

Study of chemical kinetics of poly (butylene terephthalate) based copolyesters

JOHNSON MATHEW¹, NADER AL-OTAIBI²,
ABDUL REHMAN KHAN¹ & AMIR AL-HADDAD *

¹*Chemical Engineering Department, Kuwait University, P.O.Box 5969, 13060 Safat, Kuwait*

²*Petrochemical Industries Company, Kuwait*

ABSTRACT

Copolyesterification reactions using poly (butylene terephthalate) (PBT) 70 mole % and hydroquinone diacetate (HQDA) + isophthalic acid (IPA) (30 mole %), and PBT 50 mole %/ (HQDA + IPA) 50 mole % have been carried out using a melt polymerization route. Two different polyesterification catalysts (sodium acetate and zinc acetate), were tried for this copolymerization work.

The PBT 70 mole% reactions were carried out at 265, 270, 275 and 280°C while the PBT 50 mole%/50% (HQDA + IPA) reaction were conducted at 240, 245, 250 and 255°C. A new second order kinetics model was developed and tried for these polyesterification reactions. The rate constants and activation energy have been determined and reported for this new system.

Keywords: Acidolysis, copolyesterification, melt polyesterification.

INTRODUCTION

"Xydar and "vectra", commercial acidolysis type thermotropic liquid crystal polyesters, are synthesized by transesterification between aromatic diacids and diacetates. Wholly aromatic polyesters based on 1,4-disubstituted benzenes melt at too high a temperature to be melt-processed (Gray *et al.* 1982). Melt processable thermotropic rigid rod polyesters can be obtained by copolyesterification through partial replacement with comonomers which has substituents, provide kinks, or change the directional effect of the ester (Hanns *et al.* 1995) groups to suppress the crystal mesophase transition temperature. It is thus imperative that the kinetics of homopolymerization be examined first to estimate whether such structural randomization is attainable through melt copolyesterification.

* Author for correspondence.

Direct polyesterifications between diacids and diols at high temperatures do not generate high molecular weight polyesters (Dean *et al.* 1989). At least one reactive monomer such as acid chloride, diacetate or diphenate is essential to get high molecular weight polyester (Lenz 1967, Morgan 1965).

Kinetics of polyesterification reactions have been extensively investigated (Flory 1937, 1953, Carothers & Natta 1930). variable orders observed by these researchers have been shown to be due to differing polarities of the medium (Fradet & Marechal 1981, 1982).

Kinetic investigations of melt acidolysis have been rather few. Vulic & Schulpen (1992) studied 4-acetoxy benzoic acid (4-ABA), biphenol diacetate (BPDA) and terephthalic acid (TAP) systems with and without catalysts. Mathew *et al.* (1992, 1994) investigated melt acidolysis of 4-acetoxy benzoic acid [OB] either alone or in the presence of poly (ethylene terephthalate) [PET] to synthesize poly (4-oxy benzoate) or PET-PB respectively (Williams *et al.* 1996) have examined in some detail the kinetics of polymerization of 4-acetoxy benzoic acid with 6-acetoxy-2-naphthoic acid. This scant literature (Koskikallio 1969, Levine & Temin 1985, Jackson 1989) is surprising since acidolysis has been known since 1958 and the synthesis of thermotropic polyesters has been thoroughly investigated. There are many uncertainties about kinetic order of the reaction, activation energy, etc. of reaction in the melt. This dearth in the literature can be attributed to the intrinsic mechanistic complexity of reactions originating from the high temperature needed to maintain the copolyesters in the molten state. Side reactions may occur at these high temperatures leading to chain growth, chain scission or changes in the chemical nature of end groups, insolubility of diacids or stoichiometric imbalances due to sublimation of reactants, and diffusion constraints which limit the effective removal of bi-product and influence the reaction rate.

Kinetics of the formation of copolyester using 1,4 naphthalene di carboxylic acid (1,4 NDCA) with methyl hydroquinone diacetate (MHQDA) and poly (Butylene terephthalate) (PBT) was investigated by Bishara *et al.* (2001). In this case the initial mole fractions of 1,4 NDCA, MHQDA, and PBT are known, the temperature of the reaction is known, and the concentration of catalyst is also known. For uncatalysed reactions, the concentration of the catalyst was set to zero. In this batch reactions, the concentration of only one of the constituents (acetic acid) was measured; therefore, the optimization model was used to estimate the values of the kinetic parameters for this tri-component system.

This work is an attempt to formulate a plausible kinetic model for the melt copolymerization reaction for PBT (70 mole%)/and HQDA + IPA (30 mole%), PBT (50 mole%)/HQDA + IPA) 50 mole%.

There is a need to understand copolyesterification kinetics since a precise control of the copolymer properties and process productivity is one of the key issues in designing or optimizing the melt transesterification process. The present system forms a sequel of the work involved in investigating the synthesis of copolymers of PBT/HQDA + IPA via melt polymerization technique. In this paper an attempt is made to employ the kinetic information already established for our present copolyesterification system.

The present work was carried out with the following objectives: (i) to develop a mathematical model capable of analysing the system which involves two competitive parallel reactions generating a common by-product (acetic acid); (ii) to determine the kinetic order with respect to concentrations of both HQDA + IPA monomer and PBT segments; and (iii) to predict the rate of acetic acid production by assuming that acetic acid is only produced on reaction of HQDA + IPA + PBT.

The work is presented as follows: first a mathematical model capable of analysing systems in which two competitive reactions occur is considered. The kinetic order is determined at various temperatures for both catalysed and uncatalysed runs to see whether kinetic order changes with a catalyst type and concentration. The kinetic parameters are then reported.

EXPERIMENTAL

Poly (butylene terephthalate) (PBT) was purchased from Century Enka Private Limited, India. It had a mesh size of 1000 microns. Isophthalic acid, 99.5% purity, was purchased from Aldrich Chemicals, U.K. Hydroquinone diacetate was prepared by a sulfuric acid catalysed reaction of hydroquinone and acetic anhydride and was recrystallised from acetone (m.p. 121°C). A 300 mL electrically heated stainless steel based reactor, depicted in Figure 1, was used for the melt transesterification reactions. Two polyesterification catalysts (sodium acetate and zinc acetate, 1.0 mole% concentration) were tried for this study. Transesterification was conducted to generate a series of copolyesters of varying compositions.

The compositions studied were PBT 70 mole%/(HQDA) + IPA) 30 mole% at 265, 270, 275 and 280°C, and PBT 50 mole%/(HQDA + IPA) 50 mole% at 240, 245, 250 and 255°C. Similar temperatures could not be used for both the compositions since degradation was noted at higher temperatures for the PBT 50 mole% system.

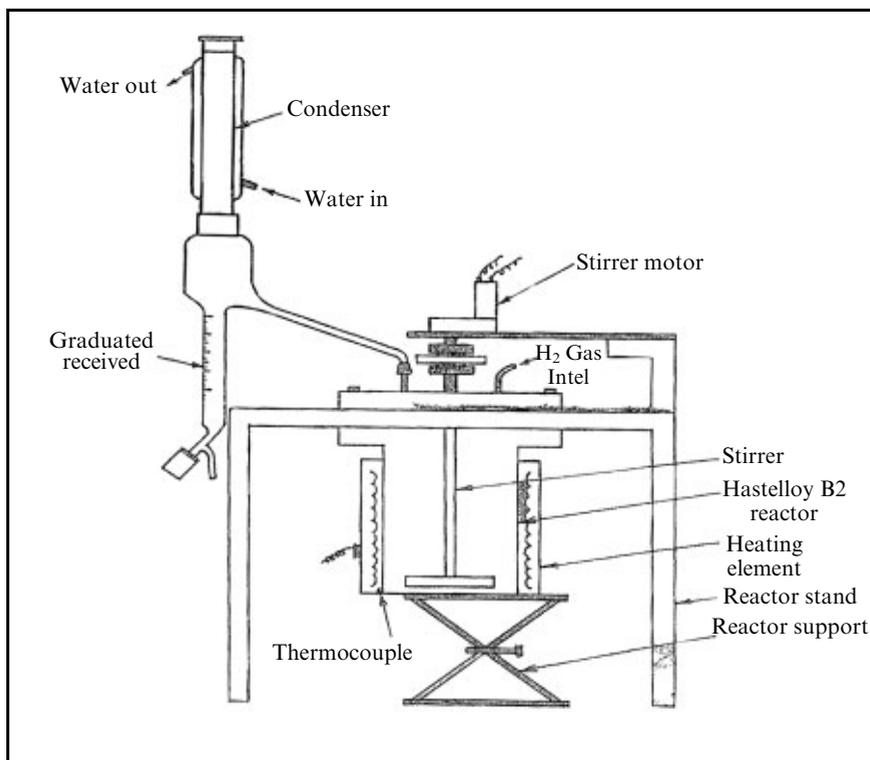


Fig.1. Polymerization Reactor

RESULTS AND DISCUSSION

The reactions when hydroquinone diacetate and isophthalic acid are heated together or maintained may be visualised as shown in Figure 2. The goal of chemical kinetic measurements for well-stirred mixtures is to validate a particular functional form of the rate law and determine numerical values for one or more rate constants which appear in the rate law.

Throughout the discussion on polyesterification of PBT, HQDA and IPA is uncatalysed or catalysed by zinc acetate or sodium acetate as the mechanism, which was presumed to occur is as indicated in Figure 2.

Acetic acid is obtained as a side product from this polyesterification reaction. The reaction is continued until an equilibrium state is attained. The acetic acid collected at atmospheric pressure will not react with the polymer product to revert back to monomers.

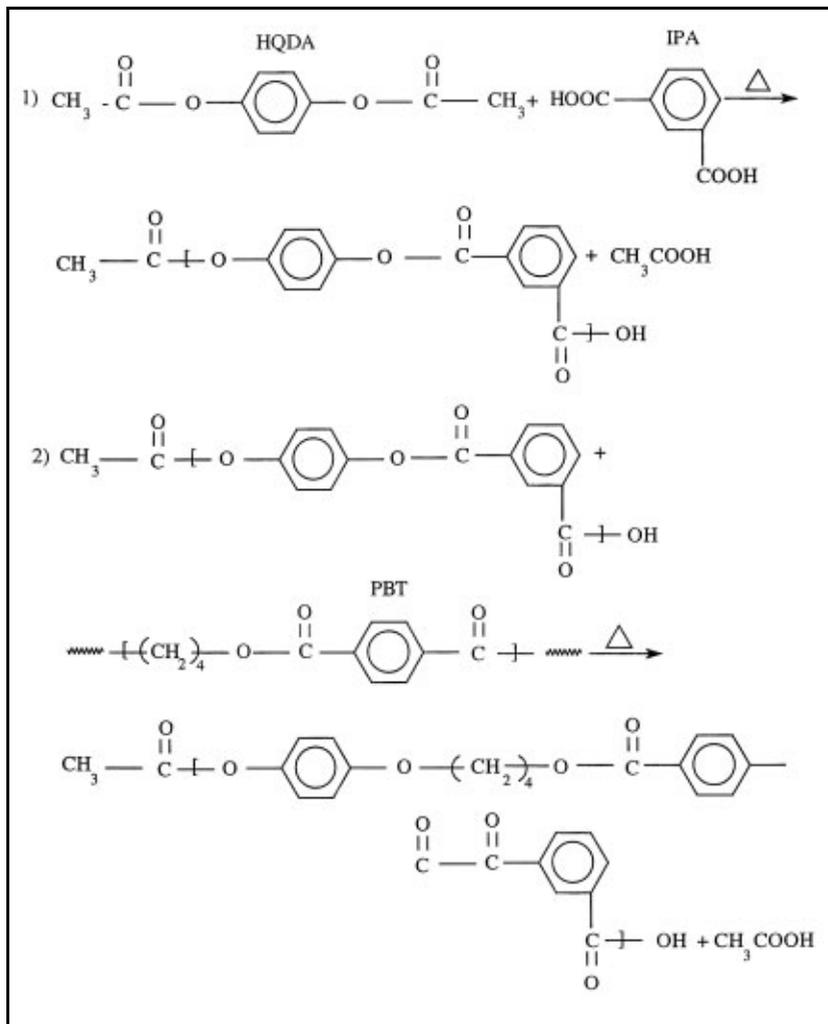


Fig.2. Mechanism indicating the reaction of HQDA and IPA with PBT

The following second order equations were derived to model the experimental data on PBT, HQDA and IPA compositions.



$$-\frac{dA}{dt} = k_1 A^2 \quad (\text{since concentration of } A = B) \quad (3)$$

$$-\frac{dC}{dt} = k_2 (AB)(C) \quad (4)$$

$$-\frac{dc}{c} = k_2 \frac{A_0}{1 + A_0 k_1 t} dt \quad (5)$$

$$-\ln(co - c) = \frac{k_2 A_0}{1 + A_0 k_1 t} dt \quad (6)$$

$$C_0 - C = (1 + A_0 k_1 t)^{-k_2/k_1} \quad (7)$$

Where A, B, C, AB, ABC and HAC correspond to HQDA, IPA, PBT, dimer of HQDA and IPA, trimer of HQDA, IPA and PBT and acetic acid. k_1 and k_2 correspond to the rate constants for the consumption of IPA and PBT respectively.

Figures 3 and 4 indicate the agreement of the model with the experimental data points for catalysed and uncatalysed data. These plots indicate the agreement of the model and the fitting obtained as the temperature of system is varied. A typical behaviour is noted for the experimental data for temperature 270°C in Figure 3. The initial rate is high at 270°C, but it crosses over the plot of 265°C at a time of 115 minutes. This could possibly be due to an almost identical rate of acetic acid evolution because of a very narrow reaction temperature difference of 5°C. The difference between these two figures is mainly quantitative. As seen from the plots, the catalyst sodium acetate plays an important role in increasing the average degree of polymerization. Table 1 indicates the comparison of the catalysed and uncatalysed experimental data for PBT 70 and 50 mole% compositions. Two rate constants k_1 and k_2 are obtained using the new model. The values of k_2 are found to be very small (indicating very little conversion). Sodium acetate was found to be the best catalyst in both of the compositions. A maximum value of 1.23 mole⁻¹min⁻¹ was obtained at 280°C for sodium acetate catalysed PBT 70 mole%/30% (HQDA + IPA) composition while 0.1 mole⁻¹min⁻¹ was obtained for 50 mole% PBT/50% (HQDA + IPA) using sodium acetate as the catalyst.

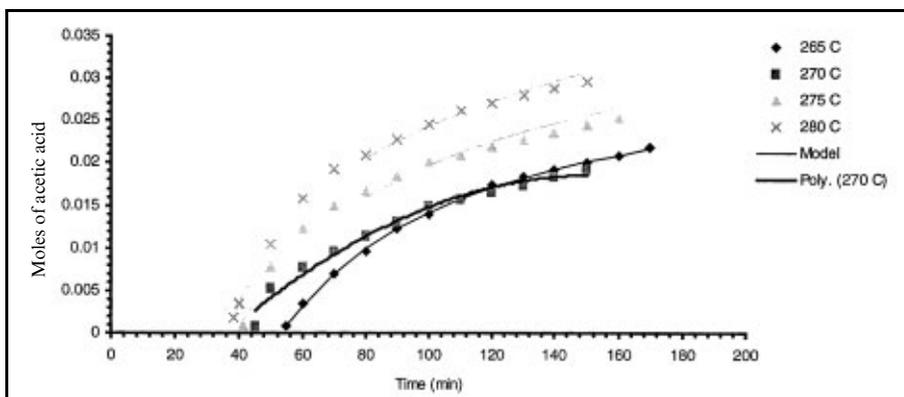


Fig.3. Second order plot indicating temperature variation for copolymerization of PBT 70/(HQDA + IPA) 30 mole% (1 mole% sodium acetate)

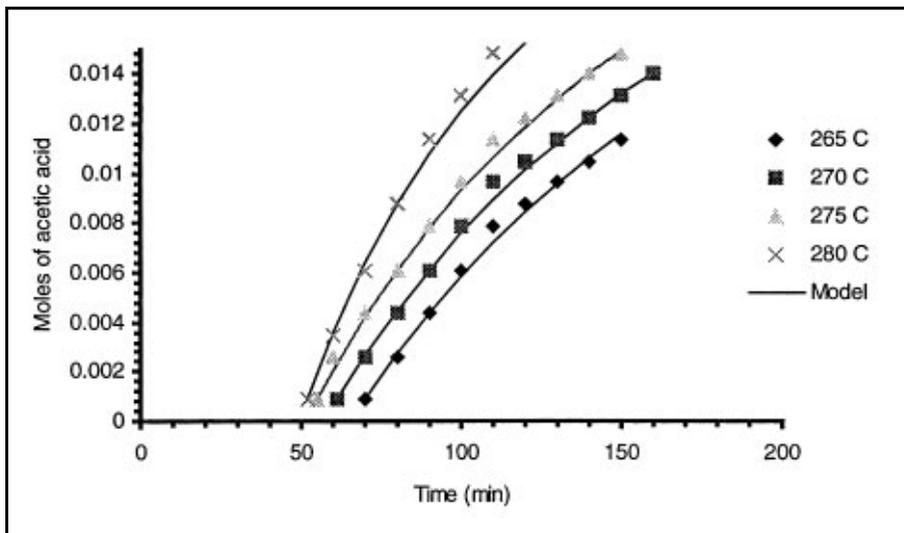


Fig.4. Second order plot indicating temperature variation for copolymerization of PBT 70/HQDA + IPA 30 mole% (no catalyst)

Figure 5 indicates the comparison of different catalysts at 1.0 mole% concentration and a typical temperature of 280°C for a polymer PBT 70 mole%. As seen from plot, higher slopes are obtained for a sodium acetate catalysed reaction.

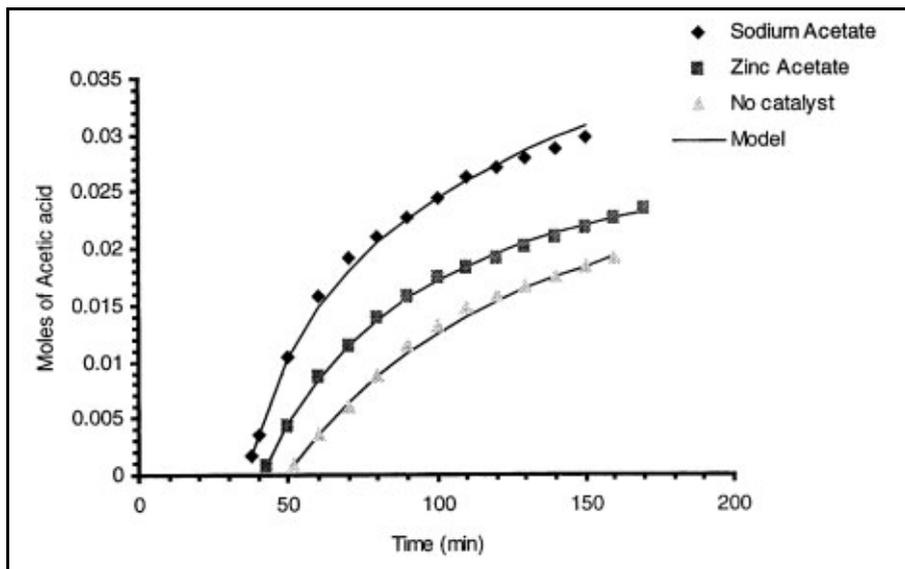


Fig.5. Second order plot for copolymerization of PBT 70/(HQDA + IPA) 30 mole% for different catalysts (1 mole%) at 280°C

Table 1. Table indicating the values of kinetic parameters obtained using second order model

Composition (mole%)	Catalyst Type	Temperature (°C)	k_1 mole ⁻¹ min ⁻¹	k_2 mole ⁻¹ min ⁻¹	Error %	E_1 kJ/mole
70 PBT	*	265	0.167	0.0000385	2.5	166.1
70 PBT	*	270	0.182	0.00035	2.02	
70 PBT	*	275	0.2114	0.000567	3.84	
70 PBT	*	280	0.328	0.000712	2.3	
70 PBT	NaC	265	0.4786	0.000232	1.35	36.4
70 PBT	NaC	270	0.54	0.0007	4.8	
70 PBT	NaC	275	0.62	0.005	3.6	
70 PBT	NaC	280	1.23	0.010667	2.5	
70 PBT	ZnC	280	0.575	0.00032	1.38	
50 PBT	*	240	0.009012	0.004078	4.95	50.1
50 PBT	*	245	0.0214	0.005	5.04	
50 PBT	*	250	0.0198	0.006711	4.65	
50 PBT	*	255	0.0477	0.00825	2.9	
50 PBT	NaC	240	0.04562	0.015034	3.56	27.6
50 PBT	NaC	245	0.1046	0.005127	1.36	
50 PBT	NaC	250	0.1052	0.008694	1.88	
50 PBT	NaC	255	0.1099	0.016521	3.98	
50 PBT	ZnC	255	0.1093	0.000435	2.06	

* = Uncatalysed reaction

ZnC = Zinc Acetate

 k_1 and k_2 = Rate constants (molar⁻¹ min⁻¹)

NaC = Sodium Acetate

E₁ = Energy of Activation for rate constants k_1

Figures 6 and 7 are two Arrhenius plots for k_1 and k_2 for the PBT 70 mole% composition. The activation energy values for the sodium acetate catalysed reaction are found to be lower (36 kJ/mole) compared to the uncatalysed reaction (166 kJ/mole). The activation energy values for rate constant k_2 were not given due to very low values with this rate constant. The activation energy values for both the catalysed and uncatalysed reactions for PBT 50 mole% composition are found to be lower than PBT 70 mole% composition. This could possibly be due to the viscosity effect of the polymer melt when PBT ratio is high.

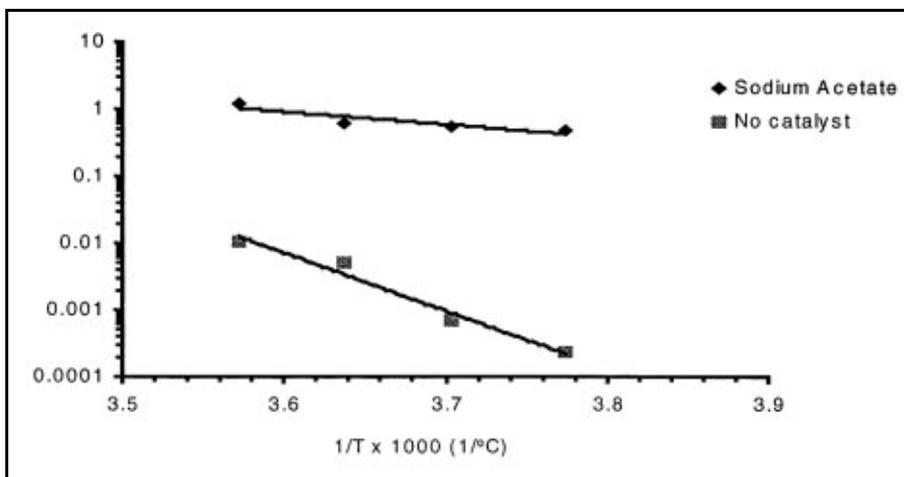


Fig.6. Arrhenius plot for copolymerization of PBT 70/(HQDA + IPA) 30% mole

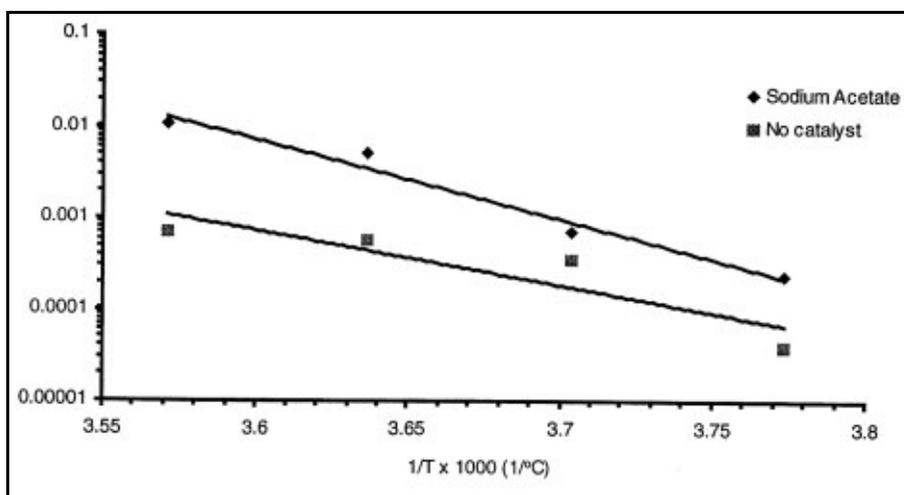


Fig.7. Arrhenius plot for copolymerization of PBT 70/(HQDA + IPA) 30 mole %

Figures 8 and 9 indicate the comparison of experimentally obtained data points and the theoretical values obtained for the model for PBT 50 mole%/50% (HQDA + IPA) composition. Higher slopes are obtained at 255°C which is the maximum reaction temperature for this composition. The uncatalysed reaction is found to terminate fast (approximately 150 minutes) with only 0.015 moles of acetic acid coming out.

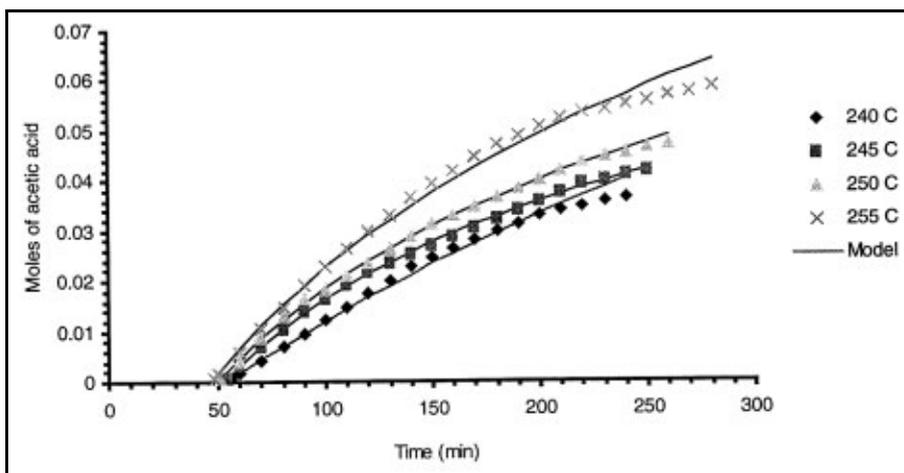


Fig.8. Second order plot indicating temperature variation for copolymerization of PBT 50/(HQDA + IPA) 50 mole% (sodium acetate 1 mole%)

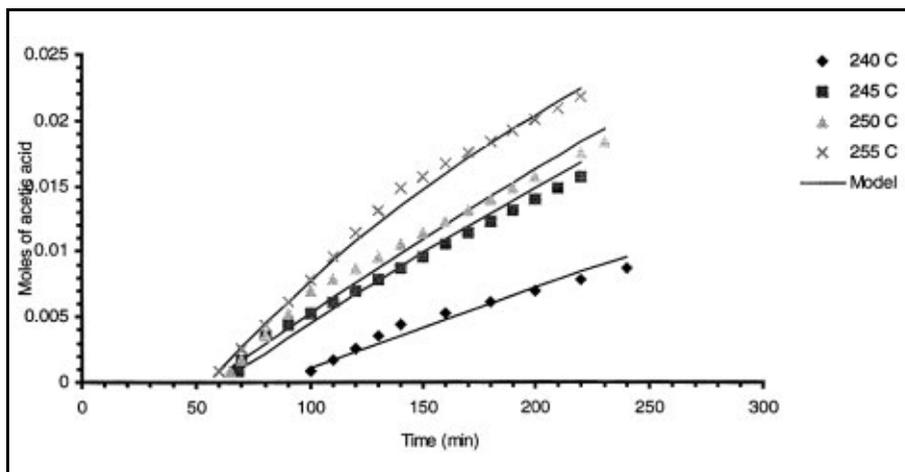


Fig.9. Second order plot indicating temperature variation of PBT 50/(HQDA + IPA) 50 mole% (no catalyst)

A higher conversion (0.05 moles of acetic acid) is obtained at 255°C for the sodium acetate catalysed reaction though the reaction time is approximately 125 minutes more than in the uncatalysed reaction. Figure 10 indicates a

comparison of different catalysts at 255°C using 1 mole% of each respective catalyst. An induction period is noted in all reactions (Figures 3-10). The induction period is found to decrease with increases in temperature. The occurrence of the induction is due to the geometry of the reactor.

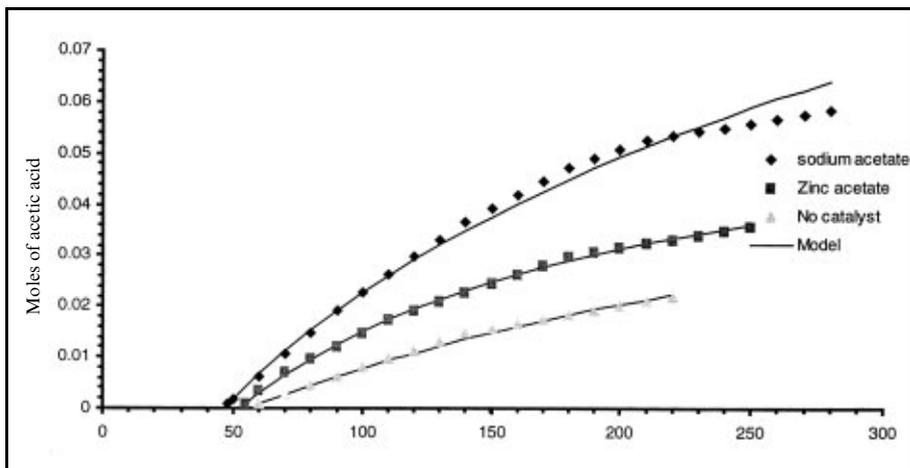


Fig.10. Second order plot for copolymerization of PBT 50/(HQDA + IPA) 50 mole% for different catalyst at 255°C (1 mole%)

Figures 11 and 12 shows the Arrhenius plots for PBT 50 mole% composition. Table 1 indicates the activation energy values for the PBT 50 mole% composition. The sodium acetate is the best catalyst that showed a lower activation energy value than the uncatalysed reaction. Sodium acetate 1.0 mole percent is found to be the best catalyst for PBT 70 and 30 mole% compositions.

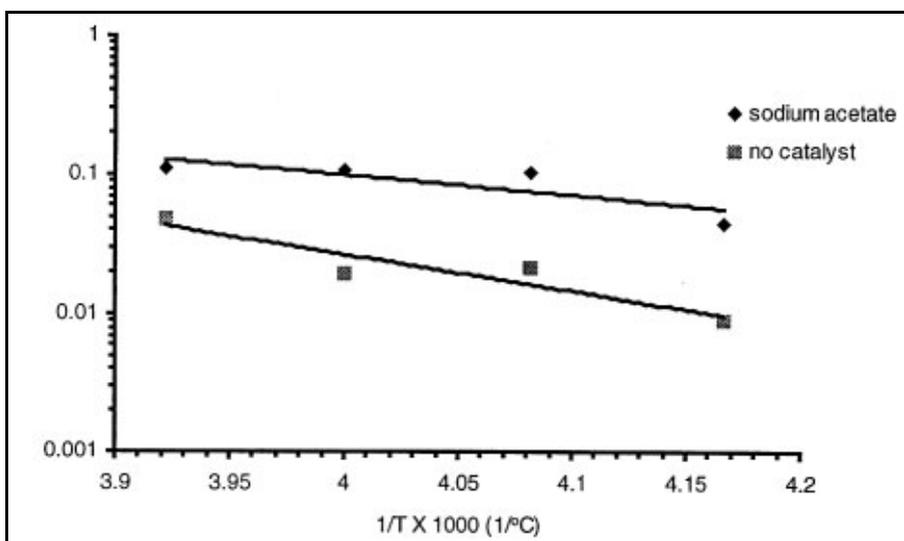


Fig.11. Arrhenius plot for copolymerization of PBT 50/(HQDA + IPA) 50 mole%

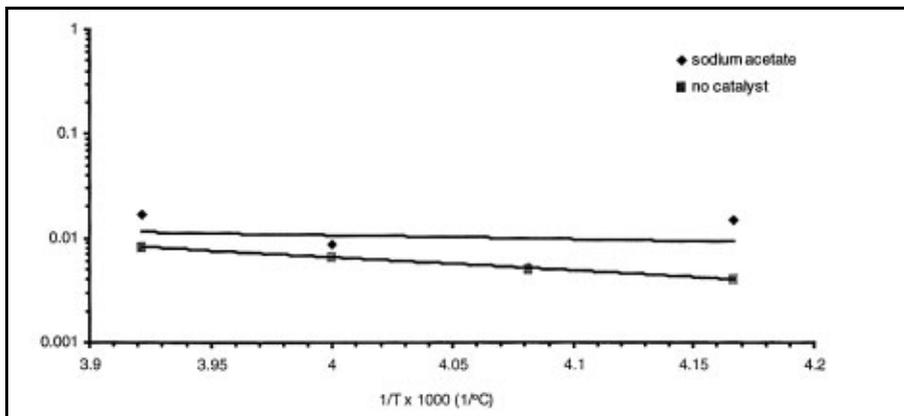


Fig.12. Arrhenius plot for copolymerization of PBT 50/(HQDA + IPA) 50 mole%

CONCLUSION

The copolyesterification kinetics of a novel polymeric system containing PBT 70 mole%/(HQDA + IPA) 30 mole% and PBT 50 mole%/(HQDA + IPA) 50 mole% has been reported. The experimental work indicated that similar reaction temperatures cannot be used for differing PBT compositions. A second order kinetic model with two rate constants k_1 and k_2 has been developed for these systems. Ideally, 1 mole% sodium acetate at 280°C is found to be the best temperature for PBT 70 mole% reaction, while 1 mole% sodium acetate at 255°C is found to be the best condition for the PBT 50 mole% composition. A good match has been obtained between experimental and theoretical values using the new model.

Sodium acetate (1.0 mole%) is found to be a good polyesterification catalyst for these systems. An induction period is found to be present for all the reactions. It decreases with increasing temperatures.

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***Submitted* :** 27/10/2002

***Revised* :** 15/4/2003

***Accepted* :** 8/6/2003

دراسة كيناتيكا الكوبولسترات المنتجة من البولي بيوتلين تيريفثاليت

ج. مانيوس¹ و نادر العتيبي² و عبدالرحمن خان^{1*} و أمير الحداد

¹ جامعة الكويت كلية الهندسة - قسم الهندسة الكيميائية

² شركة الصناعات البتروكيمياوية

خلاصة

تفاعلات الأسرته المتعددة باستخدام بولي بيوتل تيريفثاليت (PBT) بتركيز (70%) مع الهيدروكيونونداي إستيت (HQDA) + حمض أيوفثاليت (IPA) بتركيز (30%) وتفاعل آخر (50%) PBT مع (HQDA + IPA) 50% تمت دراسة كل هذه التفاعلات باستخدام طريق البلورة.

استخدمت هذه التجارب مادتان حفازان هما أستيات الصوديوم وأستيات الزنك.

تفاعلات (70% PBT) أجريت عند درجات الحرارة 265، 270، 275 درجة سيليزية وتفاعلات (50% HQDA, IPA + PBT 50%) أجريت عند درجات الحرارة 240، 245، 255/250 درجة سيليزية.

تم إيجاد معادلة جديدة من الدرجة الثانية لهذه التفاعلات الهامة كما وتم حساب قيم ثابت طاقة التنشيط وثابت جميع التفاعلات.