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Kinetics of polyesterification: modelling and simulation of unsaturated polyester synthesis involving 2-methyl-1,3-propanediol

K. Nalampang, A.F. Johnson*

Department of Chemistry, Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK

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Dedicated to Prof. Ian M. Ward on the occasion of his 75th birthday

Abstract

The kinetics of the individual key reactions involved in the formation of unsaturated polyester resins have been studied using the very reactive glycol, 2-methyl-1,3-propanediol (MPD). This diol has been reacted in turn with maleic anhydride (MA), phthalic anhydride (PA) and isophthalic acid (IA) under isothermal conditions in the temperature range 180–210 °C and the kinetic constants for the following reactions have been obtained MA + MPD, PA + MPD, IA + MPD, MA + PA + MPD and MA + IA + MPD. The relative reactivities of MPD with MA and PA measured by monitoring the loss of carboxyl groups at 180 and 200 °C were found to be 2.26 and 1.70, respectively. At 200 °C PA is more reactive than IA (ratio approximately 1.31) in homopolyesterification. In the copolyesterifications involving PA and IA where cross catalysis can occur, the PA reacted approximately 1.25 times faster than IA at 200 °C. The differences in reactivity might be expected to have a significant effect on the coreactant sequence lengths in prepolymers formed by the concurrent reaction of PA, IA and MPD particularly at low conversions thus on the final properties of the cured resins in which they are employed. The properties of the products are not examined in this paper.

Keywords: Unsaturated polyester; Polyesterification; 2-Methyl-1,3-propanediol

1. Introduction

The kinetics of polyesterification reactions involving dicarboxylic acids and diols has been reviewed comprehensively by Fradet and Marechal and others [1–3]. There are several reported rate constants and Arrhenius parameters for the reactions involving maleic or phthalic anhydride with industrially important glycols such as 1,2-propylene glycol [2,4–6]. Recently, there have been a number of reports [7–10] of 2-methyl-1,3-propanediol (MPD) being used for the synthesis of unsaturated polyester resins and it has been suggested that this diol leads to improved processability of the resins and better properties of final cured products. The perceived advantages of using MPD include the fact that it reacts at faster rates because it contains primary hydroxyl groups, which are inherently more reactive than the primary and secondary hydroxyl groups found in 1,2-propylene glycol. Furthermore, the methyl group which MPD introduces into the polymer side chain helps to inhibit crystallisation of prepolymers making them more soluble in styrene [7].

The overall aim of the present work is to gain a fuller understanding of the reactivity of MPD in polyesterification reactions in order to assess the impact of coreactant sequence length in prepolymers on the final properties of cured polyester resins. The approach taken has been to obtain the experimental rate constants for the reaction of MPD with maleic anhydride (MA), phthalic anhydride (PA) or isophthalic acid (IA) (scheme 1) at different temperatures under isothermal condition. The data obtained have then been used to construct kinetic models, which have been simulated using deterministic and time-dependent Monte Carlo methods, the latter being particularly useful for the prediction of sequence arrangement of coreactants in prepolymer chains. Particular attention has been given to the measurement of the relative reactivities of the isomeric reactants phthalic and isophthalic acid.

The first quantitative studies of polyesterification involving the reaction of a dicarboxylic with a diol were carried out by Flory [11]. In the absence of an acid catalyst the

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* Corresponding author. Tel.: +44-113-343-3913; fax: +44-113-247-0676.

E-mail address: a.f.johnson@chem.leeds.ac.uk (A.F. Johnson).

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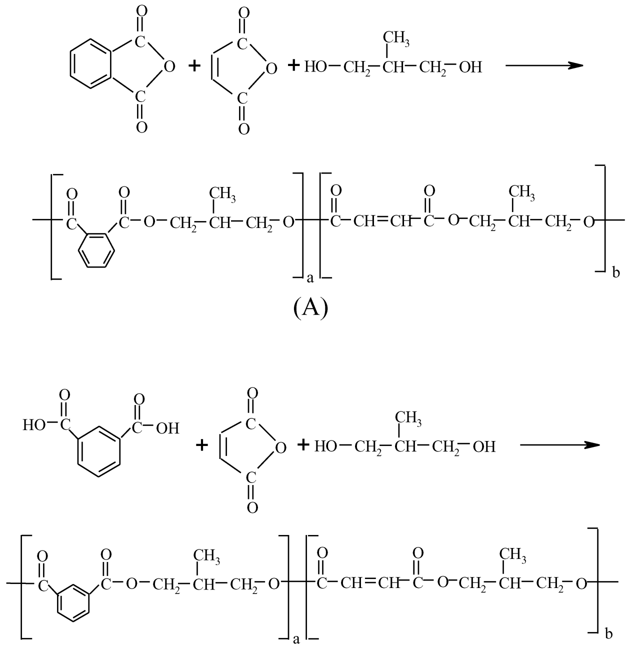

Scheme 1.

esterification kinetics were found to be initially first order with respect to the hydroxy groups, the order increasing to second order at high conversion. This was explained by the fact that dielectric constant of the reaction medium decreases with increasing of conversion and viscosity which affect to ionic equilibria during the polyesterification [5,12]. Beigzadeh et al. [13] studied the kinetics of polyesterification carried out via a two stage process using adipic acid, ethylene glycol, and fumaric acid in both absence and presence of acid catalyst at constant reaction temperatures.

The kinetic models proposed by Flory [11], Tang and Yao [14], Fang et al. [12] and Lin and Hsieh [15] were incapable of fitting the experimental data whereas that of Chen and Wu [1] did so very well. Recently, Zetterlund et al. [2] have extended the Chen and Wu [1] model to deal with the difference in reactivity of two hydroxyl groups of 1,2-propylene glycol. They proposed a 'cross-catalysis' model for reactions between MA and PA with 1,2-propylene glycol which predicted well the observed experimental conversion data. The models proposed by Chen and Wu [1] and Zetterlund et al. [2] are examined further in the work reported here.

2. Experimental

2.1. Materials

Maleic anhydride, phthalic anhydride, isophthalic acid and 2-methyl-1,3-propanediol were kindly supplied by Resinous Chemicals Ltd (Dunstan, UK) and were used without further purification. The methanol, toluene, potassium hydroxide, and phenolphthalein indicator used were reagent grade.

2.2. Polymerisation procedures

Reactions were carried out in a five necked round bottom flask (500 ml) fitted with a condenser, mechanical stirrer operated at approximately 300 rpm and a nitrogen gas inlet to facilitate the removal of water and oxygen from system. The temperature of the reactants was continuously monitored and controlled using a mantle heater. Since the viscosity of polymerisation system increases as the reaction proceeds the heat transfer from the reactants changes with conversion. It is essential to measure the reactant temperature to ensure isothermal conditions.

In the case of the homopolyesterification reactions, the mole ratios MA/MPD and PA/MPD were 1/1.1 for each. For the copolyesterification reactions involving MA/IA/MPD and MA/PA/MPD the mole ratios employed were 0.6/0.6/1.32 in each.

The reactants were independently heated to the required reaction temperature before being charged into the preheated reactor which was also at the desired temperature. The preheating of the reagents was important as this ensured both rapid mixing and temperature equilibration to that desired allowing kinetic measurements to commence immediately the reaction vessel had been fully charged. In the case of reactions involving IA, reaction rates were slow and it took a few minutes for the reaction mixture to become clear during the mixing. In this case, reaction rate measurements were started as soon as the mixture became clear.

The progress of the reaction was determined by taking small (relative to the reaction mass) and accurately weighed samples (approximately 0.5 g) at appropriate time intervals and measuring the carboxyl group content. Each sample was dissolved in approximately 50 ml of a neutralised toluene–methanol mixture (1:1) and titrated with 0.1N methanolic potassium hydroxide using phenolphthalein as indicator.

A range of syntheses were carried out at different temperatures under well controlled isothermal conditions in order to obtain individual rate constants for the two components reactions MA + MPD, PA + MPD, and IA + MPD. Three component reactions involving MA + PA + MPD and MA + IA + MPD were also examined. In all cases, a 10% molar excess of glycol was used.

2.3. Computer modelling and simulation

An interactive numerical integration package (ULEDA) developed in-house was employed for the solution of the sets of kinetic equations. Integration was carried out using either an Euler or Runge–Kutta procedure and solutions were obtained in a matter of seconds in almost all cases using a standard PC (DAN, Pentium II, 300 MHz).

3. Polyesterification models

The homopolyesterification rate equation proposed by Chen and Wu [1] for reactions carried out at constant reaction is shown in Eq. (1). This model takes into account the effects of the equilibrium involving water as the condensation product (i.e. unremoved water from the reaction mixture) and the variation in the dielectric constant for self-catalyst polyesterification:

$$\frac{\mathrm{d}[\mathrm{RCOOR'}]}{\mathrm{d}t} = kK_{\mathrm{e0}}\exp(\alpha p)[\mathrm{RCOOH}]^2[\mathrm{R'OH}] - k_{\mathrm{h}}[\mathrm{H_2O}][\mathrm{RCOOR'}] \tag{1}$$

If p is the conversion of the acid group ($p = ([\mathrm{COOH}]_0 - [\mathrm{COOH}])/[\mathrm{COOH}]_0$), and r is the ratio of diol to diacid at the beginning of the reaction ($r = [\mathrm{OH}]_0/[\mathrm{COOH}]_0$), Eq. (2) is obtained.

$$\frac{\mathrm{d}p}{\mathrm{d}t} = kK_{\mathrm{e0}}\exp(\alpha p)C_0^2(1-p)^2(r-p) - k_{\mathrm{h}}[\mathrm{H_2O}]p \tag{2}$$

In these equations, k is the polyesterification rate constant (kg mol^{-1} min^{-1}), k_{h} is the rate constant for hydrolysis of ester bonds (kg mol^{-1} min^{-1}), K_{e0} is the equilibrium ionisation constant at zero fractional conversion (p) (kg mol^{-1}), α is a constant where term $\exp(\alpha p)$ accounts for the increase in K_{e0} as decreasing of the dielectric constant with increasing p.

Zetterlund et al. [2] extended the Chen and Wu model by giving attention to the asymmetry of 1,2-propylene glycol i.e. the reactivity between the primary $(\mathrm{OH})_1$ and secondary $(\mathrm{OH})_2$ which has been reported to differ by a factor of 2.6 [19]. In addition, they proposed a cross-catalysis model for situations where two different polymerisable acids are employed, e.g. MA and PA where the possibility exists of one acid acting as a catalyst for the other.

The 2-methyl-1,3-propanediol employed in this work has two primary hydroxyl group (Scheme 1) and any difference in the reactivity of the hydroxyl group has been ignored allowing some simplification of the rate equations derived by Zetterlund et al. [2]. On the basis of Chen and Wu [1] and Zetterlund et al. [2] models it is possible to define the kinetic equations for reacting systems such as MA + PA + MPD or MA + IA + MPD in the absence of a non-polymerisable acid catalyst as shown in Eqs. (3)–(6).

Copolyesterification system contains MA + PA + MPD

$$\frac{\mathrm{d}p_{\mathrm{MA}}}{\mathrm{d}t} = k_{\mathrm{MA}}K_{\mathrm{e0,MA}}\exp(\alpha p)C_{0,\mathrm{MA}}^2(1-p)^2(r-p) + k_{\mathrm{MA/PA}}K_{\mathrm{e0,MA}}\exp(\alpha p)C_{0,\mathrm{MA}}C_{0,\mathrm{PA}}(1-p)^2 \times (r-p) - (k_{\mathrm{h}}[\mathrm{H_2O}])_{\mathrm{MA}}p \tag{3}$$

$$\frac{\mathrm{d}p_{\mathrm{PA}}}{\mathrm{d}t} = k_{\mathrm{PA}}K_{\mathrm{e0,PA}}\exp(\alpha p)C_{0,\mathrm{PA}}^2(1-p)^2(r-p) + k_{\mathrm{PA/MA}}K_{\mathrm{e0,PA}}\exp(\alpha p)C_{0,\mathrm{PA}}C_{0,\mathrm{MA}}(1-p)^2 \times (r-p) - (k_{\mathrm{h}}[\mathrm{H_2O}])_{\mathrm{PA}}p \tag{4}$$

Copolyesterification system contains MA + IA + MPD

$$\frac{\mathrm{d}p_{\mathrm{MA}}}{\mathrm{d}t} = k_{\mathrm{MA}}K_{\mathrm{e0,MA}}\exp(\alpha p)C_{0,\mathrm{MA}}^2(1-p)^2(r-p) + k_{\mathrm{MA/IA}}K_{\mathrm{e0,MA}}\exp(\alpha p)C_{0,\mathrm{MA}}C_{0,\mathrm{IA}}(1-p)^2 \times (r-p) - (k_{\mathrm{h}}[\mathrm{H_2O}])_{\mathrm{MA}}p \tag{5}$$

$$\frac{\mathrm{d}p_{\mathrm{IA}}}{\mathrm{d}t} = k_{\mathrm{IA}}K_{\mathrm{e0,IA}}\exp(\alpha p)C_{0,\mathrm{IA}}^2(1-p)^2(r-p) + k_{\mathrm{IA/MA}}K_{\mathrm{e0,IA}}\exp(\alpha p)C_{0,\mathrm{IA}}C_{0,\mathrm{MA}}(1-p)^2 \times (r-p) - (k_{\mathrm{h}}[\mathrm{H_2O}])_{\mathrm{IA}}p \tag{6}$$

The procedure for simulation of reactions involving one or two acids was the same. The conversion range explored in the simulations was that measured in the experiments i.e. each started from the point where isothermal conditions were reached in the reaction vessel and measurements were taken of the residual carboxylic group concentrations at appropriate time intervals. In the case where two acids are involved in the reaction, the conversion relates to the total conversion of both and it is impossible to determine conversion of individual acids by the titration technique. It has been assumed that in such situations, individual acid concentrations can be obtained by using the rate constants from the homopolyesterification rate studies at the same reaction temperature.

3.1. Estimation of the kinetic constants

The rate constants and Arrhenius parameters were estimated by fitting the calculated acid conversion-time result to the experimental data over the entire conversion range thus avoiding any uncertainty in the experimental data during the short period when the reactants were being mixed and thermally equilibrated. Even during the start up period, there is substantial loss of acid groups due to the rapid rate of reaction, which was difficult to avoid on the scale with which reactions were carried out (sufficient material was prepared to carry out down-stream studies on the pre-polymers and cured resins). In the reactions carried out with a single acid (homopolyesterification) the Chen and Wu [1] model has been employed to fit data using the three unknown parameters kK_{e0}, $k_{\mathrm{h}}[\mathrm{H_2O}]$ and α. The compound rate constant kK_{e0} was assumed to obey an Arrhenius temperature dependence. In the early stages of the reaction, water levels change with time in the reactor until a balance is reached between the rate of water formation and its removal. For calculation purposes, it has been assumed that the water content of the reaction mixture was constant i.e. the term $k_h[H_2O]$ is constant throughout the reaction process [1,2,13]. The constant, α, was given a value of 0.61 as suggested by Chen and Wu [1], Zetterlund et al. [2] and Beigzadeh et al. [13] for self-catalysed polyesterification. It is also accepted [1,13] that all three parameters in the model are independent of the stoichiometric ratio $[OH]_0/[COOH]_0$, r, but increases with increasing temperature in accordance with an Arrhenius's form of expression.

For copolyesterification reactions involving two acid reactants, the cross-catalysis model proposed by Zetterlund et al. [2] was employed. The number of parameters in this model are greater but can be reduced if a number of simplifying assumptions are made. The rate constant of cross-catalysis indicates the rate of polyesterification compared with homopolymerisations. It is reasonable to assume, therefore, that the cross-catalysis rate constants are essentially the same i.e. $k_{MA/PA}K_{e0,MA} = k_{PA/MA}K_{e0,PA}$ It is also thought reasonable to assume that the rate constants for ester hydrolysis are similar i.e. $k_h[H_2O]_{MA} = k_h[H_2O]_{PA}$. These assumptions reduce the number of unknown parameters to two only as the rate constants for homopolymerisation are known from the experimental measurements.

4. Results and discussion

4.1. Homopolymerisation

The conversion-time curves for self-catalysed homopolymerisation, both experimental and those calculated, are shown in Figs. 1–3. The kinetic parameters, kK_{e0} and $k_h[H_2O]$, for the reactions MA + MPD, PA + MPD and IA + MPD as a function of temperature are shown in Table 1. Arrhenius plots of the constant kK_{e0} for each of these polyesterification reactions are shown in Fig. 4.

From Figs. 1–3, it can be seen that the agreement between model predictions and experimental data is satisfactory, although the model underestimates reaction rate in the later stages of the polymerisations. The activation energies obtained from Arrhenius plots were as follows: MA + MPD, $E = 65250$ J mol^{-1}, ln $A = 10.45$ kg^2 mol^{-2} min^{-1}; PA + MPD, $E = 82340$ J mol^{-1}, ln $A = 14.23$ kg^2 mol^{-2} min^{-1} and IA + MPD, $E = 81610$ J mol^{-1}, In $A = 13.78$ kg^2 mol^{-2} min^{-1}. These values are comparable to those reported by Fradet and Marechal [3], where 50–70 kJ mol^{-1} was obtained for the aliphatic acid and 70–100 kJ mol^{-1} for the aromatic acid. Comparisons the activation energies from the literature and the present work over the temperature range 170–220 °C can be made by inspection of Table 2. The activation energy for the reaction of MA + MPD is lower than the others, probably the result of inductive effects and steric factors resulting from the alkyl group in the diol. Brauman and Blair [18] suggested that the electron-attracting power of alkyl groups increases with chain length. Since 1,2-propylene glycol has only one primary hydroxy group while 2-methyl-1,3-propanediol has two primary hydroxy groups, then the latter might be expected to be more reactive than the former.

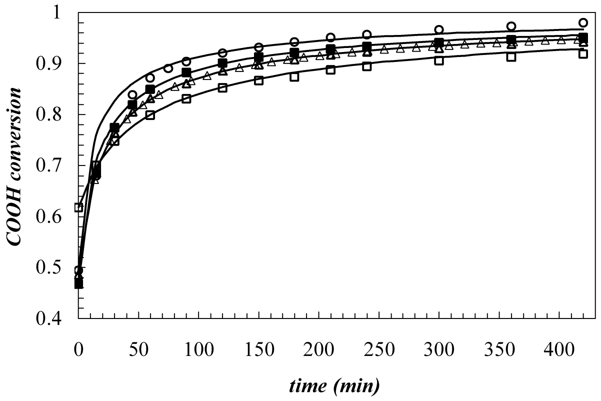

Fig. 1. Conversion of [COOH] in the polymerisations of MA + MPD at different reaction temperatures (□ = 170 °C, Δ = 180 °C, ○ = 200 °C and ■ = 190 °C).

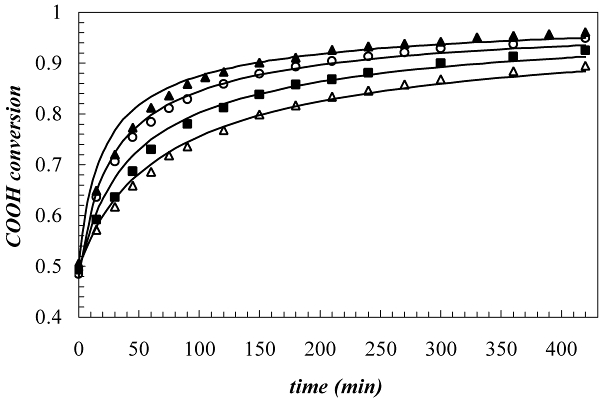

Fig. 2. Conversion of [COOH] in the polymerisations of PA + MPD at different reaction temperatures (Δ = 180 °C, ■ = 190 °C, ○ = 200 °C and ▲ = 210°C).

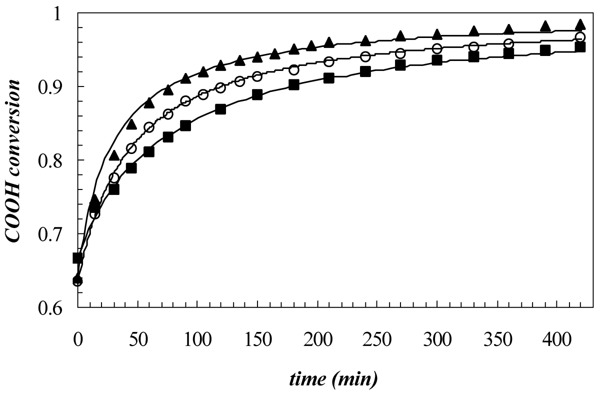

Fig. 3. Conversion of [COOH] in the polymerisations of IA + MPD at dfferent reaction temperatures (■ = 190 °C, ○ = 200 °C and ▲ = 210 °C).

Table 1
Kinetic parameters from model prediction for polymerisation of MA, PA and IA acid with MPD

System	Temperature (°C)	kK_{e0}	$K_h[H_2O]$	r
MA + MPD	170	6.71×10^{-4}	4.52×10^{-5}	1.1006
	180	1.11×10^{-3}	3.42×10^{-5}	1.1022
	190	1.40×10^{-3}	2.94×10^{-5}	1.1034
	200	2.11×10^{-3}	2.52×10^{-5}	1.1024
PA + MPD	180	4.90×10^{-4}	0	1.1049
	190	7.75×10^{-4}	1.21×10^{-5}	1.1056
	200	1.24×10^{-3}	1.42×10^{-5}	1.1058
	210	1.89×10^{-3}	1.31×10^{-5}	1.1075
IA + MPD	190	6.05×10^{-4}	0	2.0166
	200	9.35×10^{-4}	1.12×10^{-5}	2.0105
	210	1.45×10^{-3}	1.43×10^{-5}	2.0031

In the case of reactions involving PA, the parameters are similar in value.

In practice, the reaction of IA + MPD is much slower than that of MA + MPD which is the reason why an excess (10%) of the diol was employed in the reactions as suggested by Allen [16]. Using an excess of diol, the rate of reaction is independent of r, but it does increases with increasing temperature [1,13,17]. The ratio of the rate constants $(kK_{e0})_{MA}/(kK_{e0})_{PA}$ decreases from approximately 2.26–1.70 as the temperature is increased from 180 to 200 °C. In the case of $(kK_{e0})_{MA}/(kK_{e0})_{IA}$ the values are 2.31 and 2.25 at 190 and 200 °C, respectively.

The ratio $(kK_{e0})_{PA}/(kK_{e0})_{IA}$ has been calculated and an average value of 1.31 obtained indicating that the polyesterification of PA is faster than that of IA. It is not easy to account for the value found for $k_h[H_2O]$ since k_h increases with increasing temperature but amount of water in the system decreases because more water was driven off at higher temperatures [2].

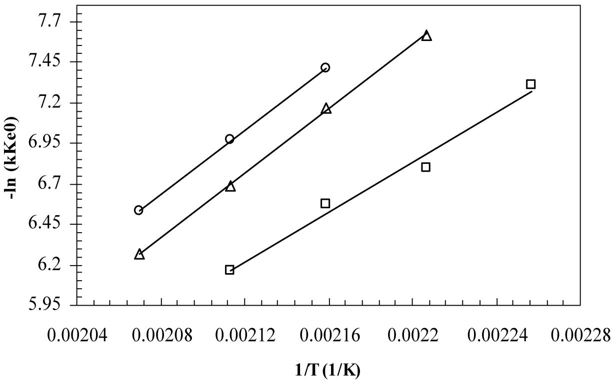

Fig. 4. Arrhenius plots of the polyesterification rate constant kK_{e0} for MA (□), PA (Δ) and IA (○).

4.2. Copolymerisation

In the copolyesterifications performed at 200 °C with MA/PA and MA/IA ratios at mole fraction = 0.5, the parameter obtained are displayed in Table 3.

The values of the constant kK_{e0} for MA, PA and IA from the homopolymerisation data using the Arrhenius form of expression. The magnitude of $k_h[H_2O]$ was estimated by curve fitting experimental results with the model. This value is not reported for homopolymerisation systems since the amount of water and rate constants for hydrolysis are very different.

The conversion-time curves for the two copolyesterification reactions examined are shown in Figs. 5 and 6. The model predictions fit well with the experimental data from 50% conversion through to 94.5 and 93.2% conversion for PA and IA reactions, respectively. Anti-synergistic effect were obtained in accordance with the findings of previous work [2], i.e. the total rate of reaction of carboxyl groups in MA/PA and MA/IA reactions is lower than the sum of total rates of reaction of individual acids. Also, the reactivity of

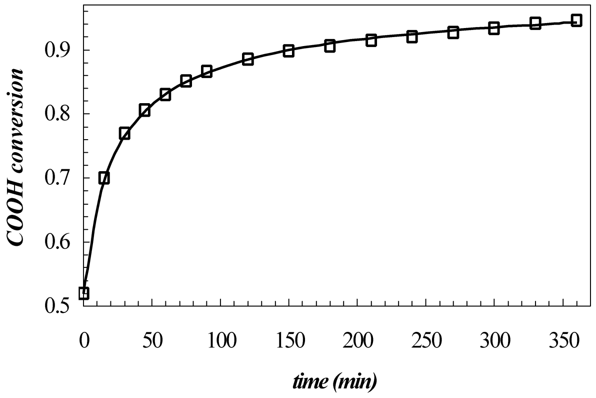

Fig. 5. Conversion of [COOH] versus reaction time of copolyesterification in MA + PA + MPD at 200 °C (symbol = experimental data, continuous line = model prediction).

Table 2
Comparison of activation energies between diacids with different glycols

Diacid	Sources	Activation energy (kJ mol^{-1})
Maleic anhydride	This work	65.2
	Zetterlund et al. [2]	89.6
	Salmi et al. [4] and Paatero et al. [5]	75.0
Phthalic anhydride	This work	82.3
	Zetterlund et al. [2]	81.7
	Salmi et al. [4]	85.0

Previous works employed 1,2-propylene glycol as diol.

Table 3
Optimization results for the copolymerisation systems at 200 °C

System	$k_{PA}K_{e0PA}$	$k_{MA}K_{e0MA}$	$k_{IA}K_{e0IA}$	$(k_{MA/PA}K_{e0MA} = k_{PA/MA}K_{e0PA})$	$(k_{MA/IA}K_{e0MA} = k_{IA/MA}K_{e0IA})$	$(k_h[H_2O])_{PA} = (k_h[H_2O])_{MA}$	$(k_h[H_2O])_{IA} = (k_h[H_2O])_{MA}$
PA	1.231×10^{-3}	2.157×10^{-3}	–	9.950×10^{-4}	–	1.150×10^{-5}	–
IA	–	2.157×10^{-3}	9.430×10^{-3}	–	7.970×10^{-3}	–	1.340×10^{-3}

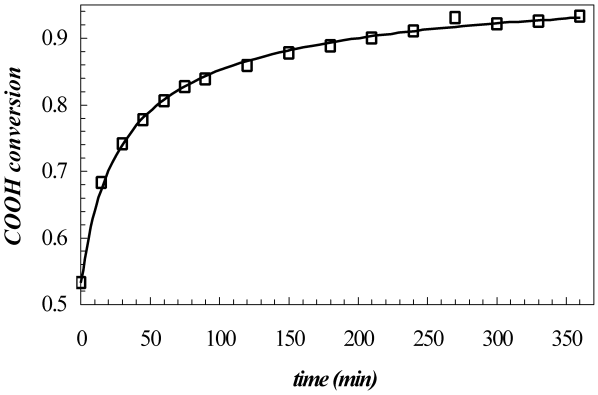

Fig. 6. Conversion of [COOH] versus reaction time of copolyesterification in MA + IA + MPD at 200 °C (symbol = experimental data, continuous line = model prediction).

PA and IA with glycol, $(k_{PA/MA}K_{e0,PA})/(k_{IA/MA}K_{e0,IA})$ has been found to be approximately 1.25 which close to relative reactivity $(kK_{e0})_{PA}/(kK_{e0})_{IA}$ from single acid system at the same temperature.

5. Conclusions

The polyesterification cross-catalysis model derived by Zetterlund et al. [2] and Chen and Wu [1] model have both proved useful for the interpretation of the kinetic data obtained in this work. The Chen and Wu [1] model has been employed to help interpret the observations made in the homopolymerisations MA + MPD, PA + MPD and IA + MPD, systems whereas modified cross-catalysis model of Zetterlund et al. [2] has been used in the copolymerisations MA + PA + MPD and MA + IA + MPD. Simple manual optimisation of the model parameters was sufficient to show that the proposed reaction models fitted the experimental results very well suggesting the theoretical models have a utility in predicting the behavior of technically important polyesterification processes given that the necessary parameters are available. The relative reactivity of maleic anhydride and phthalic anhydride toward 2-methyl-1,3-propanediol, $(kK_{e0})_{MA}/(kK_{e0})_{PA}$ decreases from approximately 2.26–1.70 as temperature increased from 180 to 200 °C. As the isophthalic acid was employed instead of phthalic anhydride the relative reactivity $(kK_{e0})_{MA}/(kK_{e0})_{IA}$ was found to be approximately 2.31–2.25 at temperature 190–200 °C. The phthalic anhydride was found to give faster reaction than isophthalic acid when reacted with 2-methyl-1,3-propanediol with the relative value approximately 1.31 of $(kK_{e0})_{PA}/(kK_{e0})_{IA}$. The anti-synergistic effect in both copolyesterifications has been obtained and is in the same way with the result from previous works [2]. This information in the present study will be employed in future computer simulation studies of the monomer sequence lengths in unsaturated polyester prepolymers.

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