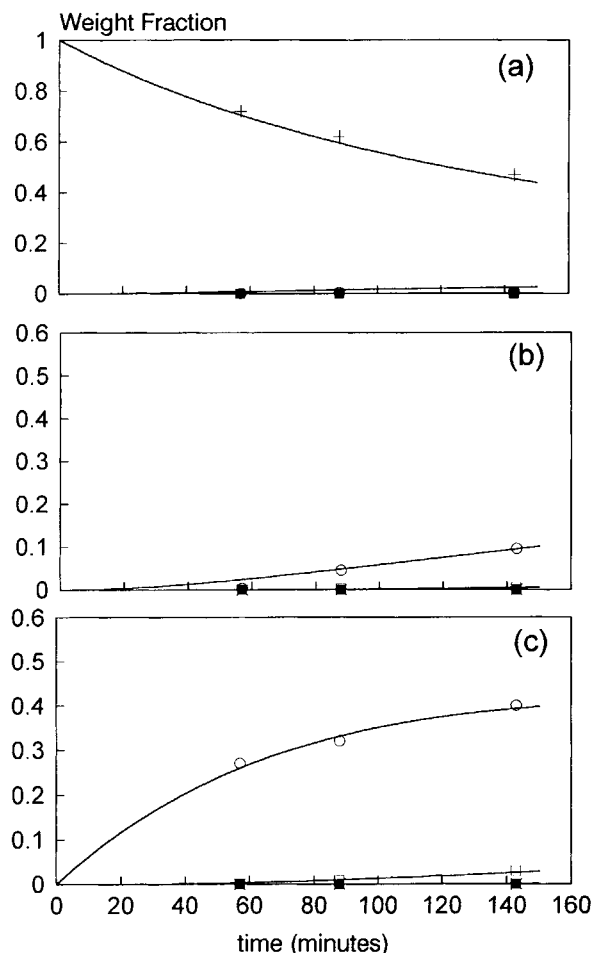
Figure 6 Example of the agreement obtained between the experimental and calculated oligomers distribution of type X (a), Y (b), and Z (c), respectively, for the kinetic run of Table I related to Sb_2O_3. Lines are calculated, symbols are experimental data and correspond to the different oligomers: (+) 0, (O) 1, ($\square$) 2, ($\blacksquare$) 3, (X) 4.

activating the corresponding carbon atom to the nucleophilic attack by the oxygen of a hydroxyl group. According to these mechanisms the maximum activity in the reaction corresponds to an appropriate acidity strength of the metal. As a matter of fact, both Tomita et al.[4] and Chung[10] have reported volcano shape plots of the catalyst activity as a function of the metal acidity strength. The number of catalysts studied in this article is too small to find a correlation between the catalyst acidity strength and the activities and selectivitis obtained, as suggested by Tomita et al.[4] and by Chung.[10] However, it is worth pointing out that such a comparison should independently be done for both the kinetic constants K_1 and K_2 determined in this article. Indeed, catalysts having comparable activities may have different selectivities.

Finally, it is well known that industry often applies a mixture of metal compounds as catalyst, probably because synergistic effects can be obtained, as reported in the literature.[5] Therefore, we performed kinetic runs with a mixture of Mg, Mn, and Zn acetate, that is , a mixture of industrial interest, in order to verify the presence of synergistic effects.

Observing the values of the constants reported in Table I and the results reported in Figure 5, it can be noted that the selectivity of this catalysts mixture to give Y type oligomers is roughly the same as Mn and Mg acetates, while the activity is greater than that shown by each metal alone, as it can be seen in Figure 8, where methanol yields at different reaction times are reported for the mixture and each component, respectively, taken at the same concentration and temperature.

CONCLUDING REMARKS

It has been shown that in order to describe the performance of several catalysts, it is necessary to analyze samples of the reaction mixture by the HPLC technique to evaluate both the activity and selectivity of the catalyst.

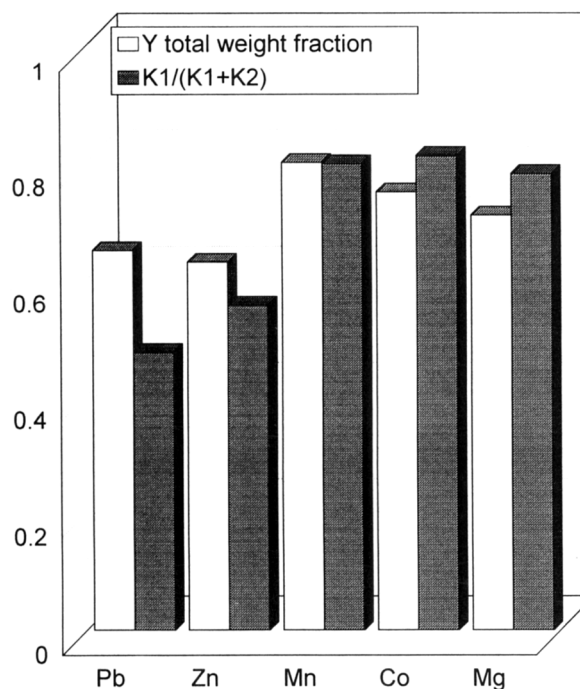The use of the proposed kinetic model is useful to homogeneously compare both the activity of the

Figure 7 Comparison of the obtained values of the Y total weight fraction and the corresponding S_1 values for different metal acetates.
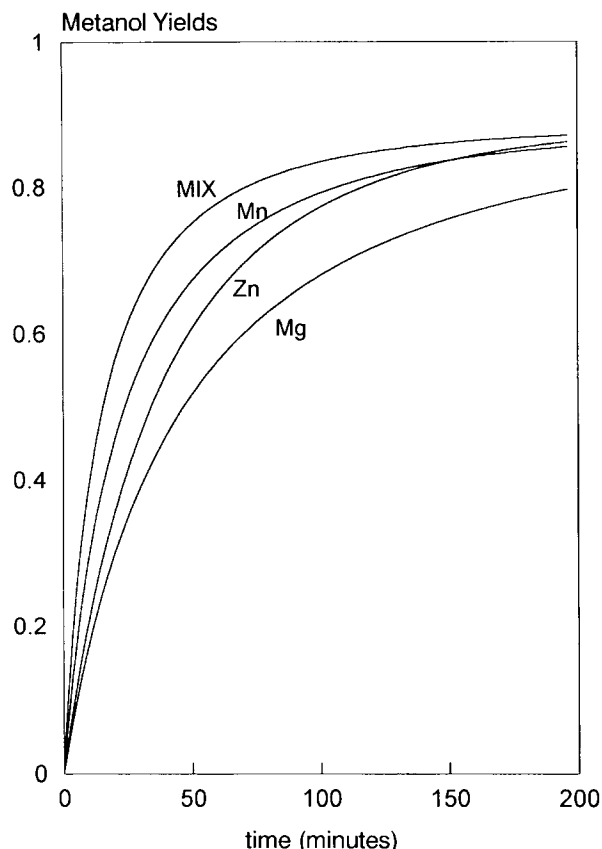
Figure 8 Comparison of methanol yields for, respectively, the mixture of Mg, Mn, and Zn acetate and any single component of the mixture, at the same temperature (180°C) and catalyst concentration (1.5 mmol/L).

catalysts expressed as the sum of the kinetic constants ($K_1 + K_2$) and the selectivity to give Y type oligomer represented by the ratio $S_1 = K_1/(K_1 + K_2)$. Moreover, applying the proposed kinetic model it is possible to extrapolate laboratory data for plant simulation and optimization.

Finally, it has been shown that the mixture of Mg, Mn, and Zn acetate has a greater catalytic activity than the single component the mixture. These effects are probably due to metal interactions with the formation of more active mixed clusters. This aspect is worth to be further studied.

LIST OF SYMBOLS

C_i = Concentration of component i

[CH_3OH] = Methanol concentration (mol/L)

K_1 = Kinetic constant of transesterification involving EG(L^2 mol^{-2} min^{-1})

K_2 = Kinetic constant of transesterification not involving EG(L^2 mol^{-2} min^{-1})

K_{eq1} = Equilibrium constant of transesterification involving EG.

K_{eq2} = Equilibrium constant of transesterification not involving EG.

r_i = Rate of i formation or disappearance (mol/min)

r_j = Vector of the possible reactions

[X_i] = Concentration of the X_i species with i = 0, n (mol/L)

x_M = Molar fraction of methanol in the reaction mixture

T = Absolute temperature (K)

$P°$ = Vapor pressure (atm)

[Y_i] = Concentration of the Y_i species with i = 0, n (mol/L)

[Z_i] = Concentration of the Z_i species with i = 1, n (mol/L)

Greek Symbols

α_{ij} = Stoichiometric matrix

REFERENCES

1. J. M. Besnoin, G. D. Lei, and K. Y. Choi, *AIChE J.*, **35**(9), 1445 (1989).
2. E. Santacesaria, F. Trulli, L. Minervini, M. Di Serio, R. Tesser, and S. Contessa, *J. Appl. Polym. Sci.*, **54**, 1371 (1994).
3. K. Tomita and H. Ida, *Polymer*, **14**, 55 (1973).
4. K. Tomita and H. Ida, *Polymer*, **16**, 185 (1975).
5. T. H. Shah, J. L. Bhatty, G. A. Gamlen, and D. Dollimore, *J. Macromol. Sci.-Chem.*, **A21**(4), 431 (1984).
6. G. Buzzi-Ferraris, *Quad. Ing. Chim. Ital.*, **4**, 171 (1968).
7. J. Otton, S. Ratton, V. A. Vasnev, G. D. Markova, K. M. Nametov, V. I. Bakhmutov, L. I. Komarova, S. V. Vinogradova, and V. V. Korhak, *J. Polym. Sci., Part A.*, **26**(8), 2199 (1988).
8. K. H. Wolf, B. Kuster, H. Herlinger, C. J. Tschang, and E. Scrhollmeyer, *Angew. Makromol. Chem.*, **68**, 23 (1978).
9. K. Yoda, K. Kimoto, and T. Toda, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, **67**, 909 (1964).
10. J. S. Chung, *J. Macromol. Sci.-Chem.*, **A27**(4), 479 (1990).