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Copolyesterification between poly(butylene terephthalate), terephthalic acid and hydroquinone diacetate: a kinetic analysis

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Abstract

The kinetics of liquid crystalline copolyester synthesis via melt transesterification between poly(butylene terephthalate) (PBT), terephthalic acid (TA) and hydroquinone diacetate (HQDA) is examined. Two different copolyester compositions PBT30/(HQDA + TA) 70 and PBT 50/(HQDA + TA) 50 mol% ratio were synthesized. The ratio of HQDA to TA was kept constant for all the reactions.

The copolyesters were synthesized via melt polycondensation route at 265°C, 275°C and 285°C using two different transesterification catalysts, zinc acetate and dibutyl tin oxide. A key postulation assumed in this work is that the reaction originates between TA and HQDA to form a dimer which slices PBT chain. The copolyesterification rate constant for a system containing butylene glycol a more nonpolar moiety compared to ethylene glycol in poly(ethylene terephthalate) has been determined. The activation energy values for the different copolymer systems has also been determined. The rate constants for the uncatalyzed and catalyzed copolyesterification reaction and the activation energy values for the reaction have been determined.

Keywords: Poly(butylene terephthalate); Reaction kinetics; Copolyesterification; Melt polycondensation

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1. Introduction

The structural organization in thermotropic liquid crystalline aromatic polyesters principally comprises of benzene rings fastened exclusively at para positions by ester groups and may be present as sequence of either 4-oxybenzoate or 1,4-oxyphenylene oxy and 1,4-carboxyphenylene carboxy units. The parent polyesters of the major components are so high melting (>600°C) that degradation precedes melting. A recourse to copolyesterification is sought, with the incorporation of flexible spacers [1,2], rigid kinks or substitution in the mesogenic core [3–5], to induce a dramatic decline in transition temperature without a discernible compromise in the mechanical properties. The PBT–OB (oxybenzoate) is formed by the transesterification between 4-acetoxybenzoic acid and poly(butylene terephthalate) (PBT). The downward shift in transition temperature, induced through aliphatic flexible moieties, displays thermotropic character within a definitive range of copolyester composition [1].

Copolymerization reactions are often an attempt to obtain properties intermediate between those of the homopolymers. The properties of PBT based copolymers depend on the composition of the reaction mixture. The composition is influenced by the reaction mechanism and kinetics, which are further influenced by the choice, purity, and the concentration of the main reaction components, by the presence and proper choice of the amount of catalyst and by the reaction temperature. The mechanism and kinetics of polyesterification, polyamidation, polyurethanes and many more have been investigated in the past as well as today [6–15].

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There has been no evidence of kinetic studies of melt transpolyesterification of PBT–TA–HQDA ternary system. An earlier study relating to copolyesterification of PET and 4-acetoxy benzoic acid did not manifest precipitation of poly(4-oxybenzoate) [12,13]. This work is an attempt to investigate the melt reaction behavior of the PBT/HQDA/TA system. The work is presented as follows: A simple reaction sequence is suggested to outline the dominant steps involved. The major reactions, which lead to acetic acid production, are taken into account in the kinetic analysis. Simple second order kinetics is found to be effective for each of the steps significant to the acetic acid production. The correctness of this procedure is justified by experimental observations. Finally, physico-chemical characterization of the copolyesters are considered.

2. Experimental

PBT of inherent viscosity 0.58 and 1600 μm particle size (M/s Century Enka Pvt. Ltd., Pune, India) and purified terephthalic acid (TA) were used as received. Hydroquinone diacetate (HQDA) was prepared by sulfuric acid catalyzed reaction of hydroquinone and acetic anhydride and was recrystallized from acetone (m.p. 121°C). A 300 mL electrically heated histalloy based reactor, depicted in Fig. 1, was used for the melt transesterification reactions. Transesterification reactions were conducted to generate a series of copolyesters of varying compositions. Melt polyesterification kinetics of two compositions were studied. The isothermal reaction temperatures chosen for the kinetic estimations were 265°C, 275°C and 285°C. Dry nitrogen blanket was maintained through out the experiments to prevent oxidative degradations. The rate of evolution of by-product, acetic acid, was monitored volumetrically to estimate the kinetic parameters. Dibutyl tin oxide and zinc acetate (0.25, 0.5 and 1.0 mol% of HQDA) were used as catalysts for the melt transesterification reactions. Thermal transitions were obtained with a Mettler DSC 30 apparatus under nitrogen atmosphere using a sample size of 10–15 mg. Samples were analyzed in the temperature range of 50–250°C in the first and second heating cycles.

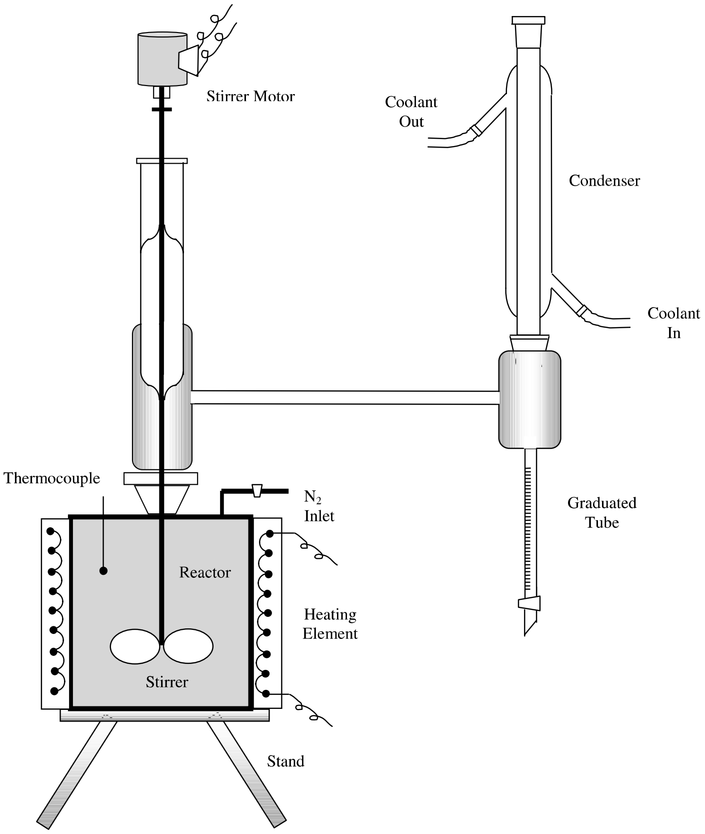

Fig. 1. Experimental setup.

3. Results and discussion

The reactions when PBT, HQDA and TA are heated together or maintained isothermally at temperature in excess of isotropic temperature of crystalline PBT may be visualized as follows: (i) PBT chain cleavage with TA resulting in the formation of two PBT segments of similar or differing in chain lengths but terminated with carboxylic acid end group, ($S_{PBT}T$), (ii) the segment of (i) react with HQDA to form PBT segment $S_{PBT}TH$ with acetoxy end group, (iii) segments $S_{PBT}T$ and segment $S_{PBT}TH$ could then react to reform the PBT chain with insertion of hydroquinone–terephthalate unit, (iv) transesterification of HQDA and TA leads to form hydroquinone terephthalate (TH) and (v) the insertion of hydroquinone–terephthalate unit into PBT chain PB(TH)T (Fig. 2).

Thus, one can visualize the existence of many variables (rate constants) for these independent reactions. It is difficult task to analytically solve for these kinetic variables. Hence the following assumptions are made to simplify the kinetic picture: (1) the reaction between HQDA and TA leads to the formation of dimers (TH); (2) an oligomer (dimer) of HQDA and TA can cleave

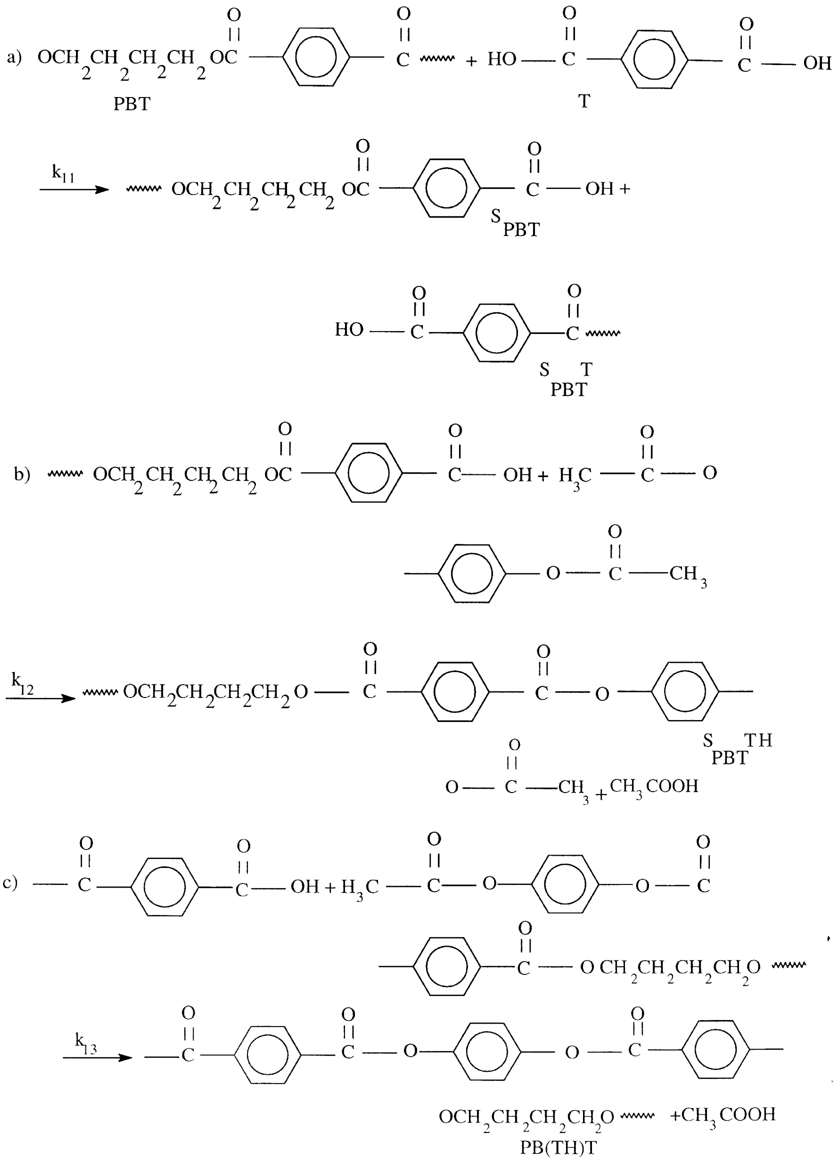

Fig. 2. Mechanism of PBT–HQDA–TA copolyesterification.

the PBT chain to form PBT segments $S_{PBT}T$ and $S_{PBT}TH$; (3) these segments then react to reform PBT chain with insertion of TH moiety. Hence, the reactions leading to the copolyester of interest are given by Eqs. (A) and (B). If c denotes the dimer formed by the reaction of HQDA and TA, then the following steps can be presumed for the copolyesterification reactions.

$$\underset{(a-x)}{\mathrm{H}} + \underset{(a-x)}{\mathrm{T}} \xrightarrow{k_1} \underset{(c)}{\mathrm{TH}} + \underset{(x+y)}{\mathrm{CH_3COOH}} \tag{A}$$

$$\underset{(q-y)}{\mathrm{PBT}} + \underset{(c)}{\mathrm{TH}} \xrightarrow{k_2} \underset{(y)}{\mathrm{PB(TH)T}} + \underset{(x+y)}{\mathrm{CH_3COOH}} \tag{B}$$

where, H, T, TH, PBT, PB(TH)T, CH_3COOH, a, c, x, y and q denote hydroquinone diacetate, terephthalic acid, dimer of HQDA and TA, poly(butylene terephthalate), copolyester, acetic acid, initial concentration of HQDA and TA, initial concentration of dimer number of moles of H or T converted, number of moles of PBT chains converted and initial concentration of PBT respectively. k_1 and k_2 denote the rate constant of homopolyesterification and copolyesterification respectively. Rate of formation of the dimer can be given as

$$\frac{dx}{dt} = \frac{-dH}{dt} = \frac{-dT}{dt} = k_1(a-x)^2 \tag{1}$$

Rate of formation of the copolyester can be given as

$$\frac{dy}{dt} = \frac{-d\mathrm{PBT}}{dt} = k_2c(q-y) \tag{2}$$

$$\frac{dc}{dt} = k_1(a-x)^2 - k_2c(q-y) \tag{3}$$

total rate of acetic acid production is given by the algebraic sum of Eqs. (1) and (2).

$$\frac{d\mathrm{CH_3COOH}}{dt} = \frac{dx}{dt} + \frac{dy}{dt} = k_1(a-x)^2 + k_2c(q-y) \tag{4}$$

From the conservation of residues of H and T, we have $c = x - y$. Eq. (2) now becomes

$$\frac{dy}{dt} = k_2(x-y)(q-y) \tag{5}$$

Eq. (4) can now be written as

$$\frac{d\mathrm{CH_3COOH}}{dt} = k_1(a-x)^2 + k_2(x-y)(q-y) \tag{6}$$

A simple numerical procedure [11] was applied to Eq. (6) to calculate theoretically the values of k_1 and k_2. A number of reactions were carried in steps of 10°C from 265°C to 285°C.

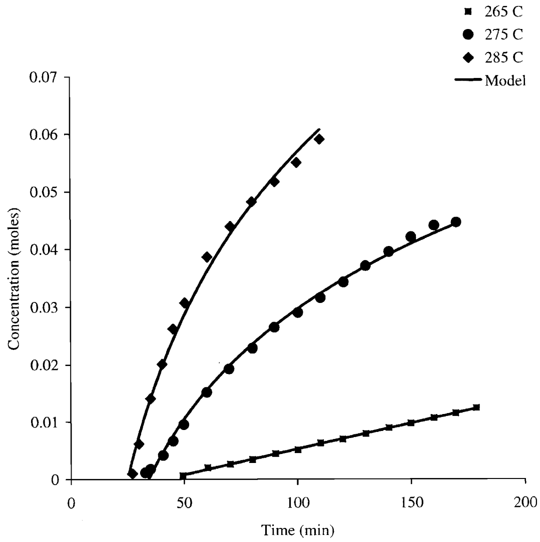

Fig. 3. Second order plot for uncatalyzed PBT (50%) and (HQDA + TA) (50%) with the model.

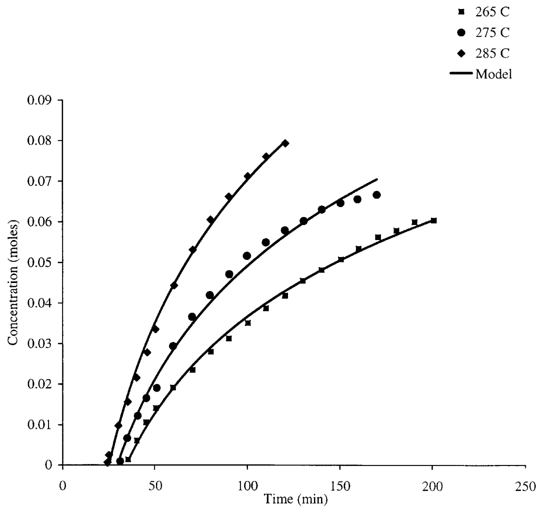

Fig. 4. Second order plot for PBT (30%) and (HQDA + TA) (70%) with the model.

Figs. 3 and 4 indicate the experimental data points at three different temperatures and fitting curves according to Eq. (6) for PBT 50/(HQDA + TA)50 and PBT 30/(HQDA + TA)70. The reaction rate is also adequately modeled by second-order kinetics for catalyzed reactions (Fig. 5).

Figs. 6 and 7 are two typical plots for different compositions indicating that the kinetic model adheres well to the experimental data obtained from different catalysts. Figs. 8 and 9 are two typical figures indicating

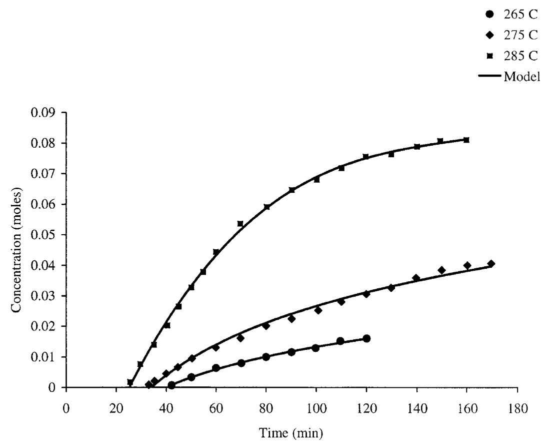

Fig. 5. Second order plot of 0.25 mol% dibutyl tin oxide catalyzed reaction for PBT (30%) and (HQDA + TA) (70%) with the model.

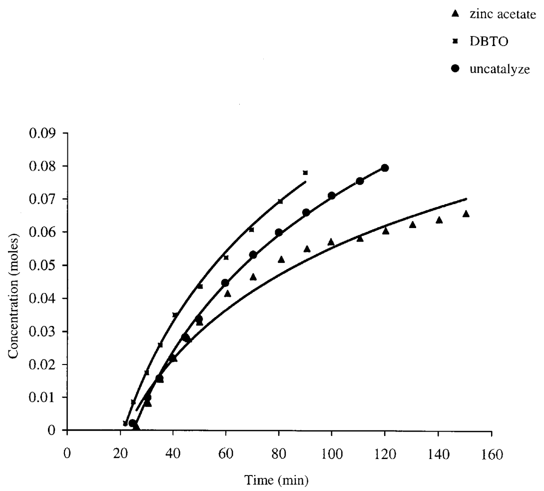

Fig. 7. Second order plot of uncatalyzed and 0.5 mol% catalyzed reactions for PBT (30%) and HQDA + TA (70%) at 285°C with model.

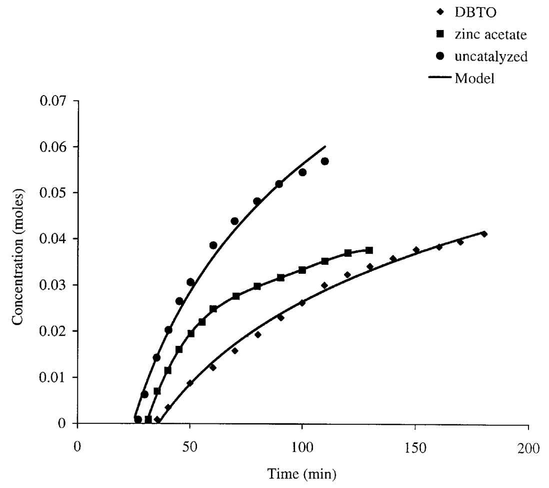

Fig. 6. Second order plot of uncatalyzed and 0.5 mol% catalyzed reactions for PBT (50%) and HQDA + TA (50%) at 285°C with the model.

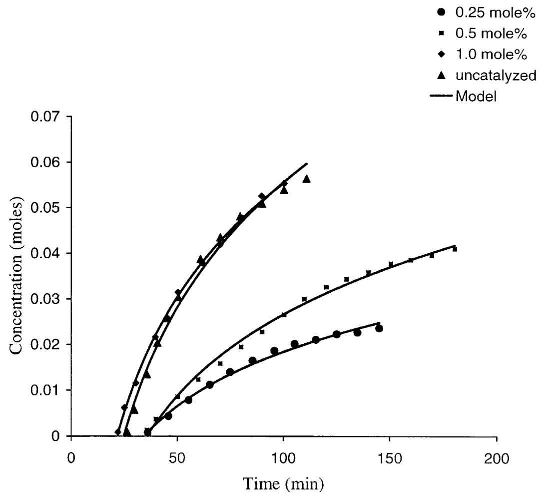

Fig. 8. Second order plot of uncatalyzed and dibutyl tin oxide catalyzed reactions for PBT (50%) and HQDA + TA (50%) at 285°C with the model.

that the model adheres well to the experimental data analyzed for different catalyst concentrations.

A typical Arrhenius plot is shown in Fig. 10. As seen in the plot the experimental data can be adequately modeled by Eq. (6).

Table 1 indicates the rate constants (k_1 and k_2) and activation energies (E_1 and E_2) for zinc acetate and dibutyl tin oxide catalyzed reactions for PBT 50 and HQDA + TA 50 mol% concentration. The values of k_1 are found to be the range of 0.03136–0.5 kJ/mole while for k_2 it is in the range of 0.004–0.1 kJ/mole. No major decrease in the value of the rate constants k_1 and k_2 are noticed. The activation energy values indicate that DBTO at 0.25 mol% concentration is a suitable catalyst for the PBT 50 mol% concentration.

Table 2 indicates the activation energy values for PBT 30 mol% concentration. The activation energy values for the catalyzed reaction are found to be almost similar to that of uncatalyzed reactions. The activation energy values for the PBT 30 mol% uncatalyzed and catalyzed reactions are found to be in the range of 20–100 kJ/mole.

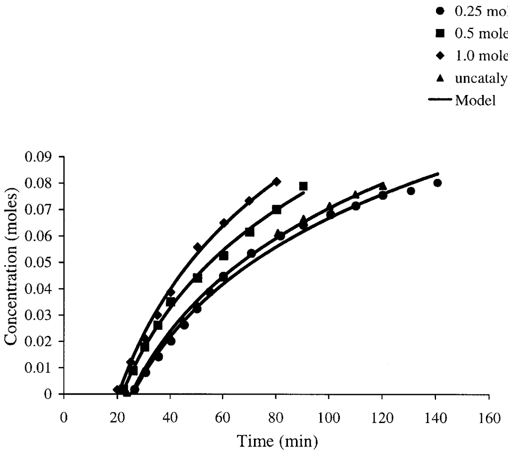

Fig. 9. Second order plot of uncatalyzed reactions and dibutyl tin oxide catalyzed reactions for PBT (30%) and HQDA + TA (70%) at 285°C with the model.

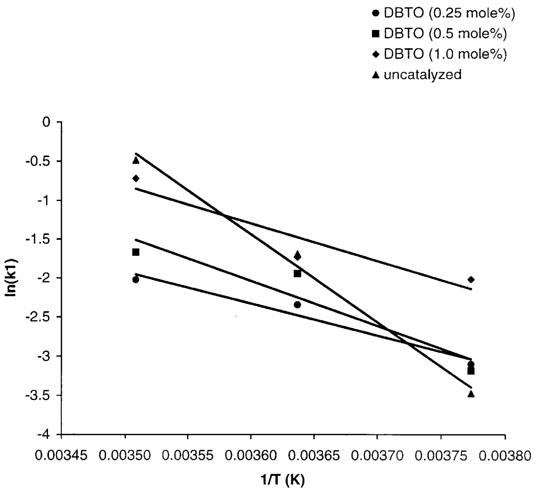

Fig. 10. Arrhenius plots for uncatalyzed and dibutyl tin oxide catalyzed reaction for 50 mol% PBT.

Table 1
Table indicating the effect of catalyst type and temperature on the rate constant and activation energy for PBT (50 mol%): HQDA + TA (50 mol%)

Catalyst type	Temperature (°C)	k_1	k_2	E_1	E_2
Uncatalyzed	265	0.03136	0.00424	94.35	100
	275	0.18459	0.04532		
	285	0.6298	0.10079		
Zinc acetate 0.25 mol%	265	0.10337	not found	–	–
	275	0.14269	0.00635		
	285	0.10362	0.07107		
Zinc acetate 0.5 mol%	265	0.13539	0.00335	39.25	20.19
	275	0.14084	0.00425		
	285	0.47981	0.00609		
Zinc acetate 1 mol%	265	0.12109	not found	51.89	–
	275	0.37561	0.02924		
	285	0.628	0.3966		
DBTO 0.25 mol%	265	0.04446	not found	34.11	–
	275	0.09474	0.01406		
	285	0.13114	not found		
DBTO 0.5 mol%	265	0.04079	not found	48.22	–
	275	0.14447	0.02804		
	285	0.18729	0.02776		
DBTO 1 mol%	265	0.13093	0.03195	40.884	36.922
	275	0.17568	0.03669		
	285	0.48601	0.10477		

k_1: rate constant for the first stage (1/concentration). k_2: rate constant for the second stage (1/concentration). E_1: Activation energy for the first stage (kJ/mole). E_2: Activation energy for the second stage (kJ/mole).

Characterization of the copolyesters were carried out using differential scanning calorimeter. Two typical uncatalyzed runs (Figs. 11 and 12) are shown. The plots reveal that the polyesters are liquid crystalline in nature.

Table 2
Table indicating the effect of catalyst type and temperature on the rate constant and activation energy for PBT (30 mol%) HQDA + TA (70 mol%)

Catalyst type	Temperature (°C)	k_1	k_2	E_1	E_2
Uncatalyzed	265	0.18321	0.05105	24.06	63.91
	275	0.27352	0.10398		
	285	0.2819	0.39422		
Zinc acetate 0.25 mol%	265	0.08231	0.01275	43.05	53.62
	275	0.31723	0.0512		
	285	0.31931	0.06947		
Zinc acetate 0.5 mol%	265	0.13539	0.00335	35.47	101.3
	275	0.24545	0.04195		
	285	0.42037	0.08257		
Zinc acetate 1 mol%	265	0.07715	0.00792	51.57	84.55
	275	0.54779	0.01826		
	285	0.38802	0.11866		
DBTO 0.25 mol%	265	0.04895	not found	55.56	–
	275	0.10813	0.02376		
	285	0.28821	0.33379		
DBTO 0.5 mol%	265	0.07692	0.02644	56.81	73.76
	275	0.15035	0.05978		
	285	0.47282	0.27982		
DBTO 1 mol%	265	0.08912	0.2305	41.55	46.02
	275	0.16944	0.6996		
	285	0.33507	0.98971		

k_1: rate constant for the first stage (1/concentration). k_2: rate constant for the second stage (1/concentration). E_1: Activation energy for the first stage (KJ/mole). E_2: Activation energy for the second stage (KJ/mole).

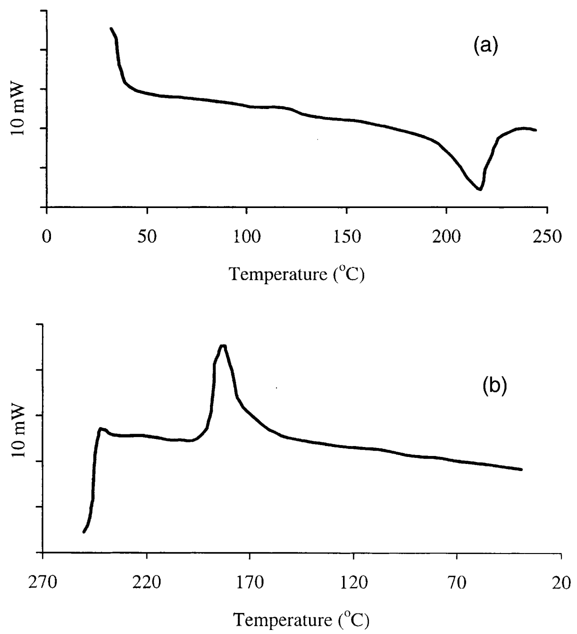

Fig. 11. DSC (a) heating and (b) cooling cycle of uncatalyzed reaction for PBT (50%) (HQDA + TA) (50 mol%) system.

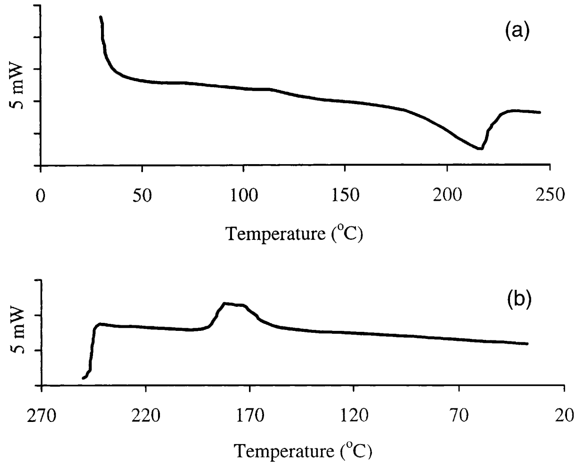

Fig. 12. DSC (a) heating and (b) cooling cycle of uncatalyzed reaction for PBT (30%) (HQDA + TA) (70 mol%) system.

4. Conclusion

Kinetics of a three component (PBT, HQDA and TA) melt polymerization system has been analyzed for the compositions PBT 50, (HQDA + TA)50 and PBT 30 + (HQDA + TA)70. Compared to one and two component systems, the kinetics of this ternary system would be extremely complex due to possibility of several reactions occurring in parallel. Due to the complexity of the ternary system many rate constants are present for the independent reactions.

To reduce the complexity of the kinetic analysis it was assumed that HQDA and TA react to produce a dimer and acetic acid and a dimer can only react with a PBT molecule forming the copolymer and acetic acid. A simple differential equation predicting the rate of generation of acetic acid was developed and the rate constants for the copolymerization reaction was estimated.

The activation energy for the uncatalyzed reaction containing 50 mol% PBT ranges between 94–100 kJ/mole while that for 30 mol% PBT the value lies between 24–64 kJ/mole.

Dibutyl tin oxide (0.25 mol%) is found to be the best catalyst (for PBT 50 mol% reaction) with a energy of activation of 55 kJ/mole, while for PBT 30 mol% concentration neither zinc acetate or dibutyl tin oxide at different concentrations seem effective. DSC studies reveal that PBT50 and 30 (mol%) compositions are liquid crystalline in nature.

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References

[1] Jackson Jr WJ, Kuhfuss HF. J Polym Sci Polym Chem Ed 1976;14:2043.

[2] Roviello A, Sirigu A. J Polym Sci Polym Lett Ed 1975;13:455.

[3] Goodman I, McIntyre JE, Simpson JW. British Patent 895 552 (1965); US Patent 3 321 437 (1967).

[4] Goodman I, McIntyre JE, Alfred DH. British Patent 993 272 (1965); US Patent 3 368 998 (1967).

[5] Kuhfuss HF, Jackson Jr. WJ. US Patent 3778 410 (1973); 3 804 805 (1974).

[6] Wong S-W, Frisch KC. J Polym Sci Part A Polym Chem Ed 1986;24:2867.

[7] Wong S-W, Frisch KC. J Polym Sci Part A Polym Chem Ed 1986;24:2877.

[8] Thompson CM, Taylor SG, McGee WW. J Polym Sci Part A 1990;28:333.

[9] Park KCh, Kim SCh. J Appl Polym Sci 1990;39:639.

[10] Sato M. J Am Chem Soc 1960;82:3893.

[11] Chapra SC, Canale RP. Numerical methods for engineers. 3rd ed. New York: McGraw-Hill; 1998.

[12] Mathew J, Bahulekar RV, Ghadage RS, Rajan CR, Ponrathnam S, Prasad SD. Macromolecules 1992;25:7338.

[13] Mathew J, Ghadage RS, Prasad SD, Ponrathnam S. Macromolecules 1994;27:4021.

[14] Hamb FL. J Polym Sci Polym Chem Ed 1972;10:3217.

[15] Mathew J, Ghadage RS, Prasad SD, Ponrathnam S. Macromolecules 1994;27:4021.