

## **Application of parameter estimation techniques to analyze the kinetics of liquid crystalline copolyesters**

GHAZI AL-ENEZI, JOHNSON MATHEW, MANSOUR KARKOUB AND ALI ELKAMEL

*College of Engineering and Petroleum, Kuwait University, P. O. Box 5969, 13060 Safat, Kuwait*

### **ABSTRACT**

Kinetics of copolyesterification between poly(butylene terephthalate) PBT and 4-acetoxy benzoic acid (ABA) in the melt have been analyzed using a simple approach. A simple second order reaction sequence summarizes catalysed and uncatalysed reactions between ABA and PBT. The kinetic parameters for the copolymerization reaction were determined using a simultaneous non-linear programming method. This technique was used to compute the moles of ABA reacted. This data was compared to that of the experimentally determined data. Close comparison (R.M.S. error  $\pm 0.003$ ) was obtained between the experimental and theoretical data. The kinetic data support block copolyester formation. The thermal data also gave support to this behavior.

**Keywords:** Copolymers; kinetics; LCP's; poly(butylene terephthalate)

### **INTRODUCTION**

A polymer exhibits thermotropic liquid crystalline behaviour, if

- (i) it can melt or become liquid-like, and
- (ii) the oriented aggregates of rod-like moieties are stable in the melt state.

Some para-linked aromatic polyesters such as poly(p-hydroxy benzoate) decompose before melting. If flexible aliphatic groups are incorporated into the main chain, the melting temperatures of para-linked aromatic polymers are depressed. Poly(ethylene terephthalate) (PET) was incorporated into various para-linked aromatic polymers to give thermotropic liquid crystalline polymers (Jackson & Kuhfuss 1976, 1985, McFarlane *et al.* 1977, Krigbaum *et al.* 1980, Mackley *et al.* 1981, Prasadarao *et al.* 1982, Joseph *et al.* 1985, Mitchell & Ishic 1985, Muramatsu & Krigbaum 1985, Hedmark *et al.* 1987).

Among these liquid crystalline polymers, copolyesters of PET and p-hydroxybenzoic acid (PHB) have been investigated to a great extent by some researchers (Balachander *et al.* 1979, Zachariades *et al.* 1982, Lenz *et al.* 1983, Zachariades & Logan 1983, Viney *et al.* 1985).

Poly(butylene terephthalate) (PBT) has a similar structure to that of PET; poly(p-oxybenzoate) (ABA) incorporated with PBT would be expected to exhibit liquid crystalline behaviour at certain suitable compositions.

This work is an attempt at formulating a kinetic model for the PBT/ABA melt copolyesterification reaction. The commercial importance of these copolyesters, coupled with an interest in the more theoretical aspects of the kinetics of such copolymerising systems and the mechanism of this copolyesterification reaction indicates that a study of this field is justified.

The purpose of this paper is:

- (i) to develop a mathematical model capable of analyzing the copolymerization of ABA and PBT;
- (ii) to determine the kinetic order with respect to the concentration of ABA and PBT segments; and
- (iii) to determine whether a procedure analogous to those involved in modeling solution kinetics can adequately describe melt polyesterification kinetics.

Accurate modeling of copolyesterification of PBT and ABA is important if an industrial melt transesterification process is to be designed, simulated, optimized, or controlled. A good understanding of the reaction kinetics would also help in enhancing the product properties and the productivity of the process.

The remainder of this paper is organized as follows: First, the experimental procedure that was used to study the copolyesterification between PBT and ABA is outlined and the experimental apparatus is described in detail. Second, a mathematical model capable of analyzing systems in which two competitive reactions occur is considered. The kinetic order is determined at various temperatures for both catalyzed and uncatalyzed runs to see whether kinetic order changes with catalyst and to check whether the temperature behaviour of the kinetic constants for poly(p-oxybenzoate) homopolyesterification shows any compensation effect in the presence of PBT. In order to determine the correct mechanism for the copolyesterification, the solution of the differential-algebraic optimization model of the kinetics of the reaction was investigated. The mechanism whose estimated parameters best fit the experimental results was chosen as the observed mechanism. It was found that the homopolymerization step is not necessary and that direct incorporation of ABA into PBT was what was actually happening during the process of the copolyesterification. Lastly, thermal characterization of the PBT/ABA copolyesters synthesized in this study is analyzed using a differential scanning calorimeter.

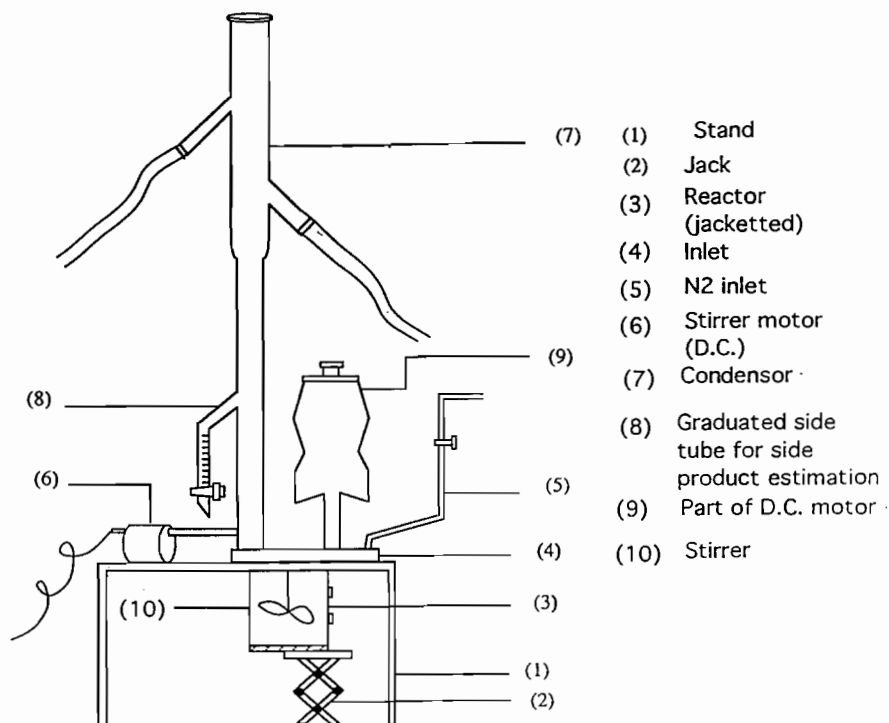
## EXPERIMENTAL SECTION

*Materials:* 4-acetoxybenzoic acid was synthesized by a sodium hydroxide catalyzed reaction of 4-hydroxybenzoic acid with acetic anhydride and was recrystallized with methanol. The product yield was 70% and had a melting point of 184°C.

**Reactor:** A 100 ml hastalloy-based, electrically-heated reactor depicted in Fig. 1 was used for polymer synthesis. The reactor had two ports for charging/stirring the reactants and for nitrogen purging. It could be maintained isothermally between ambient and 450°C. A provision for measuring the side product was made, as shown in Fig. 1.

**Preparation of Polymers:** All melt polymerization studies were conducted as indicated in Table 1. A dry purge of nitrogen gas was used throughout the reaction to prevent oxidation and degradation. All experiments were conducted at atmospheric pressure. The amount of 4-acetoxybenzoic acid lost by sublimation at 275 and 290°C accounted for about 0.25% of the monomer charged. This was collected from the flange of the reactor. The progress of the reaction was monitored by measuring the rate of formation of the side product acetic acid as a function of time.

**Measurements:** Infra-red spectra of the samples were recorded on a Perkin Elmer IR spectrophotometer using KBr discs. Thermal transitions of the PBT/ABA systems were obtained with a Mettler DSC 30 apparatus, interfaced with a thermal analysis



**Fig. 1.** Polymerization reactor.

**Table 1.** Reaction scheme used for copolyester synthesis

ABA: PBT (moles)	Temperature	Catalyst (mole % w.r.t. PABA)		
		Zinc Acetate		
7:3	(i) 260	0.25	0.25	0.25
	(ii) 275	0.5	0.5	0.5
	(iii) 290	0.1	0.1	0.1
6:4	(i) 260	0.2	0.25	0.25
	(ii) 275	0.5	0.5	0.5
	(iii) 290	0.1	0.1	0.1
5:5	(i) 260	0.2	0.25	0.25
	(ii) 275	0.5	0.5	0.5
	(iii) 290	0.1	0.1	0.1

data station under nitrogen atmosphere using a sample size of approximately 10 mg. A heating rate of 10°C/min was employed in all cases. Indium was used to calibrate the enthalpy values. A three metal (In-Pb-Zn) standard was used to calibrate the temperature scale. Samples were analyzed in the temperature range of 30–275°C in both heating and cooling cycles.

The purity of acetic acid was checked by gas chromatography. The purity was found to be about 98% at 260°C. It decreased to about 96% at 275 and 290°C. The average degree of polymerization was computed based on the moles of acetic acid produced. Most of the experimental runs were completed in a span of two hours.

## RESULTS AND DISCUSSION

### Kinetics and mechanism

The principle reactions occurring in a transesterification reaction between poly(butylene terephthalate) and 4-acetoxybenzoic acid are indicated in Fig. 2. Figure 2 indicates that acetic acid can be generated through two different routes. The first reaction is homopolymerization of 4-acetoxybenzoic acid and the second reaction is the incorporation of the dimer into poly(butylene terephthalate). The other possible route or mechanism assumes that homopolymerization is not important and the production of acetic acid is through direct incorporation of 4-acetoxybenzoic acid into poly(butylene terephthalate). There are many possible ways by which acetic acid can be generated, like the dimer reacting with dimer or trimer or tetramer and so forth. When a reactive polymer like poly(butylene terephthalate) is incorporated into this reaction (to make it amenable to processing) the kinetic analysis becomes even more difficult. Thus one can visualize the existence of many variables (rate constants) for these independent reactions. It is a difficult task to analytically solve for these kinetic variables. Hence the following assumptions are made to simplify the kinetic picture:

- (1) Only dimers are formed,
- (2) An oligomer (dimer) can react only with PBT molecules and
- (3) Processes exist in which dimers react with higher oligomers without generating acetic acid.

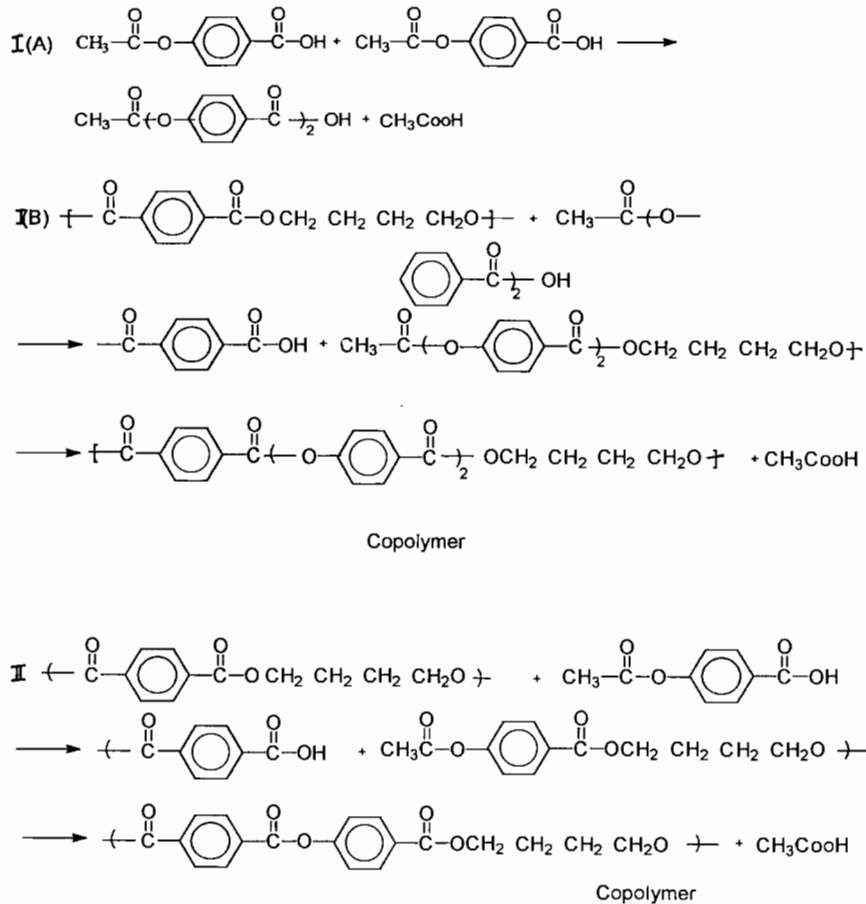
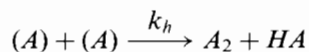


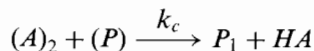
Fig. 2. Reaction scheme indicating principal events occurring in a transesterification reaction of PBT and ABA.

These reactions are assumed to be too slow and thus of no consequence in the overall mass balance. Hence, the formation of a copolymer of interest based on the reactions of Fig. 2 can be given by the mechanism outlined below:

If ( $A_2$ ) denotes a dimer formed by the reaction of ABA with ABA, then the following steps can be presumed for the polymerization reaction:



and



where  $[A]_2$  is the dimer concentration of ABA;  $k_h$  and  $k_c$  indicate the homopolymerization and copolymerization rate constants; and  $P$  and  $P_1$  represent the PBT and the copolymer, respectively.  $HA$  denotes the moles of acetic acid generated through both channels. The rate equation for the decrease in the concentration of ABA, which is also equal to the rate of formation of acetic acid, is given by

$$\frac{-dx}{dt} = \frac{-d[A]}{dt} = k_h[A]^2 + k_c[A][P], \quad (1)$$

while for PBT we have

$$\frac{-d[P]}{dt} = k_c[A][P]. \quad (2)$$

Dividing Eq. (1) by (2) results in

$$\frac{d[A]}{d[P]} = \frac{k_h[A]}{k_c[P]} + 1.$$

The reactivity ratio  $k_r$  can be given as  $k_r = (k_h/k_c)$ .

### Parameter estimation in the kinetic model

The experimental procedure discussed earlier was carried out for various sets of experimental conditions. Several temperatures and initial concentrations were used for both the catalyzed reactions and the uncatalyzed reactions (Table 1). Furthermore, the concentration of catalyst used was also varied. The differential equations modeling the kinetics of the reactions as presented in the previous section involve two parameters  $k_h$  and  $k_c$ . The purpose of this section is to describe the procedure that was undertaken to estimate these parameters for each of the experimental conditions carried out in this research.

Consider an experimental set of data where the initial mole fractions of ABA and PBT are known, the temperature of the reaction is known and the concentration of catalyst is also known. For uncatalyzed reactions the concentration of catalyst would be set to zero. Since in this kind of experiment it is possible to measure only the concentration of one of the constituents (i.e. ABA), the optimization model to estimate the values of the kinetic parameters can be posed as follows:

$$\text{Min} \sum_{d=1}^{Nd} \{ [ABA]_d^{\text{exp}} - [ABA]_d^{\text{cal}} \}^2 \quad (3)$$

subject to Eqs. (1) and (2).

Equation (3) above is the objective function representing the sum squared error over all data points  $Nd$  (for a given experimental condition) between the experimental concentration and the calculated concentrations from the differential equation model. Only concentrations of ABA are used in the objective function. This is because the concentration of PBT is not experimentally measurable either directly or indirectly. The objective of the model is to estimate the kinetic parameters in order to minimize this error. Equations (1) and (2) are the constraints of the model and represent the differential equations modeling the kinetics of the reactions. In addition to these two constraints the concentrations of each of the two species ABA and PBT are restricted to values ranging from zero to one. The initial concentrations of [ABA] and [PBT] are also known.

The above optimization problem is a parameter estimation problem. Various methods can be used to tackle this problem including iterative methods, feasible path or sequential non-linear programming methods and simultaneous non-linear programming methods (Guthrell & Biegler 1987, Jang *et al.* 1987, Hicks & Ray 1990). In this work, a simultaneous non-linear programming method is used. The differential equations will be converted to a set of approximating algebraic equations by using orthogonal collocation. These algebraic equations are then written as part of a non-linear programming (NLP) problem that is solved using successive quadratic programming (SQP) (Reklaitis 1983). Before discretizing the differential Eqs. (1) and (2) representing the constraints to the parameter estimation model ( $P_i$ ), the concentrations [ABA] and [PBT] are first parameterized as piecewise polynomials written in Lagrangian form. Using notation [ABA]  $\equiv A$  and [PBT]  $\equiv P$  we have:

$$A_{K+1}(t) = \sum_{i=0}^K A_i \phi_i(t) \quad (4)$$

$$P_{K+1}(t) = \sum_{i=0}^K P_i \phi_i(t) \quad (5)$$

where

$$\phi_i(t) = \prod_{k \neq i} \frac{(t - t_k)}{(t_i - t_k)}. \quad (6)$$

$A_{K+1}(t)$  and  $P_{K+1}(t)$  above denote  $(K + 1)$ -th-order polynomials. The notation  $k \neq i$  indicates that  $k = 0, \dots, i - 1, i + 1, \dots, K$ .

Substitutions of Eqs. (4) and (5) into (1) and (2), respectively, yields the residual equations:

$$R_1(t) = \sum_{i=0}^K A_i \dot{\phi}_i(t) + k_h A_{K+1}^2(t) + k_c A_{K+1}^{(t)} P_{K+1}(t) \quad (7)$$

and

$$R_2(t) = \sum_{i=0}^K P_i \dot{\phi}_i(t) + k_c A_{K+1}^{(t)} P_{K+1}(t). \quad (8)$$

Discretization of the above residuals is done in a manner similar to Guthrell and Biegler (1987) using the method of collocation. This yields the following set of algebraic equations:

$$R_1(t_i) = \sum_{i=0}^K A_i \dot{\phi}_i(t_i) + k_h A_i^2 + k_c A_i P_i \quad i = 1, \dots, K \quad (9)$$

and

$$R_2(t_i) = \sum_{i=0}^K P_i \dot{\phi}_i(t_i) + k_c A_i P_i \quad i = 1, \dots, K \quad (10)$$

with:  $A_o = [ABA]_o$  and  $P_o = [PBT]_o$ . Using the above set of algebraic equations instead of the differential Eqs. (1) and (2) in the original model ( $P_1$ ), one gets the following non-linear optimization program ( $P_2$ ):

$$\text{Min} \sum_{d=1}^{Nd} \{A_d^{exp} - A_d^{cal}\}^2$$

subject to:

$$\left. \begin{aligned} R_1(t_i) &= \sum_{i=0}^K A_i \dot{\phi}_i(t_i) + k_h A_i^2 + k_c A_i P_i \quad i = 1, \dots, K \\ R_2(t_i) &= \sum_{i=0}^K P_i \dot{\phi}_i(t_i) + k_c A_i P_i \quad i = 1, \dots, K \end{aligned} \right\} (P_2)$$

with

$$\begin{aligned} A_o &= [ABA]_o, \\ P_o &= [PBT]_o, \quad \text{and} \\ 0 &\leq A_i \leq 1, \\ 0 &\leq P_i \leq 1, \\ 0 &\leq k_c \leq k_c^u, \\ 0 &\leq k_h \leq k_h^u. \end{aligned}$$

With ( $P_2$ ), one can now solve for the optimal kinetic parameters  $k_h$  and  $k_c$ . The locations of the points  $t_i, i = 1, \dots, K$  correspond to the shifted roots of an orthogonal legendre polynomial of degree  $K$ . In addition, the collocation coefficients are initialized by Lagrange interpolation of the kinetic data.



The objective of model ( $P_2$ ) involves only the concentrations of (ABA), since as mentioned earlier the concentration of PBT is not measured. In addition, the purpose of the model is to estimate the kinetic constants  $k_c$  and  $k_h$  in order to have a best fit to the data as measured by the objective function of the model. However, since we are only interested in determining the reactivity ratio  $k_r (= k_h/k_c)$ ,  $k_c$  is arbitrarily assigned a value of 1. Then model ( $P_2$ ) involves only one parameter  $k_h$ . Model  $P_2$  is solved using SQP for the various experimental conditions considered. During optimization, certain values of  $k_r$  were found to be negative. This indicates that the observed concentrations of ABA are actually greater than those predicted by the model. The model underpredicts the amount of ABA present in the reaction mixture because the mechanism on which it is based assumes that ABA reacts both with itself and also with PBT. This mechanism cannot therefore represent the correct reaction scheme.

In our next approach we assumed that PBT cleavage with 4-acetoxybenzoic acid (ABA) results in formation of PBT segments terminated with carboxylic end-groups (terephthalic acid end-groups) and PBT segments terminated with acetoxy end-groups. Acetic acid is not generated in this step; this is considered to be an intermediate step that immediately rearranges to form the copolymer and acetic acid. Another kinetic model is developed by considering a single reaction i.e., direct insertion of ABA into PBT. In this model the major reaction can be indicated as



where A, P and PBOT correspond to ABA, PBT and the copolyester of interest. Based on this approach the amount of PBT consumed was calculated using the equation.

$$\frac{-d[P]}{dt} = k_c[A][P]. \quad (12)$$

The results of the optimization studies, for the mechanism and for the various experiments considered, are shown in Table 2. No negative values are obtained and the fit between the model and the experimental concentration is good (i.e. the sum of square error was always less than 0.009). It can be concluded therefore that this new mechanism is the appropriate mechanism to represent the copolymerization kinetics between ABA and PBT.

The second order plots were obtained by plotting the moles of acetic acid generated as a function of time. Figure 3 indicates the effect of temperature for the uncatalyzed reaction at an ABA concentration of 50 mole per cent. The figure also indicates that the reaction rate is adequately modeled by second-order kinetics. Figure 4 indicates that the reaction rate is adequately modeled by second-order kinetics even for a catalyzed reaction using 0.25 mole percent zinc acetate. Increasing the catalyst concentration from 0.25 mole % to 1.0 mole % (Fig. 5) does not alter the nature of the plots. As indicated in Table 2 the rates are also found to increase with

**Table 2.** Typical rate constant values ( $k_r$ )

ABA composition	Catalyst concentration		$k_r$	R.M.S. error
	(mole % ABA)	Temperature (°C)		
50	–	260	0.441	±0.002
	–	275	0.593	±0.002
	–	290	0.953	±0.003
50	0.25	260	0.318	±0.001
	0.25	275	0.748	±0.001
	0.25	290	0.887	±0.004
50	0.50	260	0.856	±0.0001
	0.50	275	0.911	±0.0005
	0.50	290	1.210	±0.002
50	1.0	260	0.723	±0.002
	1.0	275	0.946	±0.002
	1.0	290	1.252	±0.003
60	–	260	0.667	±0.004
	–	275	0.901	±0.005
	–	290	1.233	±0.005
60	0.25	260	0.674	±0.003
	0.25	275	0.891	±0.008
	0.25	290	1.246	±0.005
60	0.50	260	0.631	±0.002
	0.50	275	0.878	±0.007
	0.50	290	1.312	±0.003
60	1.0	260	0.672	±0.004
	1.0	275	0.917	±0.011
	1.0	290	1.766	±0.007
70	–	260	2.051	±0.004
	–	275	2.105	±0.003
	–	290	2.051	±0.004
70	0.25	260	1.104	±0.009
	0.25	275	1.812	±0.013
	0.25	290	2.891	±0.007
70	0.50	260	1.783	±0.004
	0.50	275	2.314	±0.003
	0.50	290	2.263	±0.009
70	1.0	260	2.092	±0.009
	1.0	275	1.470	±0.005
	1.0	290	2.028	±0.009

an increase in catalyst concentration within a particular composition. It is also noticed that the rate constant is found to increase with increasing amount of acetic acid generated.

Three different temperatures (260, 275 and 290°C) were employed for the copolyester synthesis. As anticipated, Table 2 indicates that the rate constant values increase with temperature. Typical second order plots indicating variation

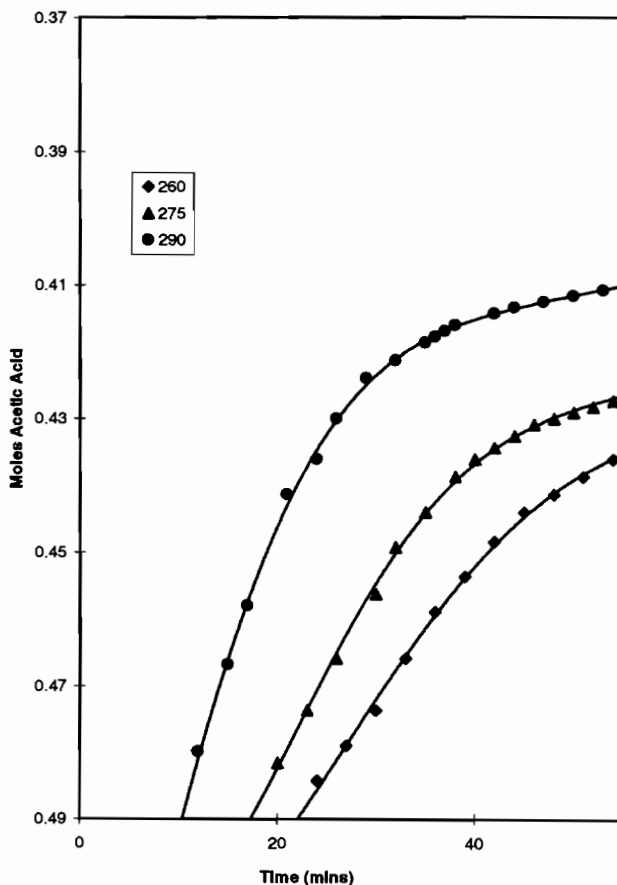


Fig. 3. Plot indicating effect of temperature for uncatalyzed 50 mole percent ABA.

of composition for uncatalyzed and catalyzed reactions are shown in Figs. 6–8. Table 2 indicates that higher  $k_r$  values are obtained with increasing ABA concentration.

### CHARACTERIZATION

All the copolymers were soluble in phenol, tetrachlorethane (60:40 wt%) solution. The DSC thermograms of PBT/ABA copolyesters are shown in Fig. 9. The melting peaks of PBT/ABA 70, PBT/ABA 60, and PBT/ABA 50 differed by approximately 10°C. The  $T_m$  of the copolyesters were found to be closer to that of PBT, plausibly indicating block copolymer formation. The peak of PBT/ABA 50 occurred at 192°C. The presence of a higher content of ABA was found to have decreased the sequence length of PBT blocks. Thus the  $T_m$ , and the breadth of the peak increased, indicating a more blocky character. This could also be explained as the homogenous reaction

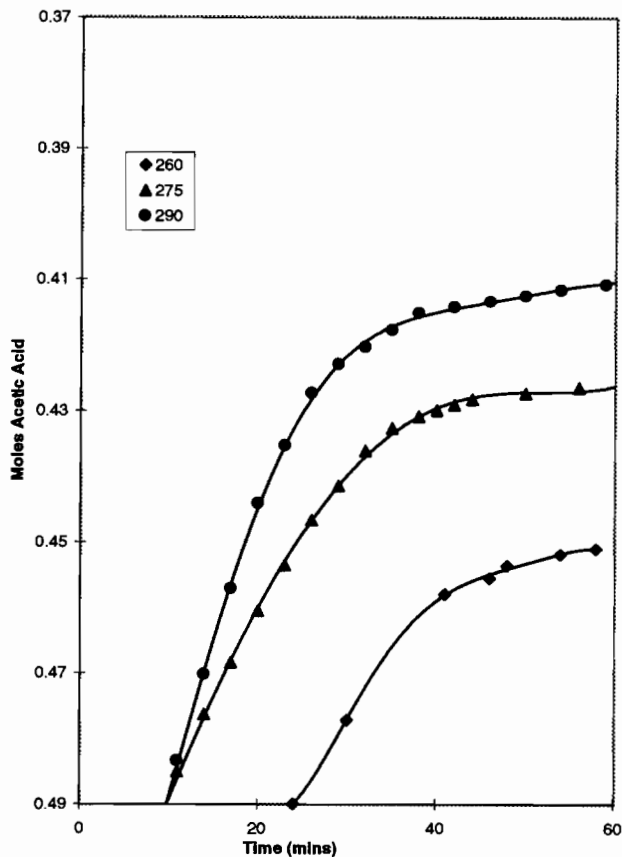


Fig. 4. Plot indicating effect of temperature for 50 mole percent ABA using 0.25 mole percent zinc acetate catalyst.

nature of polymerization of PBT and ABA. When the ABA content was low (e.g. 50 mole %), the ABA sequences and PBT sequence could be of similar length. As the content of ABA was increased (60 mole % ABA) the sample melted at 200°C with a broad peak. Not much change in the peak breadth was noted with a further increase in ABA content. This plausibly indicates that homopolymerization of ABA to form longer ABA oligomers occurs to a lesser extent supporting the model described above.

## CONCLUSION

The kinetics of melt copolyesterification of PBT/50 ABA, PBT/60 ABA, and PBT/70 ABA has been studied using simple phenomenological models. A parallel second order reaction scheme adequately represents the kinetics of PBT/ABA

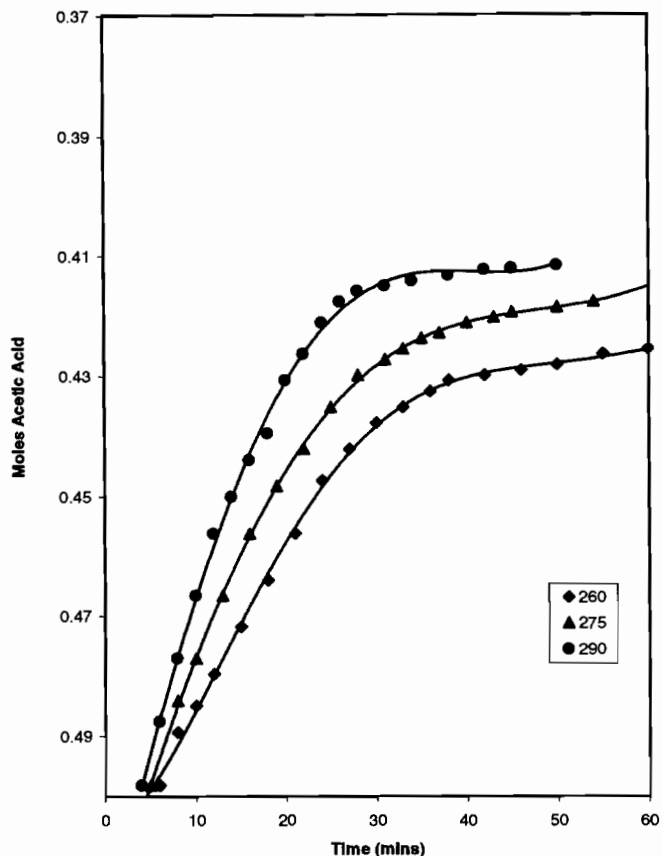


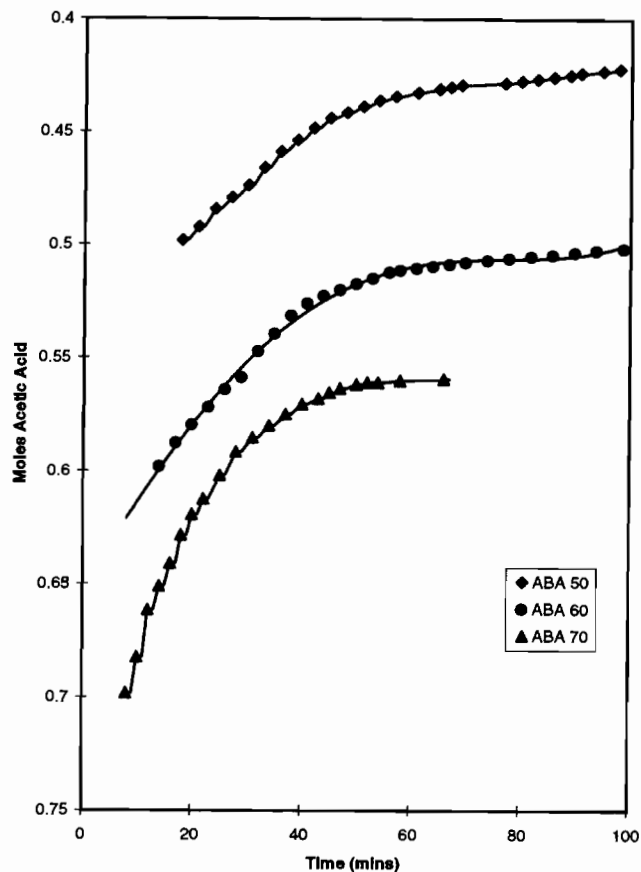
Fig. 5. Plot indicating effect of temperature for 50 mole percent ABA using 1 mole percent zinc acetate catalyst.

copolyesterification. The kinetics of catalyzed reaction also follows a path similar to homopolyesterification of ABA. This clearly implies that oxybenzoate oligomers are not formed.

A simple simultaneous non-linear programming method was used to compute the amount of acetic acid produced, and the reactivity ratios were determined by minimizing the least squares variation between the theoretical and experimental amounts of acetic acid produced. The agreement with experiment, though poor in the later stages, intuitively indicates that precipitation is not an important factor in rate acceleration.

Even through activation energies are comparatively larger for the catalysed reaction (in comparison to uncatalysed), entropy factors could drive the reaction by lowering the free energy of activation.

The copolyesterification kinetics were characterized by rate constants that were several orders of magnitude lower than those for ABA polyesterification.



**Fig. 6.** Second order indicating effect of composition for uncatalyzed reactions at 260°C.

#### ACKNOWLEDGEMENT

This work was partly supported by funds from project number EC 070 sanctioned by the research administration of Kuwait University. The authors would also like to thank Mr. Rajamony Thangakunam for help with the experiments during the course of the work.

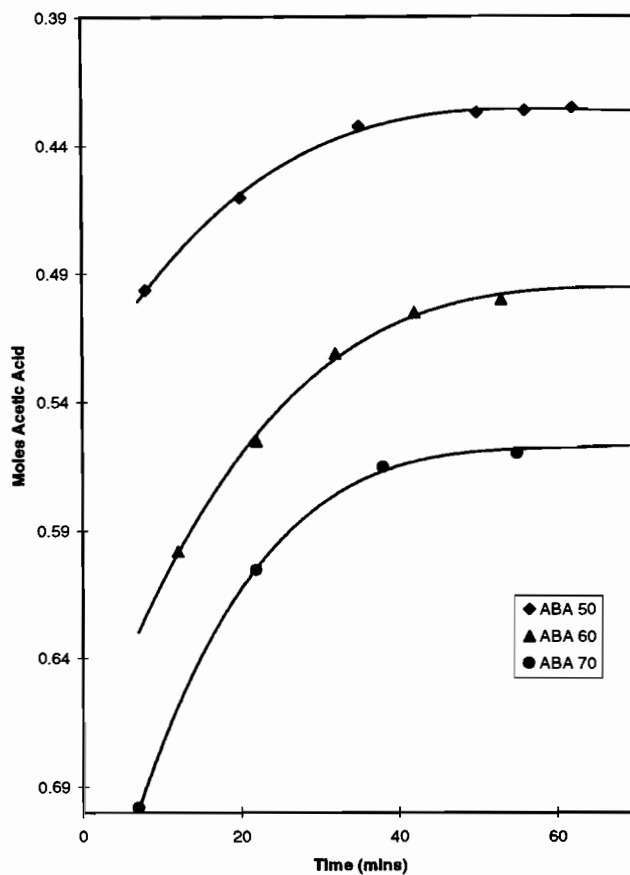


Fig. 7. Second order plots indicating effect of composition for zinc acetate (0.25 mole %) catalyzed reactions at 275°C.

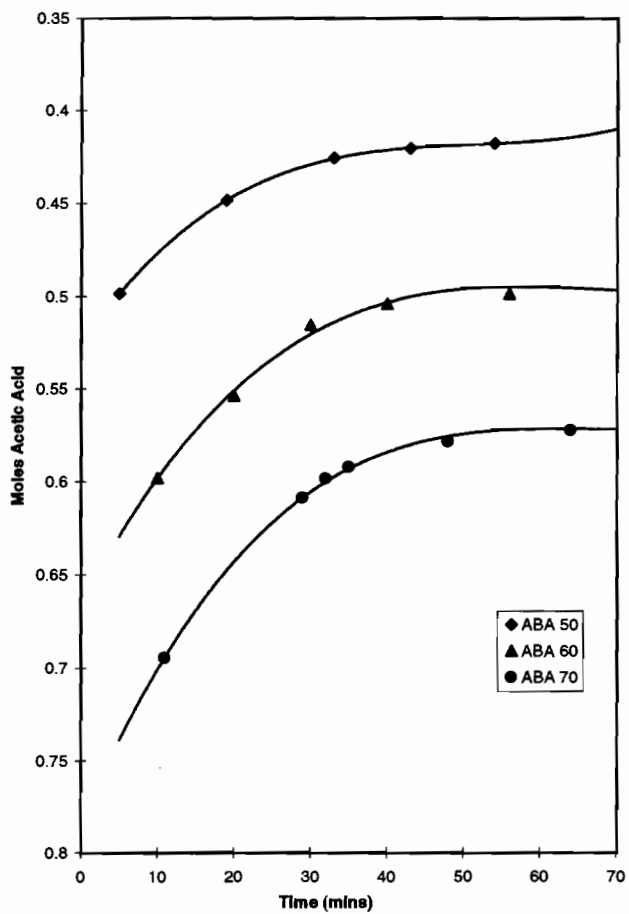


Fig. 8. Second order plots indicating effect of composition for zinc acetate (1.0 mole %) catalyzed reactions at 275°C.



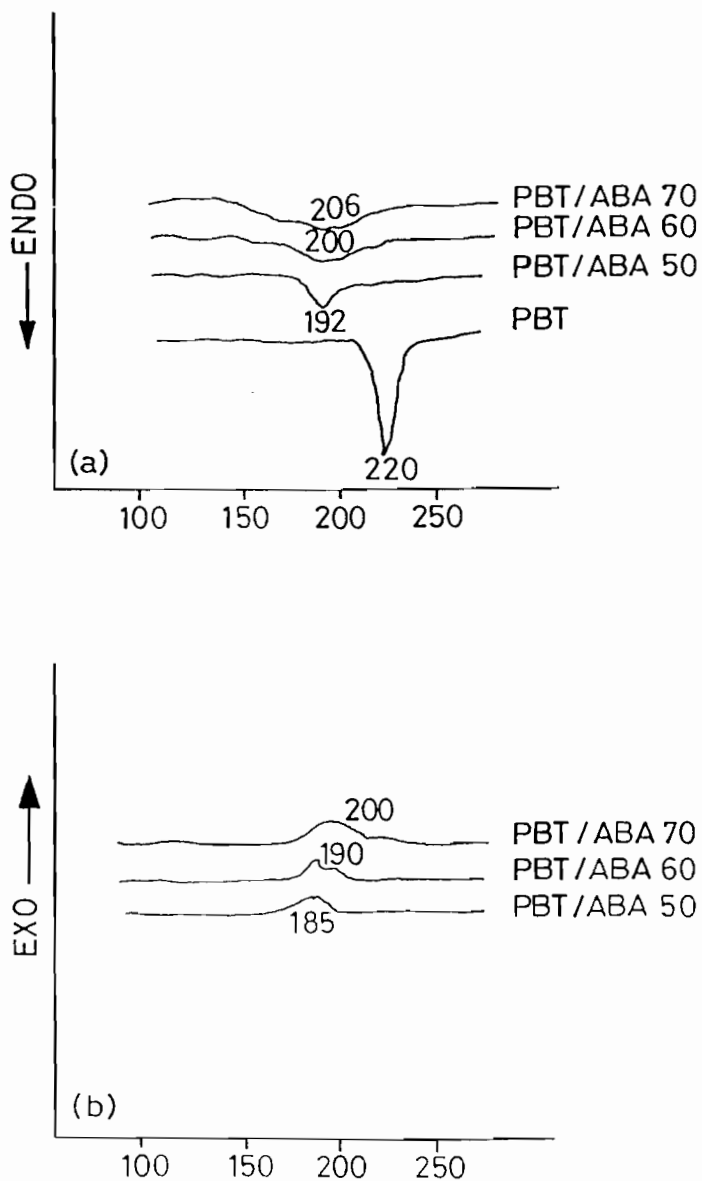


Fig. 9. DSC endotherms and exotherms for PBT/ABA systems for different PBT and ABA compositions.

## REFERENCES

- Balachander, M., Balkshnan, T. & Kothandaraman, H. 1979.** Synthesis and characterization of PET and substituted p-hydroxy benzoic acids. *Journal of Applied Polymer Science: Polymer Chemistry Edition* **17**: 3713–3721.
- Guthrell, J.E. & Biegler, L.T. 1987.** On the optimization of differential-algebraic process systems. *American Institute of Chemical Engineering Journal* **33(8)**: 1257–1270.
- Hedmark, P.G., Jansson, J.F., Hult, A., Lindberg, H. & Gedde, U.W. 1987.** Selection etching thermotropic liquid crystalline polyesters. *Journal of Applied Polymer Science* **34**: 743–762.
- Hicks, G. & Witt, R. 1990.** Effect of catalytic structure on the rate of heptane oxidation. *Canadian Journal of Chemical Engineering* **49**: 522–528.
- Jackson, W.J. Jr. & Kuhfuss, H.F. 1976.** Synthesis of polyoxybenzoate homopolymers. *Journal of Polymer Science* **14**: 2043–2058.
- Jackson, W.J. Jr. & Kuhfuss, H.F. 1985.** Synthesis and characterization of acetoxybenzoic acid based copolyesters. *Journal of Applied Polymer Science* **25**: 1980–1986.
- Jang, S.S., Joseph, B. & Mukai, H. 1987.** On-line optimization of constrained multivariable chemical processes. *American Institute of Chemical Engineering Journal* (**33**)**1**: 26–35.
- Joseph, E.G., Wilkes, G.L. & Baird, D.G. 1985.** Effect of flow history on the morphology of thermotropic liquid crystalline copolyester. *Polymer Engineering and Science* **25**: 377–388.
- Krigbaum, W.R., Lader, H.J & Cifferri, A. 1980.** Polymers with mesogenic side chain groups in liquid crystalline polymers. *Macromolecules* **13**: 554–559.
- Lenz, R.W., Jin, J.I. & Feichtinger, K.A. 1983.** Synthesis strategies in liquid crystalline polymers. *Polymer* **24**: 327–334.
- Mackley, M.R., Pinaud, F. & Siekmann, G. 1981.** Synthesis and characterization of liquid crystalline polymers using preformed resins. *Polymer* **22**: 437–446.
- McFarlane, F.E., Nicely, V.A. & Davis, T.G. 1977.** Liquid crystal polymers. II. Preparation and properties of polyester exhibiting liquid crystal melts. In: **Pearce, E.M. and Schaeffgen, J. R. (Eds.)** *Contemporary Topics in Polymer Science. Vol 2.* Plenum Press, New York, NY, USA. Pp. 109–121.
- Mitchell, G.R. & Ishic, F. 1985.** Polyesters exhibiting liquid crystalline melts. *Polymer Communications* **26**: 34–38.
- Muramatsu, H. & Krigbaum, W.R. 1985.** Liquid crystalline order in para-linked aromatic polymers. *Journal of Polymer Science B. Polymer Physics* **25**: 377–382.
- Reklaitis G.V. 1983.** *Engineering Optimization.* Wiley, New York, NY, USA.
- Viney, C., Donald, A.M. & Windle, A.H. 1985.** Synthesis and characterization of PET and p-hydroxybenzoic acid based copolyesters. *Polymer* **26**: 870–878.
- Prasadarao, M., Pearce, E.M. & Han, C.D. 1982.** Structure property modification of PET based liquid crystalline copolyesters. *Journal of Applied Polymer Science* **27**: 1343–1354.
- Zachariades, A.E., Economy, J. & Logan, J.A. 1982.** A detailed characterization of liquid crystalline copolyesters. *Journal of Applied Polymer Science* **27**: 2009–2014.
- Zachariades, A.E. & Logan, J.A. 1983.** Reactive blending of PET based liquid crystalline copolyesters. *Polymer Engineering and Science* **23**: 797–803.

*( Submitted 16 January 2000 )*

*( Revised 14 January 2001 )*

*( Accepted 2 February 2001 )*

تطبيق تقنية تحديد البارامترات لدراسة نظام كينيتيكا البلورة لمواد البولستر

غازي العنزي، جونسن ماثيو، منصور كركوب وعلي الكامل

كلية الهندسة والبتترول- جامعة الكويت

صربز 5969- الصفاة 13060- الكويت

### الخلاصة

توضح هذه المقالة دراسة كينيتيكا البلورة بين البيوتيلين تيترافلتاليت وحامض الأستوكسيبترويك. معادلات كينيتيكا من الدرجة الثانية تلخص التفاعل بفعالية. بارامترات الكينيتيكا حددت باستعمال المعادلات الأنية اللاخطية. هذه التقنية استعملت كذلك لتحديد كمية حامض الأستوكسيبترويك التي لم تتفاعل. وقد قورنت المعادلات بالتجارب وكانت المقارنت وثيقة. ولقد تم تحديد أثر العوامل المساعدة.

التجارب الكينيتيكية وكذلك الحرارية توضح بأن تكوين البولستر تم عن طريق كتل.

