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Polycondensation reaction kinetics of wholly aromatic polyesters*

A. Lodha, R. S. Ghadage and S. Ponrathnam†
Polymer Science and Engineering Group, Chemical Engineering Division, National Chemical Laboratory, Pune-411 008, India

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The kinetics of catalysed and uncatalysed acidolysis between hydroquinone diacetate–terephthalic acid (HT), hydroquinone diacetate–isophthalic acid (HI) and resorcinol diacetate–terephthalic acid (RT) were investigated at 280, 290, 300, 310 and 320°C. Two kinetic regimes were observed in the rate law plots. Kinetic behaviour in the two regimes differed with the system. Simple second order rate law describes the initial stage kinetics of these reactions most adequately. Activation energy estimates indicate the presence of compensation effect in RT system. Oligomers isolated from HT and HI polyester samples display thermotropic character. © 1997 Elsevier Science Ltd.

(Keywords: wholly aromatic; acidolysis; polyesterification kinetics)

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 temperatures to be melt processed[1,2]. Melt processable thermotropic rigid-rod polyesters can be obtained by copolyesterification through partial replacement with comonomers which have substituents, provide kinks, or change the directional effect of the ester[3] 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.

Direct polyesterifications between diacids and diols at high temperatures do not generate high molecular weight polyesters[4–6]. At least one reactive monomer such as acid chloride, diacetate or diphenate is essential to get high molecular weight polyester[7–10].

Kinetics of polyesterification reactions have been extensively investigated[11–18]. Variable orders observed by these researchers have been shown to be due to differing polarities of the medium[19–21].

Kinetic investigations of melt acidolysis have been rather few. Vulic and Schulpen[22] studied 4-acetoxy benzoic acid (4-ABA), biphenol diacetate (BPDA) and terephthalic acid (TPA) system with and without catalyst. Mathew *et al.*[23,24] 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 and most recently Hall *et al.* have examined in some detail the kinetics of polymerization of 4-acetoxy benzoic acid with 6-acetoxy-2-naphthoic acid[25]. This scant literature is surprising since acidolysis has been known[26–28] since 1958 and the synthesis of thermotropic polyesters has been thoroughly investigated[29,30]. There are many uncertainties about kinetic order of the reaction, activation energy etc. of reaction in the melt. This dearth in open literature can be attributed to the intrinsic mechanistic complexity of reaction 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, diffusion constraints which limit the effective removal of bi-product and influence the reaction rate.

The major aim of the present study is kinetic investigation of the acidolysis reaction between well known 1,4- and 1,3-benzene disubstituted acids and acetates which are the major constituents in thermotropic liquid crystalline polyesters.

The study was carried out with the following objectives: (1) Kinetic analysis of the synthesis of catalysed and uncatalysed poly(hydroquinone-terephthalate) (HT); (2) Kinetic analysis of the synthesis of catalysed and uncatalysed poly(hydroquinone-isophthalate) (HI); (3) Kinetic analysis of the synthesis of catalysed and uncatalysed poly(resorcinol-terephthalate) (RT); (4) Comparison of kinetic behaviour between catalysed and uncatalysed reactions; (5) Effect of type of the diacetate and the diacid monomer on the reaction kinetics; (6) To see whether simple kinetic laws are valid in melt/slurry as in solution polymerization.

EXPERIMENTAL

Materials

Hydroquinone diacetate (HQDA) and resorcinol diacetate (RDA) were prepared by acid/base catalysed

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* NCL Communication No.

† To whom correspondence should be addressed

method of acetylation using acetic anhydride respectively. HQDA was purified by recrystallization from mixed solvent system of methanol and water. Purity was checked by d.s.c. and h.p.l.c. and estimated to be >99.5% pure m.p. 123°C. RDA was purified by distillation under reduced pressure. Terephthalic acid (TPA) and isophthalic acid (IPA) were used as received from Aldrich.

Preparation of polymers

Melt condensation was carried out in a specially designed 60 ml capacity glass reactor[23,24]. Stoichiometric molar equivalents of reactants were charged into the reactor and electrically heated rapidly to the reaction temperature and then maintained isothermally by means of a multi-step programmable temperature controller. Reactants were continuously agitated at 300 rpm by means of a power compensating d.c. motor to facilitate the removal of bi-product, acetic acid. A steady stream of nitrogen gas was continued through the system to avoid thermo-oxidative degradation.

In addition, few reactions were carried out at 300°C under nonstoichiometric conditions to investigate the influence of variation in TPA concentration on rate. The mole ratio of HQDA : TPA was varied as 1/0.33, 1/0.5, 1/0.66 and 1/0.75.

Reaction kinetics was studied isothermally over a temperature range from 270°C to 320°C at intervals of 10°C. The mole of acetic acid collected was recorded relative to reaction time. The initial kinetics of polycondensation, wherein acetic acid distilled out under normal pressure, alone was investigated and hence a change in volume of reaction was considered to be negligible for further analysis. Reaction was allowed to proceed further under reduced pressure and the bi-product was collected to take the polymerization to high conversion. At the end, the product was isolated, crushed and purified free from the starting monomers by extraction with solvents and washing with sodium bicarbonate, water and drying under vacuum.

Measurements

Polyesters were observed under crossed polarizers using an Olympus polarizing microscope (Model BH-2). Thermal transitions were recorded on Mettler DSC-30 interfaced with TA-4000 data processor. Powder X-ray diffraction patterns were recorded on PW-1730 Philips X-ray diffractometer in the range 5Θ–40Θ.

RESULTS AND DISCUSSION

Simple second order kinetic treatment

The rate of polymerization for a second-order reaction between a diacetate and a diacid can be expressed in terms of generation of acetic acid as

$$\frac{dx}{dt} = k_2[\mathrm{COOH}][\mathrm{OAc}] \tag{1}$$

For equimolar amounts of diacid and the diacetate equation (1) changes to

$$\frac{dx}{dt} = k_2[\mathrm{C}]^2 \tag{2}$$

where 'c' is the concentration of unreacted functional groups. If 'c_0' is the initial concentration and 'p' is a fractional conversion then,

$$c = c_0(1 - p)$$

and so,

$$c_0 k t = \frac{1}{1-p} + \text{constant} \tag{3}$$

The concentration cannot be expressed in absolute units since the molar volume of the reactants in the melt were not precisely known. A second order initial rate will be given on this basis, by numerical value of the rate constant itself but will have units moles per second[23,24]. It must be stated that this difficulty in making kinetic estimates has now been successfully handled[25,27,28] but we have not addressed it in the present investigation.

Thermodynamic treatment of rate constant

The thermodynamic functions were calculated using the following equations which are in accordance with the theory of absolute reaction rates[30]

$$k = e^2\left(\frac{kT}{h}\right)\exp[(\Delta S^*)/R]\exp(-E_{\mathrm{exp}}/RT) \tag{4}$$

$$E_{\mathrm{exp}} = \Delta H + 2RT \tag{5}$$

The symbols $\Delta S^{\#}$, $\Delta H^{\#}$ and E_{exp} represent the entropy of activation, enthalpy of activation and the experimental energy of activation when two monomers react to form a dimer. Entropy of activation is usually negative for a second order bimolecular reaction[31] where two monomers add to form a dimer.

Reaction I: Hydroquinone diacetate–terephthalic acid (HT) system

This polyesterification system deals with the preparation of wholly aromatic rigid rod poly(1,4-oxy phenylene oxy-1,4-carboxy phenylene) by acidolysis between hydroquinone diacetate (HQDA) and terephthalic acid (TPA)[32]. HQDA is molten while TPA is present as solid particles (30 μm) at the temperature range over which kinetics were investigated. The transesterification reaction could originate either at the surface of the TPA particles or in the HQDA melt due to an ingress of TPA particles to first generate 4-(4-acetoxy-phenylene-1-oxy carboxy) benzoic acid. Reactions were conducted with nonstoichiometric amounts of TPA to determine whether the reaction originates on the surface of TPA particles. In this case the rate of reaction will be dependent on the number of TPA particles. The rates of the reactions were found to be independent of TPA indicating that the reaction originates in the HQDA melt and that there exists a saturation in the dissolution of TPA into molten HQDA. The product of this reaction could react with either TPA to form a product with acid end groups which melt above the reaction temperature and hence would be nonmelting at reaction temperature or with HQDA to form a product with acetoxy end groups on both the sides and hence would be isotropic at the reaction temperature[33,34]. The reaction is initially a slurry consisting of a terephthalic acid in a molten hydroquinone diacetate and changes gradually to solid state polycondensation due to the formation of intermediates with carboxylic acid end groups with melting points much above the reaction temperature.

A typical second order rate law plot for catalysed reactions between HQDA and TPA at different temperatures is shown in *Figure 1*. Induction period is noted at all temperatures. This induction period decreases with an increase in reaction temperature. An attempt to fit the data into rate expressions corresponding to different orders showed that only second order could be fitted most appropriately. It is apparent that the reaction follows second order kinetics since it is essentially bimolecular. The rate law plots show that the kinetics is adequately modelled for second order behaviour. This is true of both uncatalysed and catalysed reactions.

All the reactions are characterized by two kinetic regimes in the second order plots corresponding to dimerization and oligomerization indicating different kinetic behaviour in the two regions. This change in kinetic behaviour in both catalysed and uncatalysed reactions becomes more apparent at higher temperatures. The change in slope noted in both catalysed and uncatalysed reactions, termed as breaks, sharpen at higher reaction temperatures. The reactions follow the same order in both kinetic regimes separated by the break. The plausible explanations for occurrence of two kinetic regimes are: (i) the reactivity of the carboxylic acid group may depend on the degree of polymerization; (ii) heterogeneous (lamellar) chain growth may occur within the precipitated oligomer by stepwise addition of the monomer; and (iii) in catalysed reactions, the activity level of the catalyst could change with time. The most plausible explanation of a change in reaction order with time could not explain the breaks.

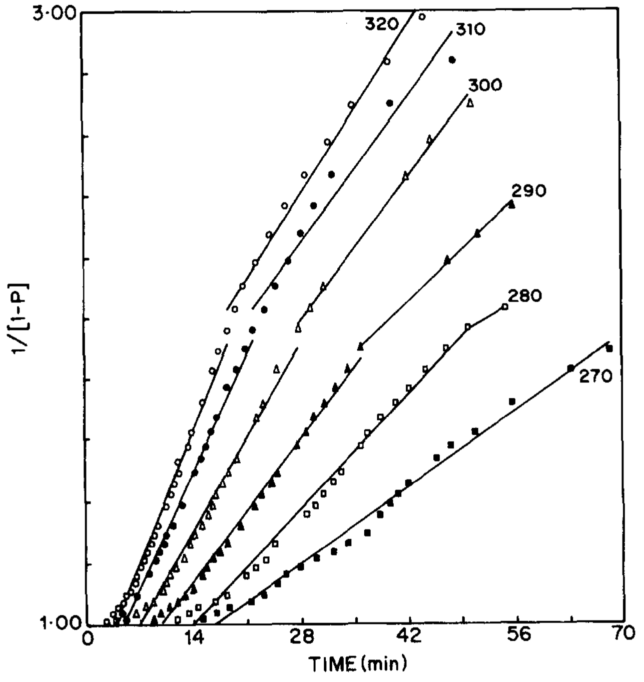

Figure 1 Second order plot illustrating the effect of temperature for HQDA/TPA catalysed reactions

The polyesterification kinetics are altered by the ionization of the dicarboxylic acid. While a direct correlation cannot be found between the ionization constant in a predominantly aqueous environment at an ambient temperature and the behaviour in melt at high temperatures, a striking similarity does seem to exist[35]. The polyesterification of diacids with low pK_1, which would ionize quite extensively, fit into a second order kinetics while the polyesterification of diacids with high pK_1, which would ionize marginally, can be fit only into an order of 2.5. It is thus apparent that the former assumes a pseudo second order due to a large excess in the hydrogen ion concentration. The ionization constant of weakest diacid in the first group of relatively stronger acids is 16 times that of the strongest diacid in the second group of weak acids. The ionization of two acids in the present study, terephthalic acid and isophthalic acid[36], are exactly half way between the two groups. The present kinetic analysis (second order) indicates that the two acids could be grouped together with acids having low pK_1.

In this (HT) system the rate decreases in the second regime. Second order rate constants of the reactions in both regimes termed as dimerization and oligomerization are calculated from the slope of the corresponding kinetic plots and are tabulated in *Table 1*. It is quite plausible that this decrease in rate in the second regime, is due to a diffusion controlled reaction[37] arising from increasing difficulty of reactants reaching the reaction site of heterogeneous system arising from oligomer precipitation, as discussed earlier.

The activation energy is calculated from the slope of the Arrhenius plots (*Figure 2*). This value for the reaction in the first regime compares well with that observed for the self condensation of 4-acetoxy benzoic acid over a similar temperature range. A glance at *Table 4* for activation energies of the HT reactions, of 18.88 kcal mol^{-1} initially and 16.22 kcal mol^{-1} in the

Table 1 Second order rate constants for uncatalysed and catalysed acidolysis between hydroquinone diacetate and terephthalic acid

			Dimerizarion		Oligomerization	
Polymn. code	Temp., °C	Induction period, min	k_1 $[c^{-1} \cdot t^{-1}]$	Corr. coeff.	k_2 $[c^{-1} \cdot t^{-1}]$	Corr. coeff.
Uncatalysed acidolysis						
1T	320	4.3	0.00645	0.99	0.00457	0.99
2T	310	5.3	0.00543	0.99	0.00273	0.99
3T	300	6.7	0.00517	0.99	0.00302	0.98
4T	290	8.4	0.00405	0.99	0.00232	0.99
5T	280	14.7	0.00220	0.99	—	—
6T	270	18.2	0.00153	0.99	—	—
Catalysed acidolysis						
1TC	320	3.0	0.0105	0.99	0.00647	0.99
2TC	310	3.7	0.00922	0.99	0.00567	0.99
3TC	300	5.6	0.00742	0.99	0.00552	0.99
4TC	290	8.5	0.00552	0.99	0.00395	0.99
5TC	280	10.6	0.00440	0.99	0.00235	0.99

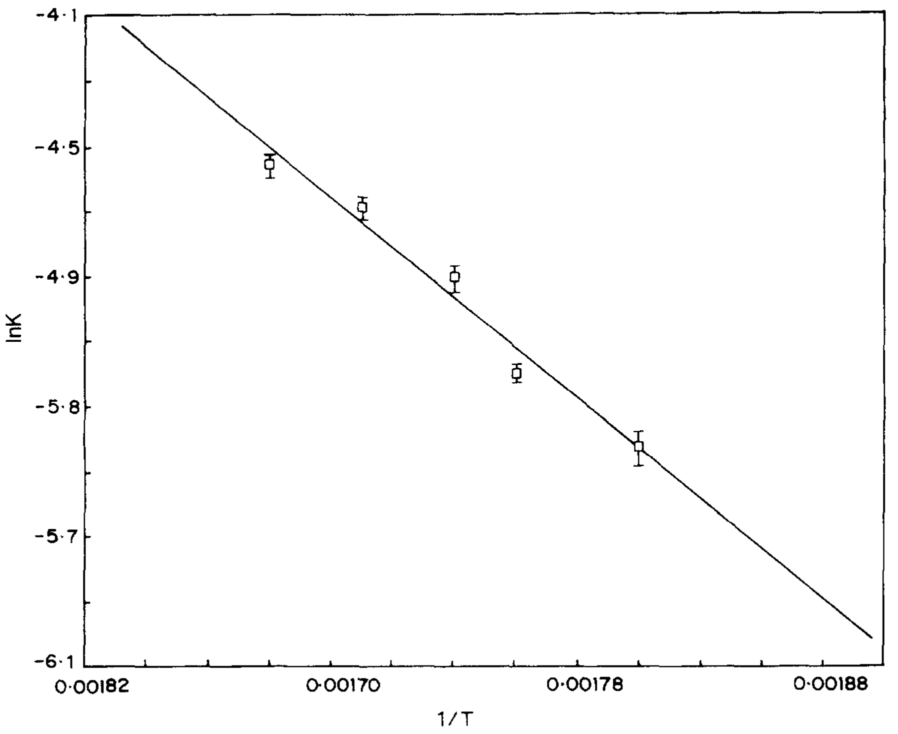

Figure 2 Error bar graph showing Arrhenius plot for HQDA/TPA catalysed reactions in the first regime (dimerization reaction)

second regime, would imply that an increase in the rate of reaction in this regime is to be anticipated. This is not borne by the analysis. The decrease in enthalpy of activation must be accompanied simultaneously by a greater decrease in the entropy of activation. The overall increase in free energy of activation thus, is the probable cause for the decrease in the observed rate.

Reaction II: Hydroquinone diacetate–isophthalic acid (HI) system

In this transesterification, the 1,4-dicarboxylic acid, TPA is replaced by the 1,3-dicarboxylic acid, isophthalic acid (IPA). This diacid provides a kink of 120° which retards the alignment of the polymer chain as a rigid-rod. Partial substitution of linear 1,4-disubstituted monomers with such kinking comomomers over a definitive composition range is known to generate liquid crystallinity in wholly aromatic polyesters by disrupting packing and thereby causing a downturn in the melting temperature[38,39].

Both catalysed and uncatalysed reactions obey second order kinetics in the two regimes occurring as a result of different kinetic behaviour over the entire temperature range of kinetic analysis, as evidenced from *Figure 3*. It is clear from *Table 2* that rate constants in the two regimes are only marginally higher than these of HT polyesterification.

In this system too, the melting point of the diacid (isophthalic acid) exceeds the reaction temperature. In a manner akin to the HT system, the reaction starts as a slurry and progressively increases in heterogeneity and ends up as solid state reaction due to continuous oligomer precipitation. The time over which these transformations occur ought to be inversely related to the reaction temperature. Since oligomers would come out of phase only when melting temperature exceeds the reaction temperature, the degree of polymerization above which the changes should be noticed would increase with the reaction temperature. While such a clear trend was noticed in the self-condensation of wholly aromatic 4-acetoxy benzoic acid, it was not so apparent in the reaction of aromatic diacids with aromatic diacetates probably because HI oligomers became nonmelting at a much lower degree of polymerization than oxybenzoate oligomers.

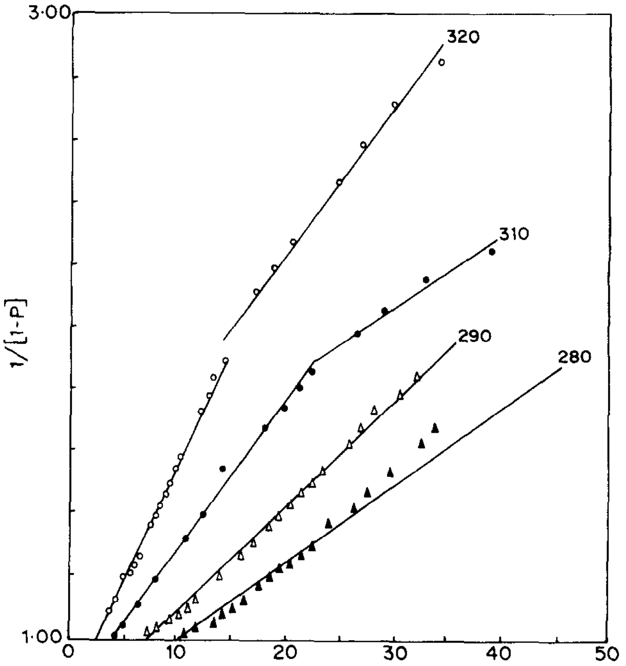

Figure 3 Second-order plot illustrating the effect of temperature for HQDA/IPA catalysed reactions

As in HT system, the rate of the reaction decreases in the second regime for apparently similar reasons. However, in uncatalysed reaction the diversion into two kinetic regimes is observed only at higher reaction

Table 2 Second order rate constants for uncatalysed and catalysed acidolysis between hydroquinone diacetate and isophthalic acid

			Dimerizarion		Oligomerization	
Polymn. code	Temp., °C	Induction period, min.	k_1 $[c^{-1} \cdot t^{-1}]$	Corr. coeff.	k_2 $[c^{-1} \cdot t^{-1}]$	Corr. coeff.
Uncatalysed acidolysis						
1I	320	3.1	0.00778	0.98	0.00537	0.99
2I	310	4.6	0.00363	0.94	—	—
3I	290	8.5	0.00452	0.99	0.00302	0.99
4I	290	9.0	0.00412	0.99	—	—
5I	280	11.9	0.00298	0.99	—	—
6I	270	15.2	0.00180	0.98	—	—
Catalysed acidolysis						
1IC	320	3.0	0.0121	0.99	0.00768	0.98
2IC	310	3.9	0.00797	0.99	0.00400	0.96
3IC	300	5.5	0.00423	0.97	—	—
4IC	290	7.8	0.00550	0.99	0.00168	0.99
5IC	280	11.1	0.00408	0.95	—	—

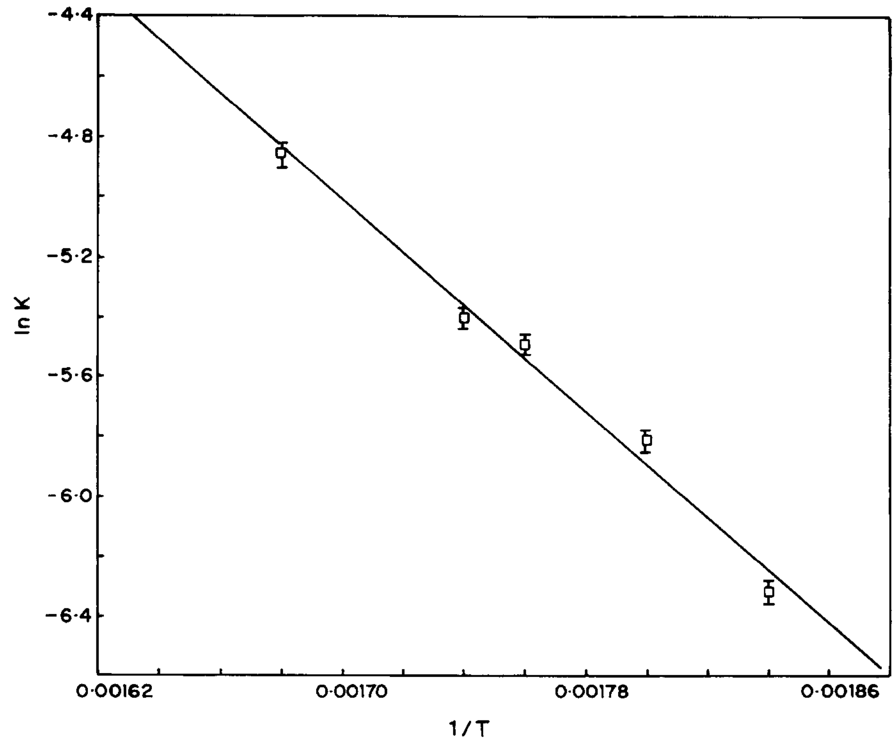

Figure 4 Error bar graph showing Arrhenius plot for HQDA/IPA uncatalysed reactions in the first regime (dimerization reaction)

temperatures of 300 and 320°C. Hence activation energy could be estimated for the reaction in the first regime only. This was estimated from Arrhenius plot (*Figure 4*) to be 17.69 kcal mol^{-1}.

Reaction III: Resorcinol diacetate–terephthalic acid (RT) system

Another kinking comonomer which could be employed to decrease the aspect ratio of a rigid-rod polyester is resorcinol diacetate (RDA), also known as 1,3-diacetoxy benzene. Thus, hydroquinone diacetate could be partially/totally replaced from the HT system. The kink introduced here is 120° as well. However, the direction of the ester groups relative to the kink along the polyester chain is exactly opposite to that in HI system. This would cause a significant difference in the extent of downturn in the transition temperature from that caused by replacement of terephthalic acid in HT polyester partially/totally with isophthalic acid[40–43].

The experimental data of both catalysed and uncatalysed bimolecular reactions are most aptly described by second order kinetic law. A typical second order plot for catalysed reaction, presented in *Figure 5*, shows that the induction period and two kinetic regimes in second order kinetic plots are a feature of this transesterification reaction as well. While the same kinetic order is retained in both regimes, the rate of reaction increases in the second regime despite an increase in the activation energy as seen from *Table 4*. Activation energies of the reactions, prior and after the break are calculated from

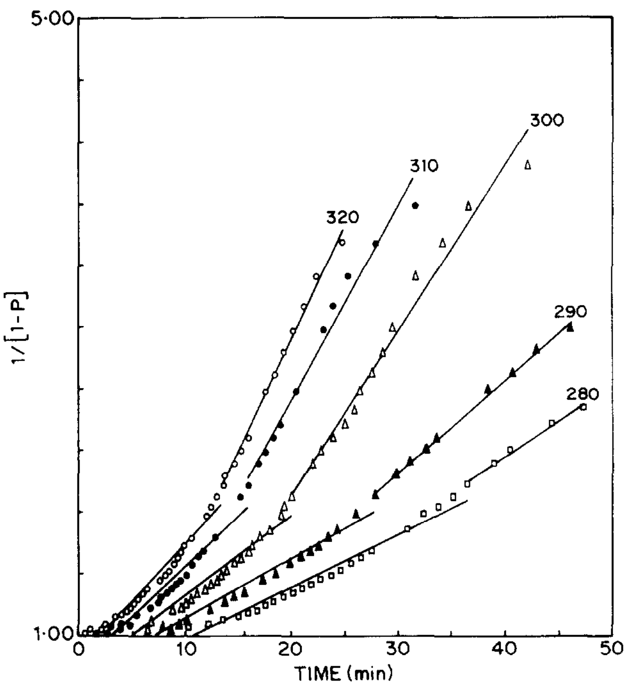

Figure 5 Second order plot illustrating the effect of temperature for RDA/TPA catalysed reactions

the slope of Arrhenius plots (*Figure 6*). A similar trend was observed for the self-polycondensation of 4-acetoxy benzoic acid[23,24]. This points to the presence of an apparent 'compensation effect'[44] wherein the entropy of activation increases at a faster rate than the enthalpy of activation thereby driving the reaction in the forward direction. In the self-condensation of 4-acetoxy benzoic acid the compensation effect, observed on oligomer precipitation, probably arose from the surface effects which increase the local concentration of the carboxylic acid units[23,24].

The transesterification reaction rates observed for the RT system (*Table 3*) are higher than those observed in the HT and HI systems under identical experimental conditions. The polyesterification between resorcinol diacetate and terephthalic acid is also intrinsically different from the HT and HI reactions in that the RDA is a liquid at room temperature. It is a very mobile liquid in the temperature range of the kinetic study. The enhanced rate in the first stage points to an increase in the concentration of the carboxyl groups due to greater solubilization of terephthalic acid in the resorcinol diacetate relative to HQDA. The reacting molecules have higher mobility even at the start of reaction. Unlike the HT and HI series, the product at the end of the reaction is found to be completely molten, as confirmed by microscopic observation at the reaction temperature.

Table 3 Second order rate constants for uncatalysed and catalysed acidolysis between resorcinol diacetate and terephthalic acid

			Dimerizarion		Oligomerization	
Polymn. code	Temp., °C	Induction period, min	k_1 $[c^{-1} \cdot t^{-1}]$	Corr. coeff.	k_2 $[c^{-1} \cdot t^{-1}]$	Corr. coeff.
Uncatalysed acidolysis						
RT1	320	0.8	0.00985	0.96	0.0178	0.98
RT2	310	2.2	0.00890	0.95	0.0199	0.99
RT3	300	3.7	0.00635	0.98	0.00893	0.99
RT4	290	8.2	0.00550	0.96	0.0104	0.99
RT5	280	8.0	0.00388	0.97	0.00530	0.99
Catalysed acidolysis						
RTC1	320	1.1	0.0124	0.95	0.0248	0.99
RTC2	310	2.1	0.00107	0.93	0.0200	0.97
RTC3	300	3.6	0.00912	0.95	0.0180	0.97
RTC4	290	5.9	0.00650	0.96	0.0100	0.99
RTC5	280	7.0	0.00568	0.95	0.00803	0.99

Table 4 Kinetic and thermodynamic parameters of acidolysis reactions of HT, HI and RT polyesters

Polymn. code	HT	HTC	HI	HIC	RT	RTC
A.E1 kcal mol^{-1}	18.88 ± 2.36	15.35 ± 1.42	17.69 ± 1.18	17.51 ± 1.78	16.18 ± 1.30	13.93 ± 1.90
ln A1	10.97 ± 0.16	8.25 ± 0.07	10.03 ± 0.07	10.22 ± 0.08	9.03 ± 0.06	7.35 ± 0.09
A.E2 kcal mol^{-1}	16.22 ± 2.51	16.57 ± 3.62		37.65 ± 2.32	21.56 ± 5.25	20.25 ± 3.65
ln A2	6.51 ± 0.18	9.00 ± 0.16		26.73 ± 0.07	14.25 ± 0.24	13.40 ± 0.17
$\Delta S1$ eu	−41.30	−46.76	−43.66	−44.11	−45.63	−48.83
$\Delta S2$ eu	−47.03	−45.22		—	−35.56	−36.45
$\Delta H1$	17.74	14.21	16.55	16.37	15.04	12.79
$\Delta H2$	15.08	15.42		-	20.42	19.11

AE is energy of activation, ΔS is entropy of activation, ΔH is enthalpy of activation, A is frequency factor and the suffix 1 and 2 represent corresponding values for reactions in two kinetic regimes

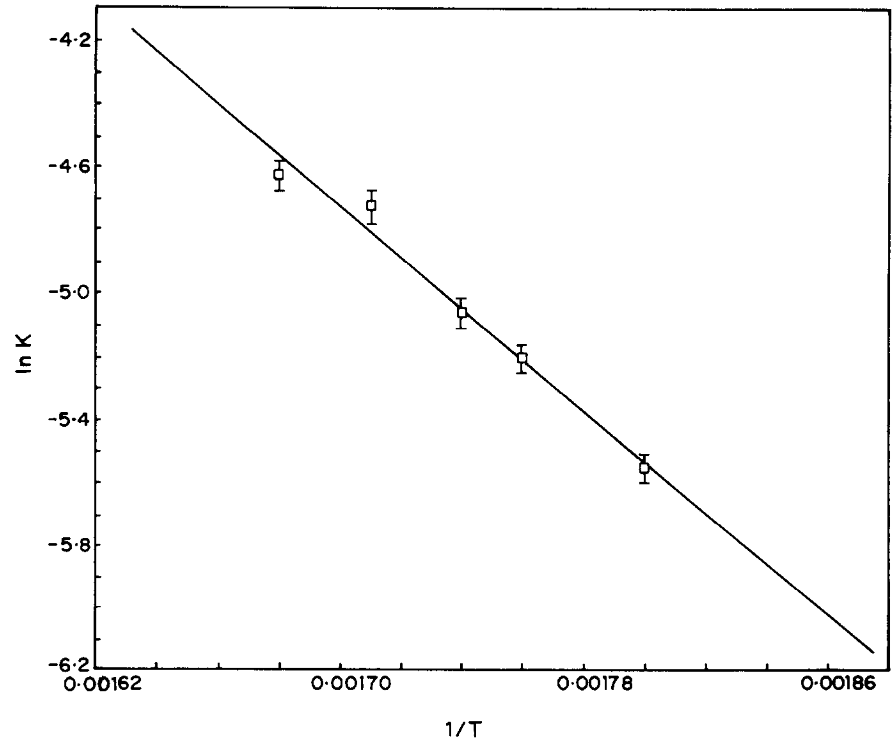

Figure 6 Error bar graph showing Arrhenius plot for RDA/TPA uncatalysed reactions in the first regime (dimerization reaction)

It is highly probable that reaction between resorcinol diacetate and insoluble terephthalic acid generates oligomers with carboxylic acid end groups which are soluble in RDA thereby increasing the concentration of carboxylic acid units in the reaction medium and resulting in enhanced rate.

The rate of polyesterification is higher for the RT system compared to the other two in both kinetic regimes. This also suggests that the electronic effect of *meta* and *para* acetoxy groups affect the rates of reaction. The mechanism[26–28] of esterification suggests the attack of carboxylate anion on electrophilic carbon of acetoxy group. The acetoxy group is *ortho*, *para* orienting and therefore the charged species responsible for the reaction are always engaged in conjugation with the benzene ring in case of HQDA. Such conjugation is not possible in RDA and therefore charged species react faster with the carboxylate anion.

The point at which separation in two kinetic regimes in the kinetic plots are observed in RT polyesterification are related to the increased concentration of carboxylic acid and hence are the reference points when the reaction acquires homogeneity *vis-a-vis* heterogeneity in HT, HI and oxybenzoate systems. The RT polyesterification starts as a slurry and gradually homogenizes, a trend dramatically opposite to that noted for HT and HI systems. Such solubilization of terephthalic acid has been noted in the melt copolyesterification of hydroquinone diacetate, 2-*tert*-butyl hydroquinone diacetate and terephthalic acid at 305°C[45]. The system was initially heterogeneous at all mole ratios of hydroquinone diacetate: 2-*tert*-butyl hydroquinone diacetate, became homogeneous during the polyesterification due to solubilization of terephthalic acid but shifted back to heterogeneity in the later stages due to phase separation of high melting oligomers.

Zinc acetate, sodium acetate and dibutyltin oxide were tested for their catalysis and it was noticed that the differences between the catalysed and uncatalysed reactions were principally quantitative and not qualitative. Thus, breaks in the second order kinetic plots and an induction are present in both these rate plots. However, breaks in the $1/(1-p)$ occur for lower values in uncatalysed reactions. Dibutyltin oxide was chosen as the catalyst[23,24]. Also, the nature of the plots were not altered by increasing the catalyst concentration from 0.1 to 1.0 mol%, but the rates were marginally enhanced. The turnover number (number of reaction events in mol/s/site) decreased with an increase in concentration of catalyst molecules. Thus, all the catalyst sites were not uniformly accessible for the second order reaction.

Characterization

Characterization of polyesters using different methods of analysis such as d.s.c., optical microscopy and X-ray diffraction confirmed the fact that wholly aromatic polyesters formed by condensation of 1,4-benzene diacid and diol degrades prior to melting. However, the oligometic product the formation of which leads to separate kinetic regimes in the reaction is thermotropic and shows peculiar characteristics on high temperature X-ray analysis.

CONCLUSION

High temperature acidolysis type transesterifications were studied using hydroquinone diacetate-terephthalic acid (HT), hydroquinone diacetate-isophthalic acid (HI) and resorcinol diacetate-terephthalic acid (RT) as model systems. In the first two the reaction starts as a slurry and progressively tend to solid state reactions. In the RT system, the initially slurry reaction homogenizes with conversion. Two different kinetic regimes were noticeable in the rate of reaction in all systems. In all three systems reactions in both regimes (separated by the break) are describable most exactly by simple second order rate law.

Specific reaction rates are in the range 10^{-2}–10^{-3} conc.$^{-1}$ time^{-1}. Rate of RT system is one order of magnitude higher than the other two. Activation energies for the reactions lie in the range 15–20 kcal mol^{-1}. Compensation effect observed in RT system indicates that these are entropy driven reactions.

Rate constants and other kinetic parameters obtained by studying polyesterification kinetics of HT, HI and RT system will be useful in studying the kinetics of thermotropic HIT (hydroquinone diacetate, isophthalic acid and terephthalic acid) and HRT (hydroquinone diacetate, resorcinol diacetate and terephthalic acid) system. In the HIT system both acids TPA and IPA are solids. The copolyesterification rate and the sequence of monomers along the chain would not only be due to their inherent reactivities but would also be dictated by the solubility and the rate of uptake of two acids into the melt. In HRT system both diols HQDA and RDA are liquids while TPA is a solid. In this system electronic effects (*para* vs. *meta* substitution) would control the kinetics.

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