

Copolyesters of Poly(ethylene terephthalate), Hydroquinone Diacetate, and Terephthalic Acid: A Simple Rate Model for Catalyzed Synthesis in Melt

HABIB I. SHABAN* and J. MATHEW

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

SYNOPSIS

Transesterification reactions between poly(ethylene terephthalate) (PET), hydroquinone diacetate (HQDA), and terephthalic acid (TA), were conducted via the melt polymerization route with the objective of analyzing the copolyesterification kinetics of a phase separated system. At first homopolymerization of HQDA and TA were conducted at 50 mol % composition of each monomer. Then the polymerization kinetics of four compositions [PET 30/70 (HQDA + TA), PET 40/60 (HQDA + TA), PET 50/50 (HQDA + TA), PET 60/40 (HQDA + TA) with 30 : 35 : 35, 40 : 30 : 30, 50 : 25 : 25, and 60 : 20 : 20 mol % PET, HQDA, and TA] were investigated. The following assumptions were made to make kinetic analysis tractable. HQDA and TA combine to form acetic acid and higher oligomers. The oligomer subsequently adds on to the PET chain to give a copolymer of PET/HQDA/TA, the product of interest. The reaction between PET, HQDA, and TA proceeds in a heterogeneous two-phase system consisting of PET-rich and PET-poor regions. The reaction sequence is HQDA and TA react to form a dimer and subsequently the dimer is added onto the PET chain. This reaction sequence is assumed to be valid for the PET-rich and PET-poor phases. Both these reactions were assumed to be second order with respect to the reactants. Reactions wherein the dimer reacts with HQDA or TA to form acetic acid exist, but the probabilities of these processes are small with respect to the main reaction postulated above, thus maintaining the overall mass balance. Moles of acetic acid found experimentally were computed using a standard procedure. The rate constant k under the conditions of phase separation was determined. The rate constant in the presence of PET was higher than that observed in the HQDA and TA reaction. An Arrhenius plot revealed that the catalyst plays a marginal role. Microscopic analysis revealed that the HQDA and TA polymer were nonmelting while copolyesters PET 30/70 (HQDA + TA) to PET 60/40 (HQDA + TA) melted and were liquid crystalline. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A global study on the structure–property relationship in thermotropic liquid crystalline polymers (LCPs) indicates that bridging groups in the mesogenic elements and their directional effects dictate a number of critical properties such as transition temperatures, mesogenic gap, etc.

Considerable literature exists on the structural organization of thermotropic liquid crystalline aromatic

copolyesters.^{1–17} The majority of these copolyesters are synthesized via the copolymerization route, which helps in tailoring the characteristic properties to the predecided values. Another major advantage of copolymerization is that it helps in conferring specific chemical properties to the major component present in the system. The homopolymer of major components may consist of benzene rings attached at para positions through carboxy groups. They may be present as a sequence of hydroquinone diacetate and terephthalic acid or sequences of 4-oxybenzoate. The polymers of these sequences have melting points above 600°C. Decomposition precedes melting in such cases. The melting temperatures of these polymers can be

* To whom correspondence should be addressed.

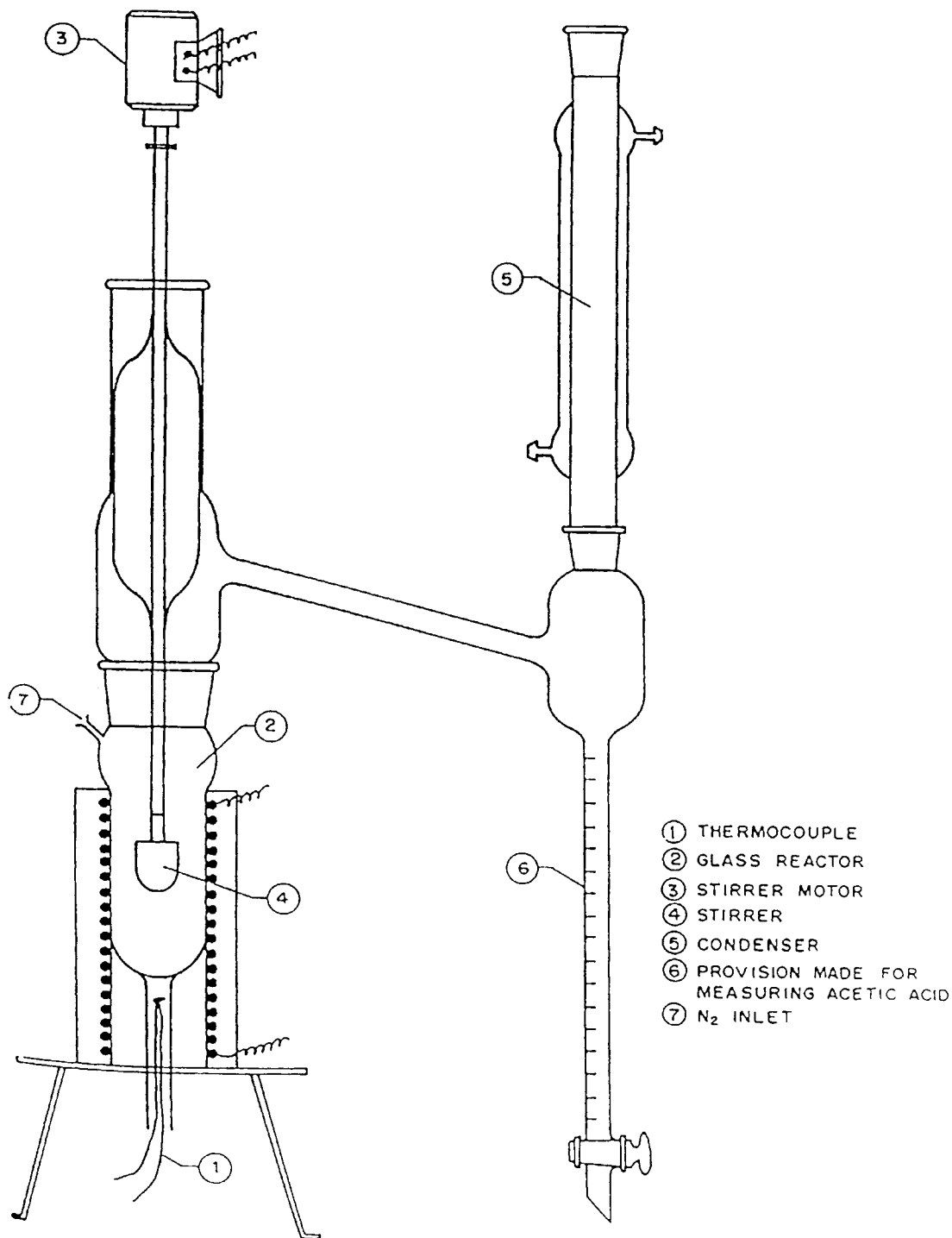


Figure 1 Laboratory scale reaction setup for the synthesis of the copolyester.

reduced by the introduction of flexible aliphatic units, rigid links, or by the addition of certain substituents in the aromatic rings.

Synthesis of aromatic polyesters using bromo, chloro, methyl, and methoxy substituted hydroquinones have been reported^{18,19} to lower the melting

temperature relative to the unsubstituted polyesters. These polyesters have applications in fabricating thermally stable high strength fibers and molding resins with unusual properties. Melt spinning of copoly(terephthalates) of phenyl hydroquinone and unsubstituted hydroquinone (up to 30 mol %) have been

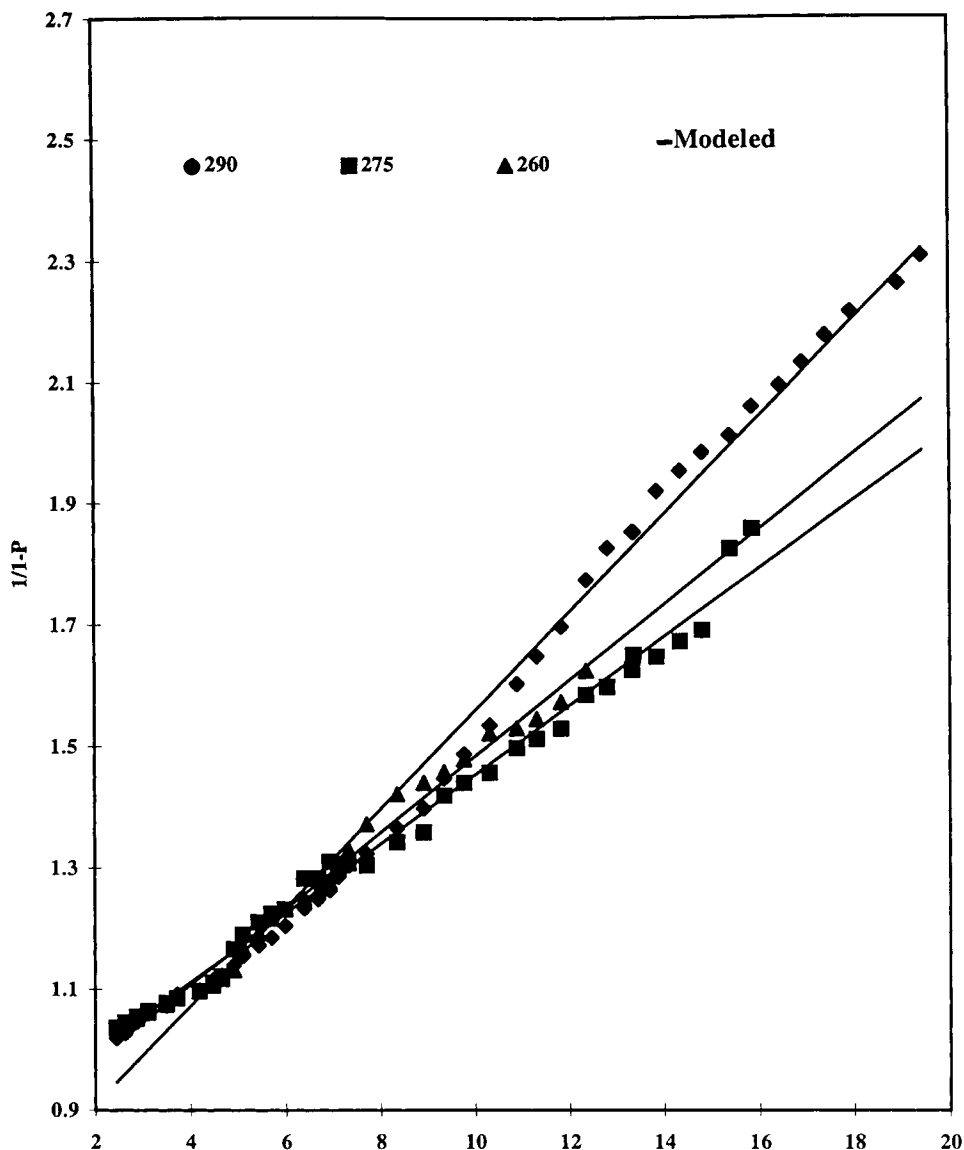


Figure 2 Second-order plot illustrating effect of temperature for uncatalyzed HQDA/TA.

reported.^{20,21} Catalytic synthesis of poly(ethylene terephthalate) (PET), terephthalic acid (TA), and 4,4-isopropylidene diphenol diacetate via melt polymerization is reported.²² It describes the preparation of copolyesters of glycols and bisphenols. The reaction mechanism between a preformed polyester (PET), a diacid, and a diacetate is discussed. This system closely resembles that generated by the reaction between PET, hydroquinone diacetate (HQDA), and TA. A baking temperature of 280°C was employed. *Precipitation of homopolymer formed between HQDA and TA occurred in the initial stages of the reaction.*²² These polymers were found to be mechanically superior to PET coxybenzoate systems. This system is commercially attractive due to its higher strength. The system differs

from 4-acetoxy benzoic acid (PET/OB) copolyester only in the directional effect of the ester unit forming a part of the mesogenic core.

An understanding of the melt polyesterification kinetics is necessary to economize on the process productivity and to improve the polymer properties. There is no published literature on the melt polyesterification kinetics of the homopolymerization of HQDA and TA or the copolymerization of PET, HQDA, and TA. Kinetic investigation of copolymerization between PET and PET/OB did not reveal precipitation of poly(4-oxybenzoate).²³ The kinetic investigations revealed that a simple second-order phenomenological model agreed well with the experimental data. The present study is a sequel to

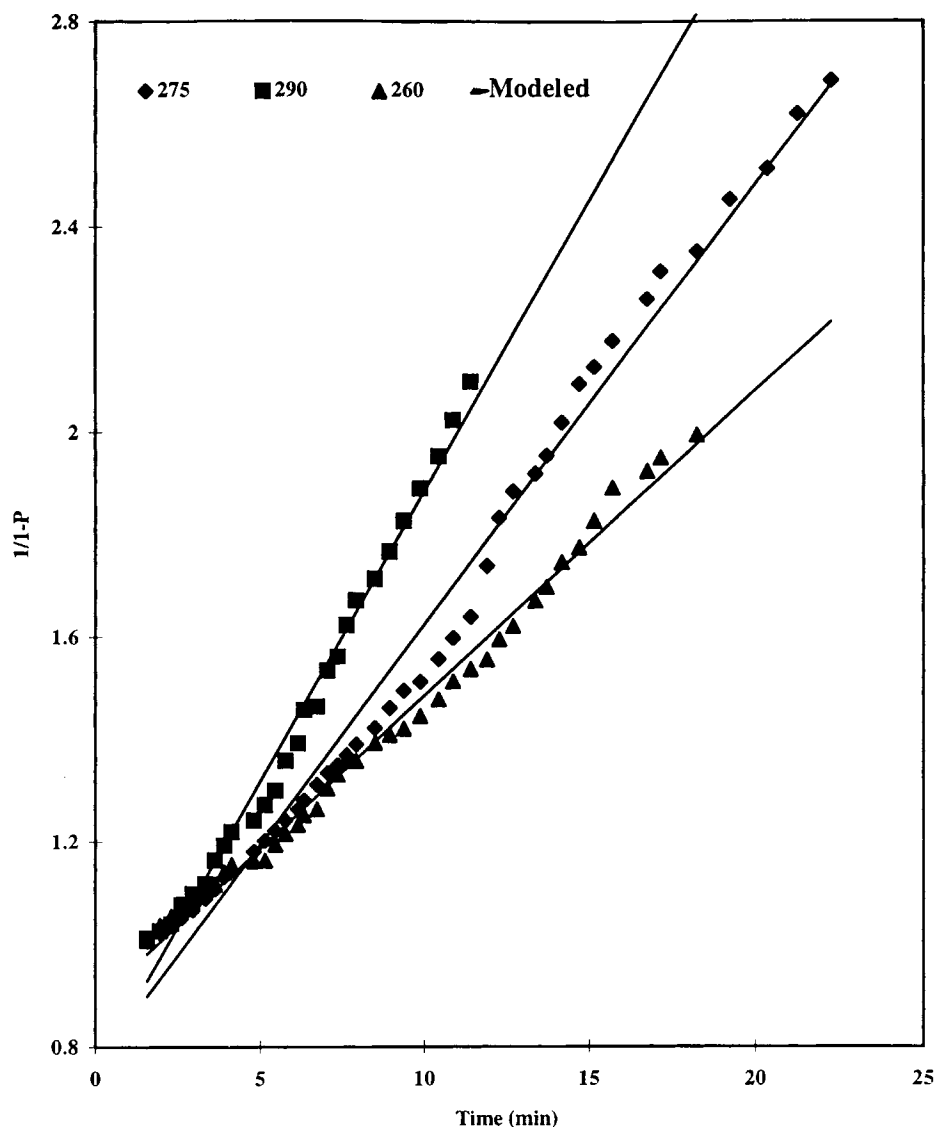


Figure 3 Second-order plot illustrating effect of temperature for catalyzed HQDA/TA system.

this earlier study. Here we explore the kinetics of a three component system, wherein many parallel reactions take place simultaneously. Precipitation was detected in such parallel systems.²²

The work was carried out with the following four objectives: to study the reaction kinetics of a two phase system; to identify plausible routes to simplify the kinetics of a three component system; to determine the kinetic order with respect to the homopolymers of HQDA and TA as well as copolymers PET, HQDA, and TA; and to predict the rates of acetic acid generation in a two phase system in a copolymerization reaction.

A simple reaction sequence is suggested that outlines the major steps involved. Major reactions, which lead to acetic acid production, are taken into account

in the kinetic analysis. Simple second-order kinetics is found to be valid for each of the steps significant to the acetic acid production. A simple kinetic picture is assumed where the rate of formation of dimer is considered as the rate controlling step. A steady-state assumption is also invoked to simplify the kinetic analysis. Last, physicochemical characterization of the homopolymer and the copolymers are considered.

EXPERIMENTAL

Materials

PET was supplied by M/s Century Enka Pvt. Ltd. (Pune, India). It had an inherent viscosity of 0.58 and

Table I Rate Constants from Second-Order Plots of HQDA/TA and PET/HQDA/TA System

System	Composition	Temperature (°C)	Rate Constants (L mol ⁻¹ s ⁻¹)		EOA (kcal mol ⁻¹)	
			Uncatalyzed	Catalyzed	Uncatalyzed	Catalyzed
HQDA/TA	50/50	260	0.0099 ± 0.004	0.0072 ± 0.003	16.2 ± 3	17.1 ± 4
		275	0.0092 ± 0.006	0.009 ± 0.005		
		290	0.034 ± 0.001	0.014 ± 0.006		
PET/HQDA/TA	30/35/35	260	0.0122 ± 0.001	0.0189 ± 0.003	15.6 ± 4	20 ± 2
		275	0.026 ± 0.02	0.0095 ± 0.001		
		290	0.04 ± 0.02	0.023 ± 0.005		
PET/HQDA/TA	40/30/30	—	—	0.035 ± 0.006	16.8 ± 2	15.8 ± 3
		260	0.0180 ± 0.002	0.0193 ± 0.003		
		275	0.0243 ± 0.001	0.024 ± 0.005		
		290	0.054 ± 0.002	—		
PET/HQDA/TA	50/25/25	305	0.068 ± 0.001	0.073 ± 0.007	13.8 ± 4	14.5 ± 3
		260	0.0194 ± 0.006	0.018 ± 0.003		
		275	0.026 ± 0.008	0.023 ± 0.006		
		290	0.033 ± 0.007	0.030 ± 0.007		
PET/HQDA/TA	60/20/20	305	0.045 ± 0.006	0.041 ± 0.001	12.3 ± 3	11.6 ± 2
		260	0.0010 ± 0.007	0.012 ± 0.001		
		275	0.028 ± 0.003	—		
		290	0.032 ± 0.004	0.029 ± 0.001		
		305	0.041 ± 0.005	0.035 ± 0.002		

the particle size was 1678 μm . Purified TA was used as received. HQDA was prepared by sulfuric acid catalyzed reaction of hydroquinone and acetic anhydride and was recrystallized with methanol. The product yield was 90% and the melting point was 121°C.

Reactor Fabrication

An 80-mL glass lined electrically heated reactor, depicted in Figure 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 at any temperature between ambient and 400°C. A provision for measuring the side product was made as shown in Figure 1.

Preparation of Polymers

The transesterification was conducted with the objective of analyzing the copolyesterification kinetics in the initial stages of the reaction wherein the distillation of the by-product, acetic acid, was completed under atmospheric pressure. Transesterifications were conducted to generate a series of copolyesters of varying compositions. At first, homopolymerization of HQDA and TA was carried out at 50 mol % composition of each monomer. The study of transesterification kinetics of the copolymerization followed as a sequel. Melt polymerization kinetics of

four compositions [PET 30/70 (HQDA + TA), PET 40/60 (HQDA + TA), PET 50/50 (HQDA + TA), PET 60/40 (HQDA + TA)] were studied, wherein 30 : 35 : 35, 40 : 30 : 30, 50 : 25 : 25 and 60 : 20 : 20 mol % PET, HQDA, and TA were used.

PET melted around 256°C and degraded when maintained isothermally for 15 min at 320°C under atmospheric pressure. The isothermal temperatures chosen for the kinetic estimation were 260, 275, 290, and 305°C during the initial stages of the reaction. The three components were assumed to be partially soluble in the temperature range under study; that is, they decompose into a PET-rich and a PET-poor phase. A dry nitrogen blanket was maintained throughout 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 (0.1 mol % HQDA) was used as the catalyst for the melt transesterification reactions. The HQDA lost due to sublimation was monitored and was found to be less than 0.075 mol % of that charged. Thus no corrections were made in the overall mass balance for the HQDA lost. The purity of acetic acid formed was also estimated at different isothermal kinetic temperatures. This was found to be 94% at 275°C and 92% at 295 and 305°C, respectively. Maximum conversion, noted on the basis of acetic acid generated, was around 75%. The light tan and opaque homo-

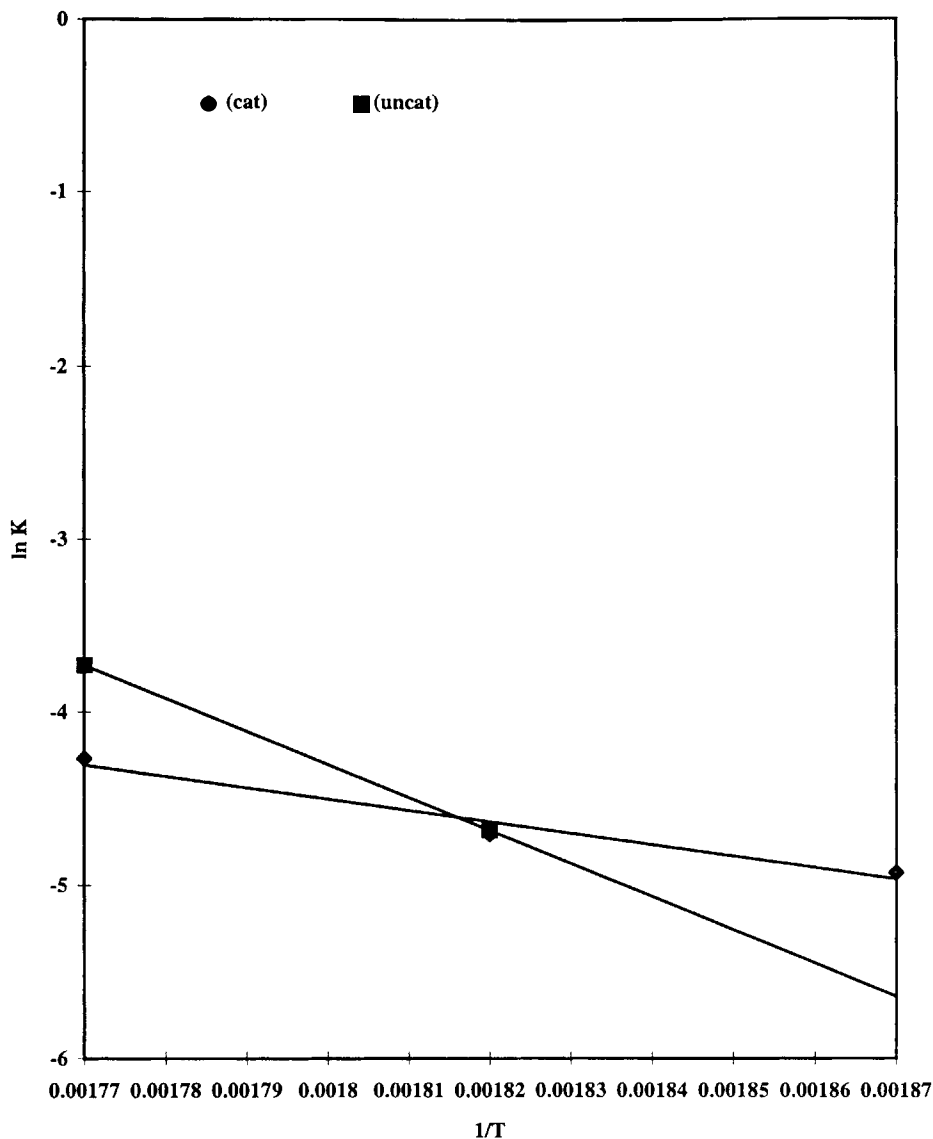


Figure 4 Arrhenius plots for uncatalyzed and catalyzed HQDA/TA reactions.

polymers and copolymers were powdered and extracted with sodium bicarbonate solution and methanol to remove the unreacted TA and HQDA prior to the characterization.

Measurements

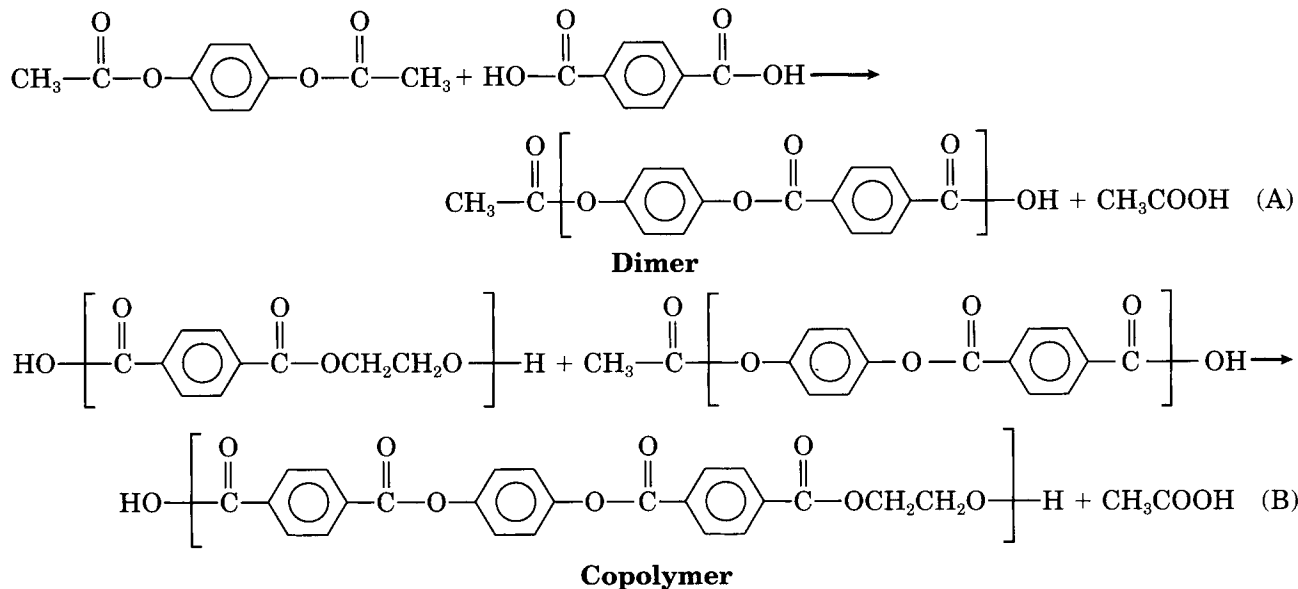
The homopolymers and copolymers were observed under a polarizing microscope equipped with a Kofler hot stage. A small amount of polymer was mounted between a slide and coverslip on the stage and heated at a constant rate. The polymers were observed under crossed polarizers.

Thermal transitions were obtained with a Mettler DSC 30 apparatus interfaced with a thermal analysis

data station under nitrogen atmosphere using a sample size of 10–15 mg. A heating rate of 20°C/min was employed in all cases. Indium was used to calibrate the enthalpy values. Three metals (In-Pb-Zn) were used to calibrate the temperature scale. Samples were analyzed in the temperature range of 50–450°C in the first and second heating cycles.

RESULTS AND DISCUSSION

The principle reaction events leading to the formation of acetic acid in a three component system involving PET segments, HQDA, and TA can be given as



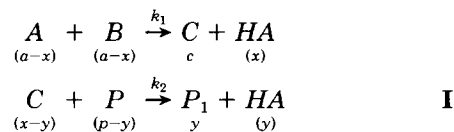
There are many possible ways by which acetic acid can be generated through route (A), like the dimer reacting with HQDA or TA or the dimer reacting with a dimer, trimer, or tetramer, and so forth. When a reactive polymer is incorporated into this reaction (to make it amenable to processing) the kinetic analysis becomes even more difficult. It is seen that an oligomer of HQDA and TA with an odd number of repeat units has two identical functional groups

at its end ($-\text{COOH}$ or $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$),

depending on the monomer that reacted preferentially. The basic criterion for the generation of acetic acid is the presence of an acid and an acetoxy end group in a molecule. To satisfy this requirement oligomer of HQDA and TA should essentially have an even number of repeat units. 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 three assumptions are made to simplify the kinetic picture: the reaction between HQDA and TA leads to the formation of dimers; an oligomer (dimer) of HQDA and TA can only react with a PET molecule; processes exist wherein HQDA and TA react with the oligomer of HQDA and TA, but without generating acetic acid. These reactions are assumed to be too slow and thus of no consequence in the overall mass balance of HQDA and TA. Hence, the reactions leading to the copolymer of interest are given by structures (A) and (B).

Neglecting for a moment phase separation, formation of the copolymer proceeds by a mechanism outlined below.

If C denotes the dimer formed by the reaction of HQDA and TA, then the following steps can be presumed for the polymerization reactions.



where A , B , C , P , P_1 , HA , a , c , x , y , and p denotes hydroquinone diacetate, terephthalic acid, dimer of HQDA and TA, PET, copolymer, acetic acid, initial concentration of HQDA and TA, initial concentration of dimer, number of moles of A or B converted, number of moles of PET segments converted, and initial concentration of PET segments, respectively.

Rate of formation of the dimer can be given as

$$\frac{dx}{dt} = \frac{-dA}{dt} = \frac{-dB}{dt} = k_1(a-x)^2. \quad (1)$$

From conservation of residues of A and B (molecular entities minus reactive end groups), we have

$$x = c + y, \quad (2a)$$

$$c = x - y. \quad (2b)$$

Rate of formation of the copolymer can be given as

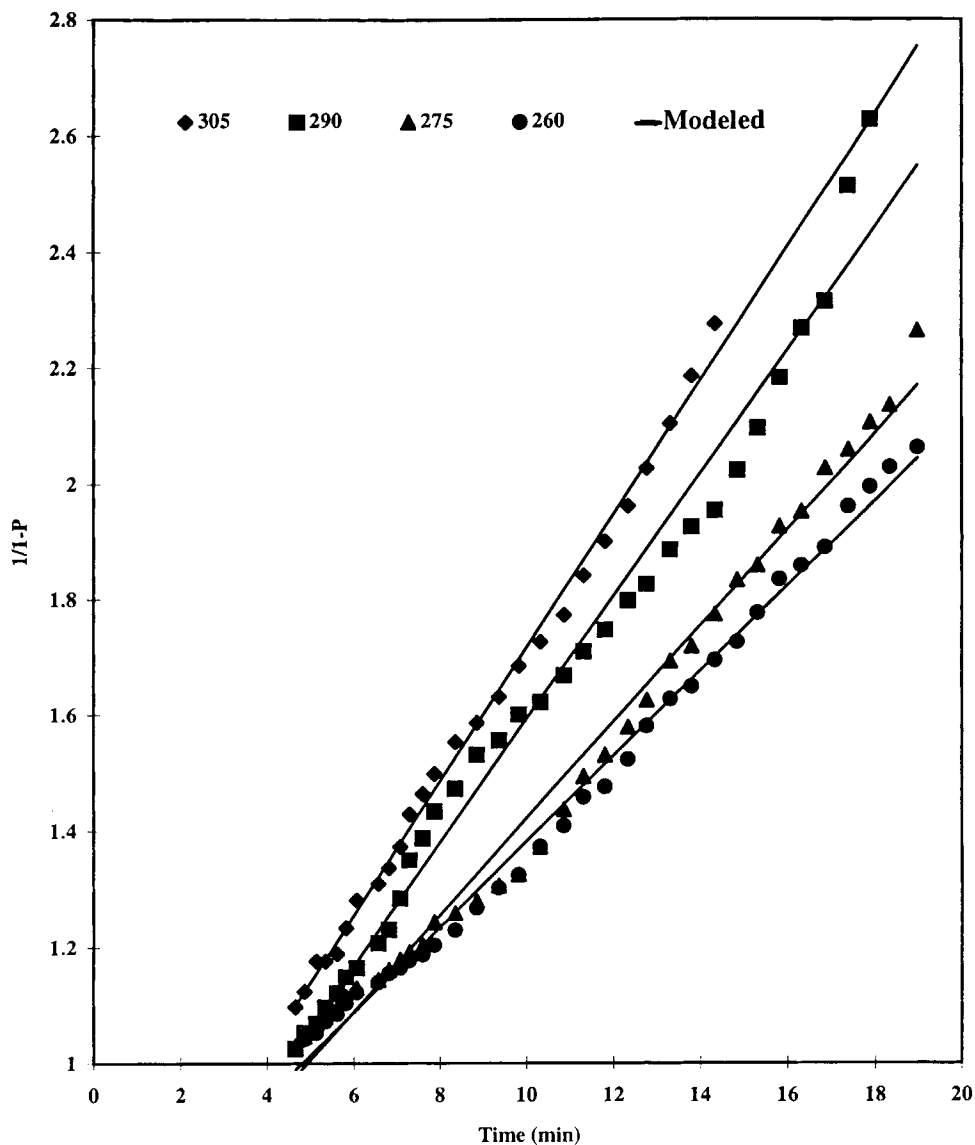


Figure 5 Second-order plot illustrating effect of temperature for uncatalyzed PET 50/50 (HQDA + TA) reactions.

$$\frac{dy}{dt} = \frac{-dP}{dt} = k_2c(p - y), \tag{3}$$

$$\frac{dy}{dt} = k_2(x - y)(p - y). \tag{4}$$

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

$$\frac{dHA}{dt} = \frac{d(x + y)}{dt} = k_1(a - x)^2 + k_2(x - y)(p - y). \tag{5}$$

Assume that the rate of formation of dimer (c) is rate controlling and the subsequent incorporation of dimer (c) into the polymer is very fast such that the steady-state concentration of (c) becomes small; then the rate of production of c can be set equal to zero. Thus,

$$\frac{dc}{dt} = \frac{d(x - y)}{dt} = k_1(a - x)^2 - k_2(x - y)(p - y) = 0, \tag{6}$$

and eq. (5) simplifies to

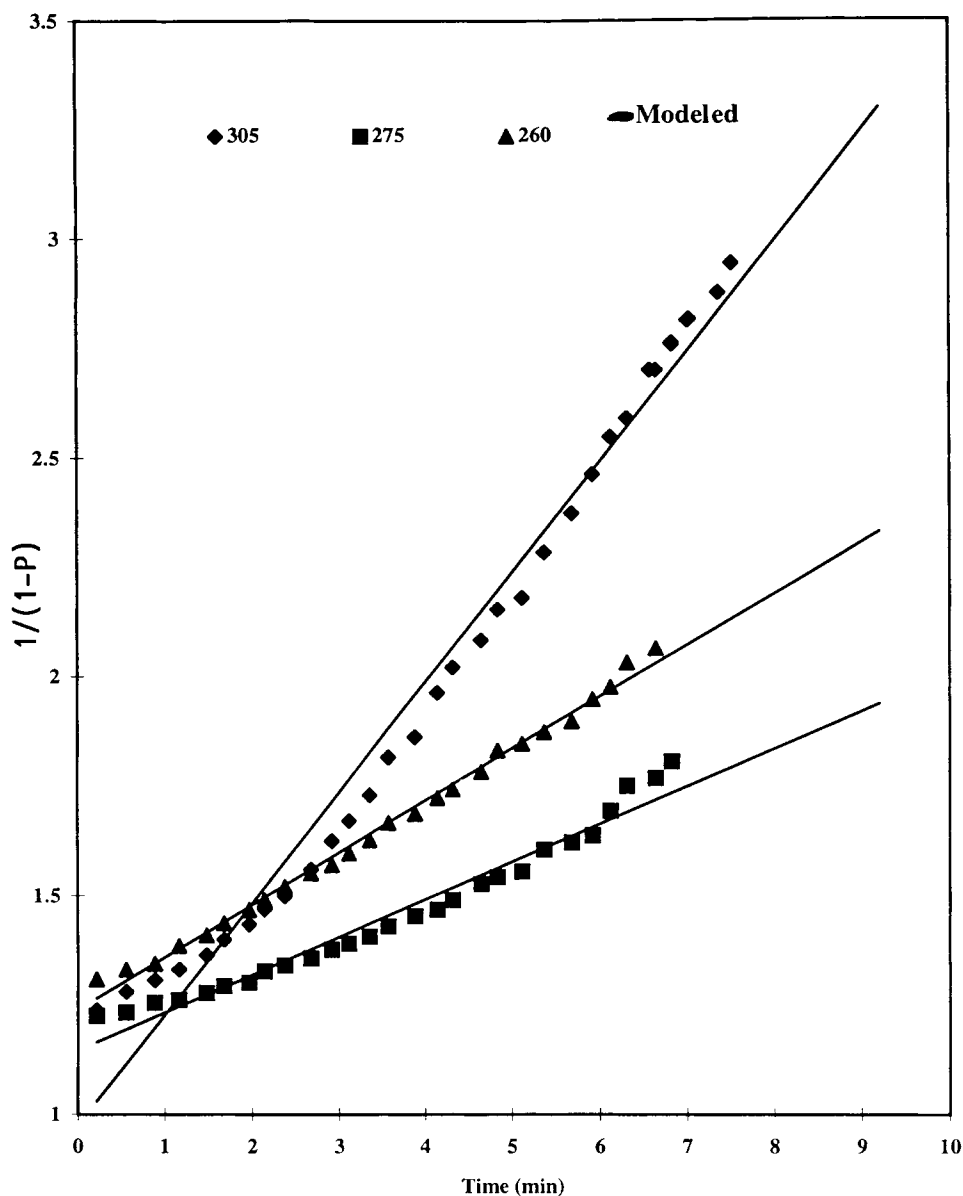


Figure 6 Second-order plot illustrating effect of temperature for PET 40/60 (HQDA + TA) catalyzed reaction.

$$\frac{d(HA)}{dt} = 2k_1(a - x)^2. \quad (7)$$

$$\frac{d(HA)}{dt} = 2k_1 \left[1 + \frac{\gamma(1 - K^2)}{1 + \gamma K^2} \right] (a - x)^2, \quad (8)$$

Now we take into account that the reacting system does not form a homogeneous system but is phase separated into a polymer-rich and polymer-poor phase leaving the respective concentrations c' and c'' . This is done by the introduction of a phase distribution coefficient, $K = c'/c''$. To proceed in an adequate way, it is assumed that reactions progress independently in both phases according to scheme I. It can be easily shown that eq. (7) must be replaced by (see Appendix)

where $\gamma = v'/v''$ is the ratio of two phase volumes and the concentrations, a , x , and HA are similar, as in eq. (7), to the overall concentrations of the respective species in the system. For $K = 1$ (no phase separation), eq. (8) reduces to eq. (7).

In the approximation leading to eq. (8), phase separation just causes a change in rate constant, k_1 has to be replaced by $[1 + \gamma(1 - K^2)/(1 + \gamma K^2)]$, which is considered as a new rate constant, k'_1 . Strictly speaking K (and also γ) should change

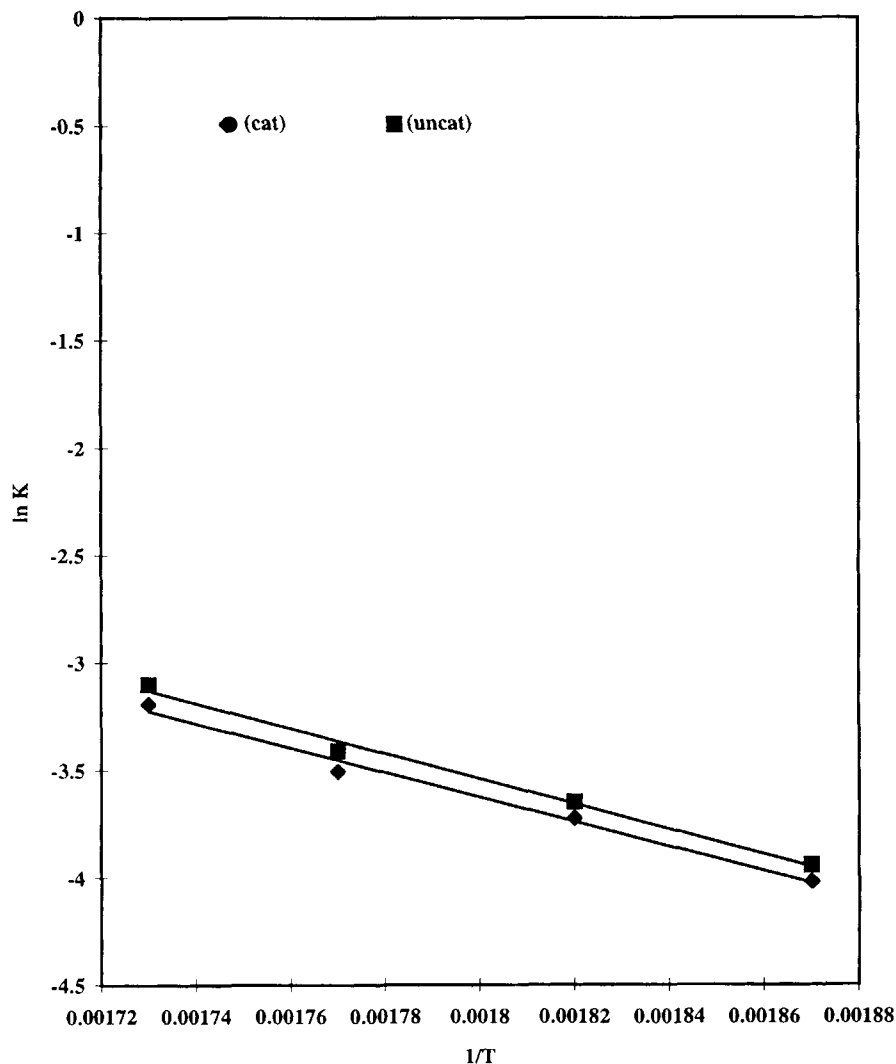


Figure 7 Arrhenius plots for uncatalyzed and catalyzed PET 50/50 (HQDA/TA) reactions.

slightly when the reaction advances. But, this variation of K in the course of time is neglected in eq. (8). Solution of eq. (8) under conditions of eq. (6) gives

$$\frac{2a}{2a - y - x} \equiv \frac{1}{1 - p} = 1 + k_1 at. \quad (9)$$

Figure 2 shows experimental data points for the uncatalyzed HQDA and TA system at three different temperatures and fitting curves according to eq. (9).

The reaction rate is also adequately modeled by second-order kinetics for catalyzed reactions (Fig. 3). Rate constants and activation energies are listed in Table I. It becomes obvious that the catalyst di-

butyl tin oxide does not play a major role. Arrhenius plots are shown in Figure 4. Kinetics in systems comprising 30–60% of PETP were also studied and evaluated according to eq. (9) for catalyzed and uncatalyzed reactions. The quantity $1/(1 - p)$ can be seen as a measure for the average of dimers added to the PET chains. A number of reactions were carried out at temperatures ranging from 260 to 305°C in steps of 15°C. Typical examples are presented in Figures 5 and 6. It becomes obvious that experimental data points can be adequately by eq. (9). Resulting rate constants are presented in Table I. Figures 7 and 8 show Arrhenius plots. Table I reveals that no remarkable changes in rate constants and activation energies occur with increasing PET content in the reaction systems.

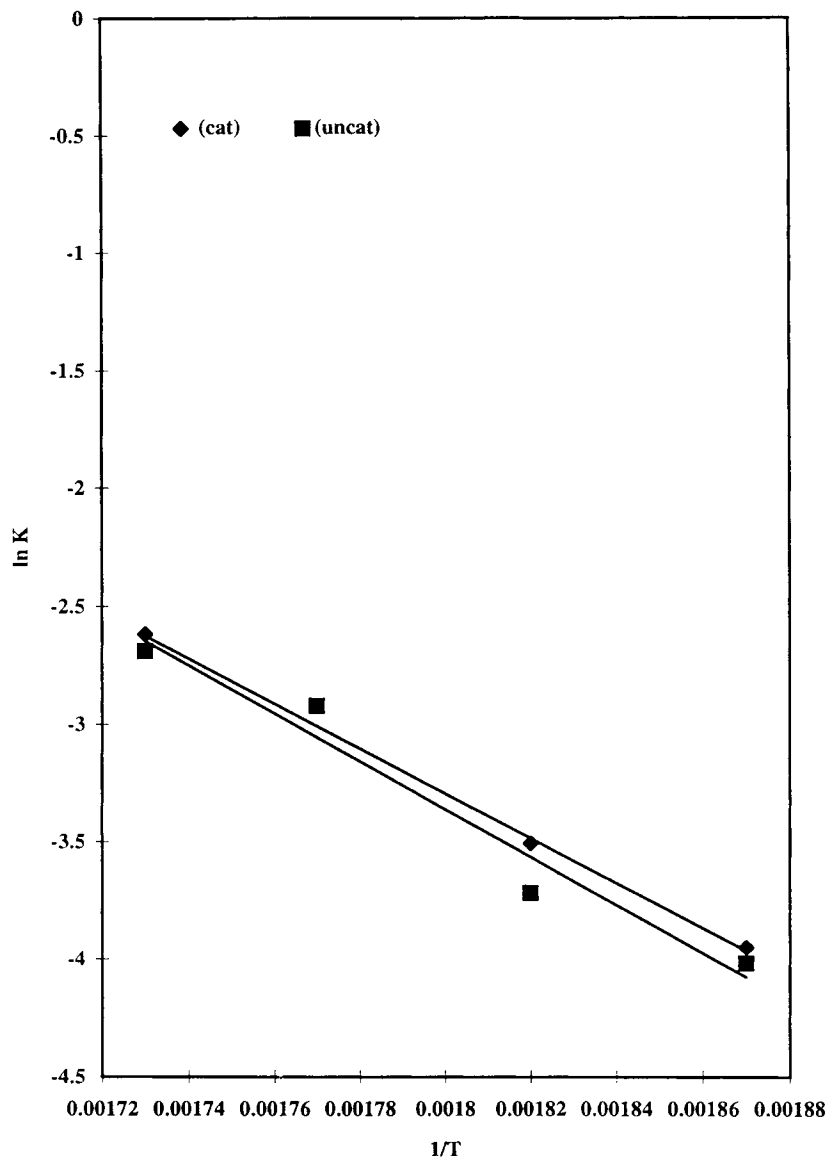


Figure 8 Arrhenius plots for uncatalyzed and catalyzed PET 40/60 (HQDA/TA) reactions.

Figures 5 and 6 shows slight periodic deviations of experimental data points from the straight line according to eq. (9), which becomes pronounced at higher temperatures. This could reflect changes of distribution coefficient K with time owing to periodic phase dissolutions and phase separations in the course of chemical reactions.

The validity of the steady-state assumption in the case of a copolyesterification reaction involving PET holds. Rate constants in Table I indeed suggest that this is true in general. This is especially true for higher temperatures. The numerical value of the rate constants, in particular, equal twice that observed for the HQDA/TA reaction. Qualitatively it

may be stated that the high melt viscosity of PET at low temperature might cause reduction of reaction rates.

CHARACTERIZATION

The homopolymers (HQDA and TA) were heated at 10°C/min from room temperature to 325°C, the upper limit of the microscope. The samples were found to be infusible. The copolyesters (PET/HQDA/TA) were analyzed in a similar manner. Depolarization of light was observed in all copolyesters, PET 30/70 (HQDA + TA) to PET 60/70

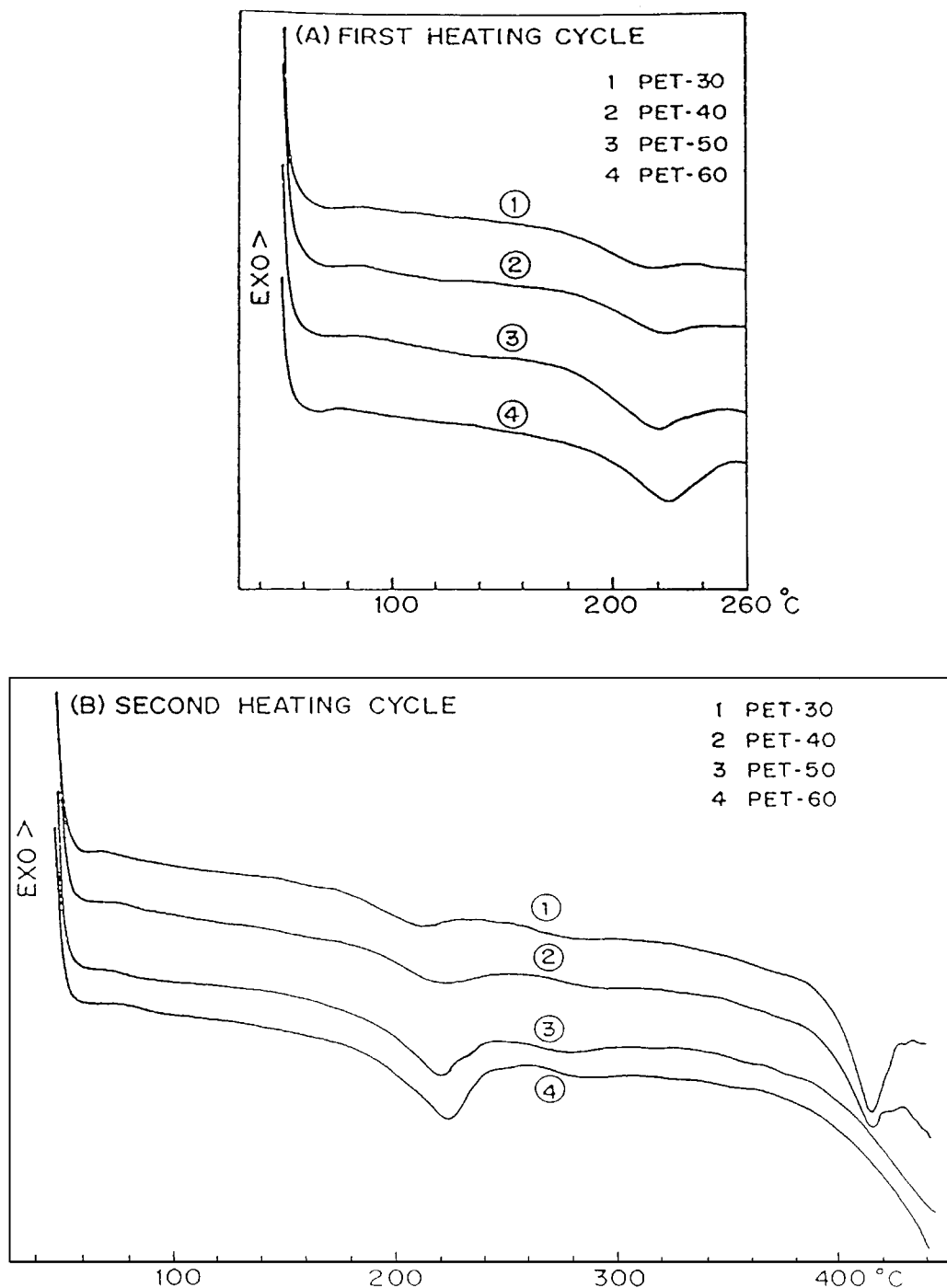


Figure 9 DSC endotherms: (a) first heating cycle; (b) second heating cycle for uncatalyzed PET/(HQDA + TA) systems at 305°C.

(HQDA + TA). The microscopic observations revealed the presence of some nonmelting homopolymers in the PET 30 and 40 copolyester compositions.

DSC thermograms of the first and second heating cycle (heating rate 20°C/min) for copolyesters PET

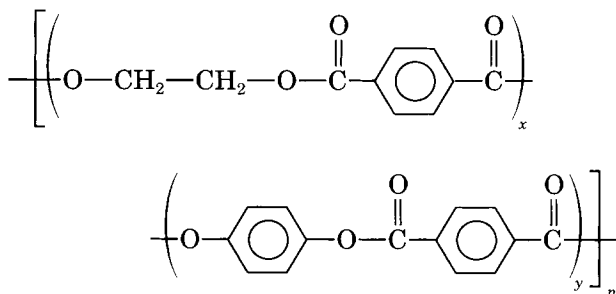
30/70 (HQDA + TA) to PET 60/40 (HQDA + TA) are shown in Figure 9. The first heating cycle consisted of heating the sample to 260°C at the rate of 20°C/min. The sample was then cooled to 50°C at a cooling rate of 20°C/min and reheated in the second heating cycle to 460°C at 20°C/min.

Table II Transition Temperatures and Thermodynamic Data of Catalyzed and Uncatalyzed Reactions

Composition (mol %)	T_{m1} (°C)	ΔH_{m1} (kJ/mol)	T_{m2} (°C)	ΔH_{m2} (kJ/mol)
PET 30/70 (HQDA/TA)	213	1.9	213	1.7
PET 40/60 (HQDA/TA)	219	3.3	221	3.4
PET 50/50 (HQDA/TA)	216	7.2	221	8.2
PET 60/40 (HQDA/TA)	223	9.85	223	10.4

The thermodynamic parameters pertinent to the first and second heating cycles are presented in Table II.

The entities present in the copolyester can be depicted by the global structure given below:



Here x and y represent the mole percent of PET and HQDA + TA units along the chain. At 50 mol % HQDA + TA the structures would resemble a rigid rod, flexible spacer type thermotropic system comprising triad mesogen with carboxylic groups coupled to 1,2-ethane diol. At lower (<50) mole percent of HQDA + TA the mesogen is diluted at the cost of PET moieties.¹

Above 50 mol % HQDA + TA in the copolyester, the averaged mesogen length would increase while the flexible spacer will remain unchanged and comprise dimethylene units of 1,2-ethane diol. At sufficiently high (>60) mole percent of HQDA + TA, the averaged mesogen formed is nonmelting and the thermotropic character disappears. When randomization occurs by the incorporation of HQDA + TA into the PET chain the structure formed will not resemble a globally averaged one. Randomization can also give a wide distribution of aspect ratios along the polymer chain. The structure in ordered systems would resemble the globally averaged one. Here, the averaged aspect ratio of the mesogens formed would be similar to those actually present along the copolyester chain.

These systems would continue to display the thermotropic character of a higher mole percent of HQDA + TA units along the chain as compared to

the randomized structure. DSC thermograms would therefore qualitatively differ depending on the microstructure of the copolyester. The PET/OB and PET/HQDA-TA copolyesters of similar composition differ marginally in their structures. The direction of the ester linkages along the copolyester chain are altered. This change is known to alter the packing and crystal structure details.²⁶

Microscopic observations made in the temperature range over which the first-order transitions were noted in the DSC revealed phase changes. Optical anisotropy was noted for all the samples. The melting temperatures of the PET/HQDA-TA system exhibited higher melting temperatures as compared to the PET/OB system of similar composition.

The melting temperatures reported in Table II in conjunction with optical microscopic observations revealed that the melting transition were liquid crystalline.

In a step growth polymerization the monomer concentration progressively decreases with reaction time. It is thus obvious that the existence of unreacted PET, at the end of reaction, is remote. Thermal analysis of a typical sample PET 60/40 (HQDA + TA) by quench cooling the melt to -25°C and reheating at a rate of $20^{\circ}\text{C}/\text{min}$ did not reveal a glass transition temperature or cold crystallization peak corresponding to PET.

The PET/HQDA-TA copolyesters exhibited higher enthalpy values when compared to PET/OB systems of similar composition. The highest enthalpy value was noted for the PET 60/40 (HQDA + TA) and was on the order of 10.4 kJ/mol. Within the copolyester series the degree of crystallinity increased with rise in PET content. This progressively increasing value of ΔH_{m1} and ΔH_{m2} can be correlated to the melttable fractions of the copolyester. A rise in ΔH_{m2} values was noted on comparing the enthalpy values of the first and second heating cycle. This could plausibly be due to continued polycondensation reactions and alterations in the crystallite size.

CONCLUSIONS

Kinetics of a three component system (PET, HQDA, and TA) in which phase separation may occur was analyzed. To retain the simplicity of the analysis few key assumptions were made to the effect that acetic acid is produced through only two channels: HQDA and TA reacting to form dimer and this dimer subsequently adding on to the PET chain. A generalized scheme in which acetic acid is generated through two channels is considered valid for the PET-rich and PET-poor phase. Kinetically, both these reactions were assumed and shown to be of second order with respect to the reactants. In the second reaction, the concentrations of PET repeat units and the dimer figured as a product. Even though in principle other reactions can also give rise to an acetic acid like dimer reacting with HQDA or TA, the probabilities for these processes are small in comparison to the main reaction postulated as above.

Transesterifications involving ester units buried within the oligomeric chain from HQDA and TA can also react, but without producing acetic acid. These reactions are extremely slow and hence are assumed to be too slow to be of any consequence in the overall mass balance. The reaction network involves a second-order reaction for which analytical expressions are not possible.

If assumption is made that the second-order reaction involving HQDA and TA is much slower than the rate of incorporation of the dimer into PET, steady approximation can be safely applied to the production of dimers, as is the standard practice in the literature. The net rate of production of the dimer is thus set equal to zero. The overall production rate of the acetic acid will be twice that of the rate of production of copolymer. Under steady-state conditions this also will be equal to twice the rate of production of dimer of HQDA/TA. One immediately obvious conclusion is that the rate of acetic acid production should obey a neat second-order plot that also holds twice as a good approximation when phase separation occurs in the reaction system. The parameters were chosen such that the least squares deviation between the moles of acetic acid produced and theoretically predicted is a minimum. Plot of $1/(1-p)$ against time should generate a linear fit. Here, p denotes the fractional conversion where HQDA and TA have the same stoichiometric conversions. This kinetic order should be independent of the starting concentration of PET. The rate constants for the dimerization steps are determined independently. The numerical value of the rate con-

stant in the presence of PET is almost equal to twice that of HQDA and TA reactions. We cannot offer a concrete explanation for the lowering of rate constants (observation of less than the stipulated doubling of rate constants). We may speculate that it may have something to do with viscosity effects prevalent in a molten system.

Microscopic observations revealed that the polycondensate of HQDA and TA is nonmelting. The copolyesters PET 30/70 (HQDA + TA) to PET 60/40 (HQDA + TA) are liquid crystalline.

The first-order transition temperature values obtained from the DSC, in conjunction with microscopic observations, revealed the liquid crystalline nature of these materials. The increasing values of the enthalpy of fusion indicated an increase in the crystalline content of the copolyester, plausibly due to the presence of unreacted PET or from the formation of copolyesters of PET/HQDA/TA and the absence of nonmelting HQDA/TA polymer.

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APPENDIX

The distribution coefficient K represents the ratio of polymer or solvent concentrations c' and c'' in the polymer-rich and polymer-poor phase, respectively.

$$K = \frac{c'}{c''} = \frac{m'}{m''} \cdot \frac{v'}{v''},$$

where m' and m'' are the corresponding masses. The volume ratio will be abbreviated by $\gamma = v'/v''$. From $m'/m'' = \gamma K$ one immediately finds with $m = m' + m''$,

$$m' = \frac{m}{1 + \frac{1}{\gamma K}} \quad \text{and} \quad m'' = \frac{m}{1 + \gamma K}. \quad (\text{A.1})$$

For both phases, we assume the validity of eq. (7),

$$\frac{d(HA)'}{dt} = 2k_1(a' - x')^2, \quad (\text{A.2})$$

and an equivalent expression for the second phase

$$\frac{d(HA)}{dt} = \frac{1}{1 + \frac{1}{\gamma}} \frac{d(HA)'}{dt} + \frac{1}{1 + \gamma} \frac{d(HA)''}{dt}, \quad (\text{A.3})$$

which leads eqs. (A.1) and (A.2) to eq. (9).

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