Chapter III

KINETICS OF POLYURETHANE FORMATION

Many industrially important polyurethanes are prepared from polyol and diisocyanates[1-3] The basic chemistry of PUR formation involves the reaction of isocyanates containing highly unsaturated -N=C=O group, which can react with almost any compound possessing an active hydrogen atom like alcohols, amines, water etc to form polymers containing various type of linkages The properties of the final product depends on the factors like, type and nature of polyol and isocyanates, reaction conditions like temperature, pressure and catalyst concentration Therefore it is of prime importance to follow the kinetics of polyurethane formation, as it helps in deciding various parameters which affect the rate of reaction and hence the properties of the product resulted Generally the kinetics of such reactions are studied by using various analytical techniques like IR and UV spectra, Gel permeation chromatography(GPC), DSC, High performance liquid chromatography(HPLC) etc and also very often by conventional volumetric titration method using di-n-butylamine[2]

Scientists have started research on this area in the early 1960's Frisch[4] and coworkers reported the kinetics of DBTDL catalyzed reaction of a polyester polyol with TDI by using infrared spectroscopy and titration technique The detailed mechanism of the catalysis in the urethane formation has been reported by Smith[5] He has proposed various mechanisms for the reaction of alcohols with isocyanates and has used IR spectra as a tool to study the complex formation of isocyanates with various catalysts during the synthesis

Techniques like HPLC, FTIR, GPC and ^{1}HNMR have been used by many authors to follow the kinetics of PUR formation[6-12] In all the above cases, various isocyanates like TDI, diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HMDI) etc have been reacted with compounds containing active H atom like polyethylene glycol (PEG), butane diol (BD) and caprolactone diols either in the presence or absence of catalyst The effect of catalyst, its concentration, NCO/OH ratio and type of starting materials used on the reaction pattern have been discussed in detail

DSC and DTA techniques have also been used by various authors[13-15] to follow the kinetics and mechanism of polycondensation of OH terminated polyether with TDI The isocyanate addition reactions with hydroxyl, carboxyl and amine groups and also the effect of carboxylic acid content and DBTDL catalyst on the reaction of a biuret of HMDI with acrylic polyols have been reported[16,17]. There are also some reports on the kinetics of formation of the reaction of hydroxyl terminated polybutadiene rubber, polyisobutylenes and siloxanes[18-22] with various isocyanates like HMDI, IPDI, TDI and MDI in solvents like toluene and nitrobenzene by volumetric titration method and also by using other methods like conduction type calorimeter[18] and viscosity measurements[23]

The type of catalyst used also play an important role in the preparation of polyurethanes Sojecki et al[14,24] have reported the synergistic effect of various catalyst systems like $SnCl_2$ + trimethylene diamine on the reaction of TDI with various macrodiols

The effect of temperature and pressure on the kinetics of PUR formation have been investigated by many researchers[15,25] Recently Krol Piotor[26,27] have reported various mathematical models for the generalization of kinetics in the reaction of isocyanates with alcohols and hydroxy ethers

Toluene diisocyanate is an interesting molecule due to the different reactivities of ioscyanate groups present in the ortho and para position of benzene ring The reactivity also varies with the type of catalyst and reaction conditions like temperature[28,29]. Various researchers have studied this effect in the reaction of TDI with various glycols and polyols[14,30-32] However little information is available on the reaction kinetics of castor oil based polyols and TDI, though they are widely used in the preparation of blends and IPNs[33,34]

Kinetics of polymerization

The materials used were already discussed in the previous chapter Both castor oil and polyols based on it (R60 and R92) were vacuum dried for about 6 h to make them moisture free All the reactions were carried out in a three necked round bottom flask having the provision for nitrogen flushing Castor oil / polyols in dry toluene was taken in the flask and was kept in a constant temperature bath with continuous stirring During this time the flask was purged with N_2 gas After attaining thermal equilibrium, calculated quantity of TDI in toluene was introduced into the flask so as to maintain an NCO to OH ratio unity The concentration of the reactants was 0 5N Samples were withdrawn from the flask at regular intervals and quenched immediately in a solution of standard dibutylamine in toluene The contents of the flask were kept at room temperature for about 1 hr to ensure complete reaction of the unreacted isocyanate with amine. The excess amine was back titrated with standard alcoholic HCl using bromophenol blue as the indicator[35] Identical experiments were carried out by varying the concentration of catalyst, DBTDL and at three different temperatures of 30, 40 and 50°C

Results and discussion

The data of experimental results were used in second order rate expression and the plots of x / a(a-x) *vs* time were found to be linear for equal initial reactant concentration

The second order rate plots for the uncatalyzed reactions of CO, R60 and R92 with TDI showed a very distinct break in continuity The representative plots for CO and R92 are shown in Fig 3.1A and 3 1B

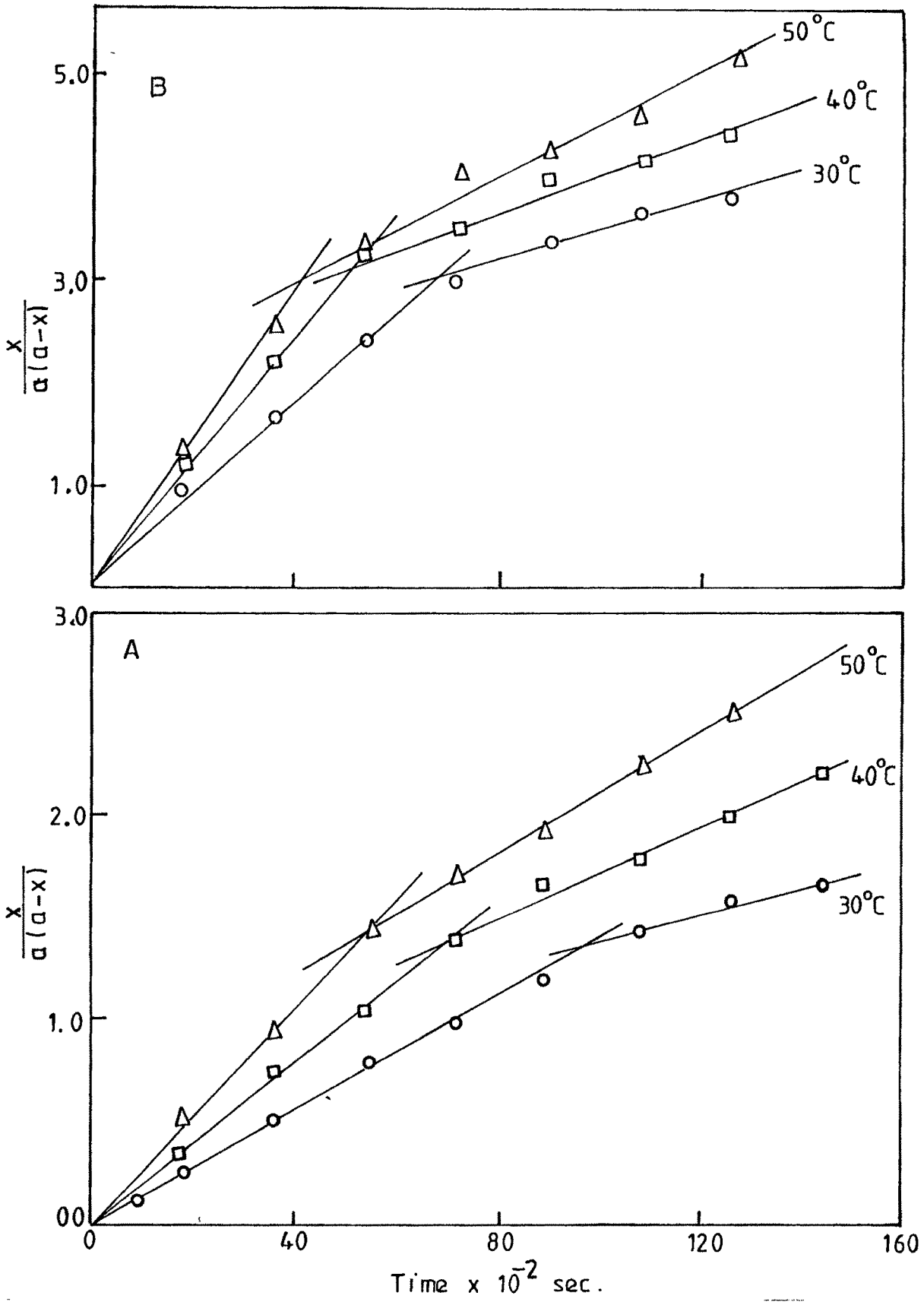

Fig 3.1 Uncatalyzed second order reaction plots of TDI-CO (A) and TDI-R92(B) at various temperatures

Table 3.1 : Rate constants and activation parameters for uncatalyzed reaction of TDI with polyols

Polyol	Temp (°C)	$k_1 x 10^4$ l mol^{-1} sec^{-1}	$k_2 x 10^4$ l mol^{-1} sec^{-1}	k_1/k_2	E_{a1} kJ mol^{-1}	E_{a2} kJ mol^{-1}	$\Delta S^{\#}_1$ JK^{-1} mol^{-1}	$\Delta S^{\#}_2$ JK^{-1} mol^{-1}
	30	1.42	0.67	2.11				
CO	40	2.01	1.09	1.84	25.3	31.7	-243	-228
	50	2.68	1.50	1.78				
	30	4.07	1.29	3.15				
R60	40	4.84	1.76	2.75	19.4	22.9	-255	-252
	50	6.67	2.27	2.93				
	30	4.51	1.43	3.15				
R92	40	6.11	1.91	3.19	19.1	21.4	-254	-256
	50	7.17	2.58	2.77				

respectively The pronounced discontinuity in the plots may be due to the difference in reactivity of both the NCO groups in TDI molecule The NCO group in the para position is more reactive than the one at ortho position as it is free from the steric hindrance due to the methyl group in the 1st position Hence the o-NCO may not react until the concentration of p-NCO group has been sufficiently depleted. However at very high temperature (~125°C), both ortho and para NCO groups almost react simultaneously as observed by other authors[30] Table 3 1 shows the rate constants and activation parameters for uncatalysed reaction of TDI with CO, R60 and R92 The rate constants k_1 and k_2 for the isocyanate groups in the para and ortho positions respectively were calculated from the slopes of the two distinct lines in the rate plots This method is generally accepted for a reaction involving two isocyanate groups present in the same benzene ring[36]

The isocyanate group in the para position shows two to three fold higher reactivity than that in the ortho position. However, some authors[37,38] have assumed that the reactivity of p-NCO group is about 8 to 10 times than that of o-NCO group, where as Brock[39] calculated the reactivity of para isocyanate group and found that it was only about 2 67 times more reactive than the isocyanate group at the ortho position The effect of temperature on the less reactive o-NCO group can be understood by calculating k_1/k_2 at different temperatures As can be observed from Table 3 1, the values decrease with increasing temperature This trend indicates that the temperature enhances the reactivity of isocyanate group in ortho position rather than that in the para position

When polyols differing in their chain length (hydroxyl value) were reacted with TDI, the numerical values of k_1 and k_2 decrease with increase in chain length These findings are in good agreement with Farkans et al[40]. Secondly, the k_1 and k_2 values for R60 and R92 are almost three times more than that of CO This may be because, the formers not only contain more hydroxyl groups but they also contain primary hydroxyl groups in addition to secondary hydroxyl groups while the latter contains only secondary hydroxyl groups Dyer and coworkers[41] also found that, the primary alcohol reacted three times as fast as the secondary alcohol during the reaction of primary and secondary butanols with phenyl isocyanates

The activation energies Ea_1 and Ea_2 (Table 3 1) for uncatalyzed reaction were calculated from the slopes of the Arrhenius plots The plots of ln k Vs I/T are shown in Fig 3 2. The values of activation energy for the reaction of isocyanate groups in the ortho position (Ea_2) were higher than the value of activation energy for the reaction of isocyanate group in the para position (Ea_1) of TDI molecule This may be attributed to the inductive and steric effects provided by the neighboring methyl substituent in

Table 3.2 : Rate constants and activation parameters for DBTDL catalyzed reaction of TDI with polyols

Polyol	Temp (°C)	Concentration of catalyst, DBTDL								
		0.85×10^{-3}M			1.70×10^{-3}M			3.40×10^{-3}M		
		$k \times 10^4$ $l\ mol^{-1}sec^{-1}$	E_a kJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$k \times 10^4$ $l\ mol^{-1}sec^{-1}$	E_a kJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$k \times 10^4$ $l\ mol^{-1}sec^{-1}$	E_a kJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}
	30	4.02			13.24			15.11		
CO	40	5.87	30.1	-219	19.89	25.3	-225	19.64	21.4	-236
	50	8.76			24.72			25.92		
	30	16.61			28.01			30.21		
R60	40	20.02	17.5	-249	37.34	17.4	-244	36.94	16.6	-247
	50	24.21			45.16			46.02		
	30	16.24			27.94			29.01		
R92	40	21.22	17.3	-249	37.21	17.9	-242	37.14	17.4	-244
	50	26.34			44.92			45.92		

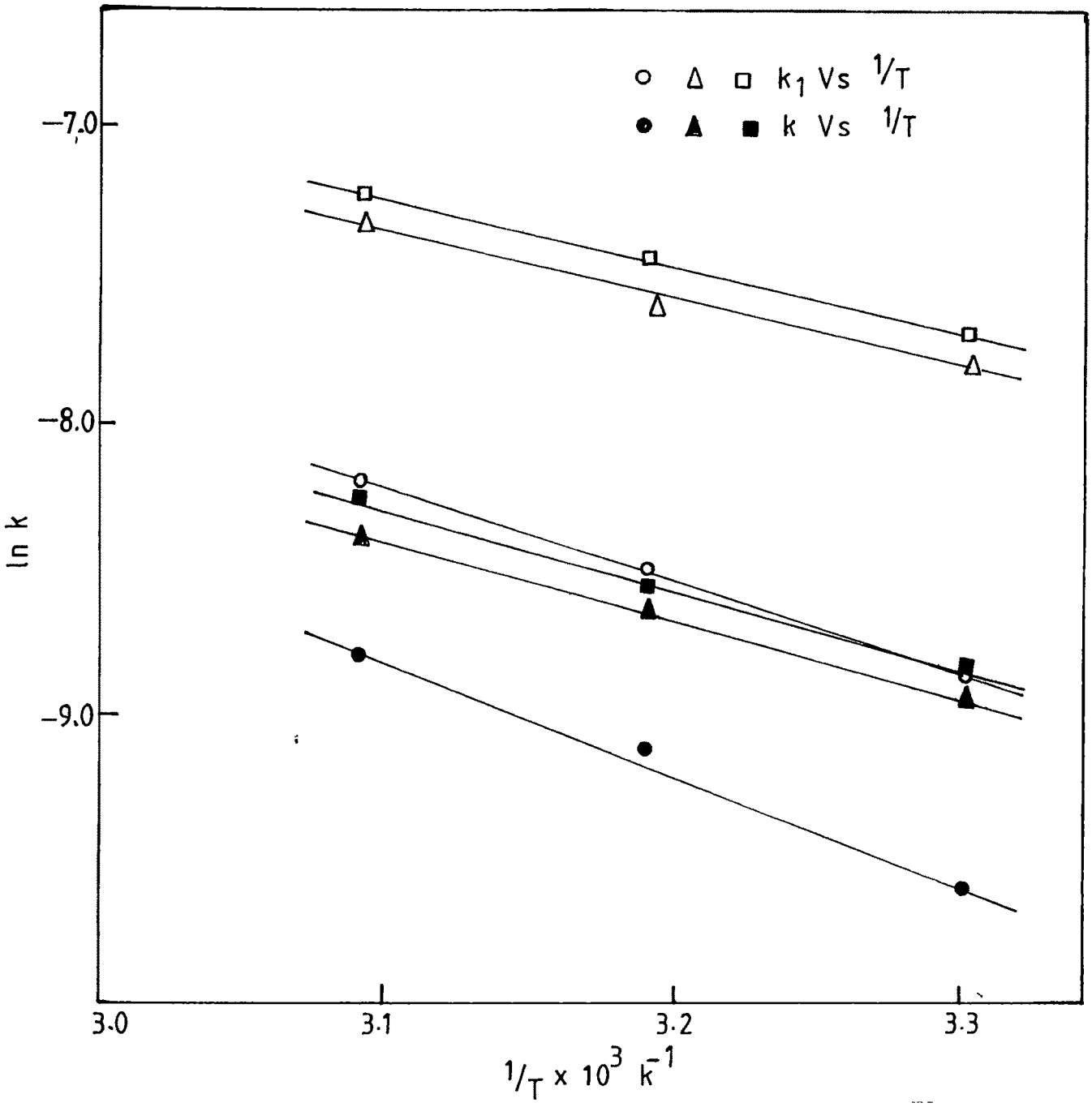

Fig 3.2 Arrhenius plots for uncatalyzed TDI-CO (O, ●), TDI-R60 (Δ, ▲) and TDI-R92 (□, ■) reactions

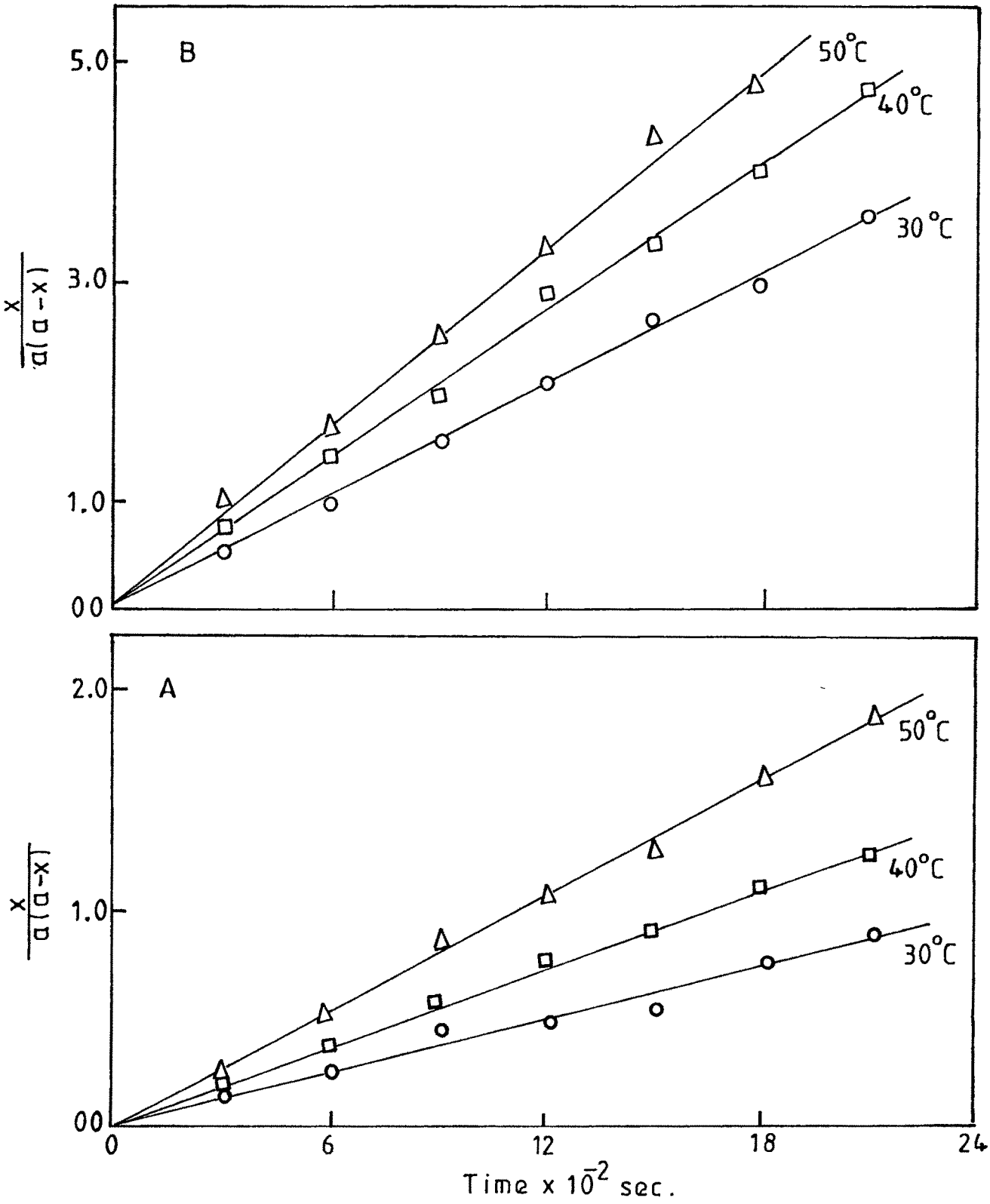

Fig 3.3 DBTDL catalyzed (0 85x10^{-3}M) second order reaction plots of TDI-CO (A) and TDI R92 (B)

the 1st position of the benzene ring The values of Ea_1 and Ea_2 for uncatalyzed reaction of TDI with the polyols are in the order R92 > R60 > CO, which may be due to the difference in reactivities of the polyols with isocyanate

The entropy of activation ΔS^* was calculated for both CO and the polyols using the equation

$$\Delta S^* = \left[\log \frac{k^1}{T} - \log \frac{k}{h} + \frac{\Delta H^*}{2\,303\ RT} \right] 2\,303\ R$$

where

$\Delta H^* = Ea - RT$, k^1 = Rate constant and k = Boltzmann constant

The apparent entropies of activation showed high negative values in all the cases which may be due to the formation of a rigid complex between the catalyst and isocyanate in the transition state in the catalyzed system and more ordered transition state of the reactants in the uncatalyzed system[31].

The concentration of catalyst play an important role in the formation of polyurethane network and also in the formation of interpenetrating polymer networks (IPNs), as it decides the gel time of the system at a particular temperature The rate constants and activation parameters for the reaction of TDI with polyols using different catalyst concentration are shown in Table 3 2 The representative rate plots for CO and R92 using a catalyst concentration of 0 85 x 10^{-3}M are shown in Fig 3 3A and 3.3B at three different temperatures The plots do not show any break in continuity unlike in the case of uncatalyzed system. In view of the enhanced rate of reaction, the discontinuity in the plots due to different reactivities of the two isocyanate groups does not manifest here. With increase in catalyst concentration, rate constant increases and it attains leveling value at a catalyst concentration of 3.4×10^{-3}M. Returning to Table 3.2, it was also found that decrease of E_a with increase of catalyst concentration is significant only in the case of CO Beyond the catalyst concentration of $0\ 85 \times 10^{-3}$M, no significant decrease of E_a is observed in case of R60 and R92

The percentage conversion of NCO is plotted as a function of time for polyol R92 (Fig 3.4) The values are found to increase with increase in temperature and catalyst concentration up to 1.7×10^{-3}M Further increase in catalyst concentration has no profound effect on the conversion The polyols R60 and R92 showed higher conversion compared to parent CO at all temperatures and catalyst concentration

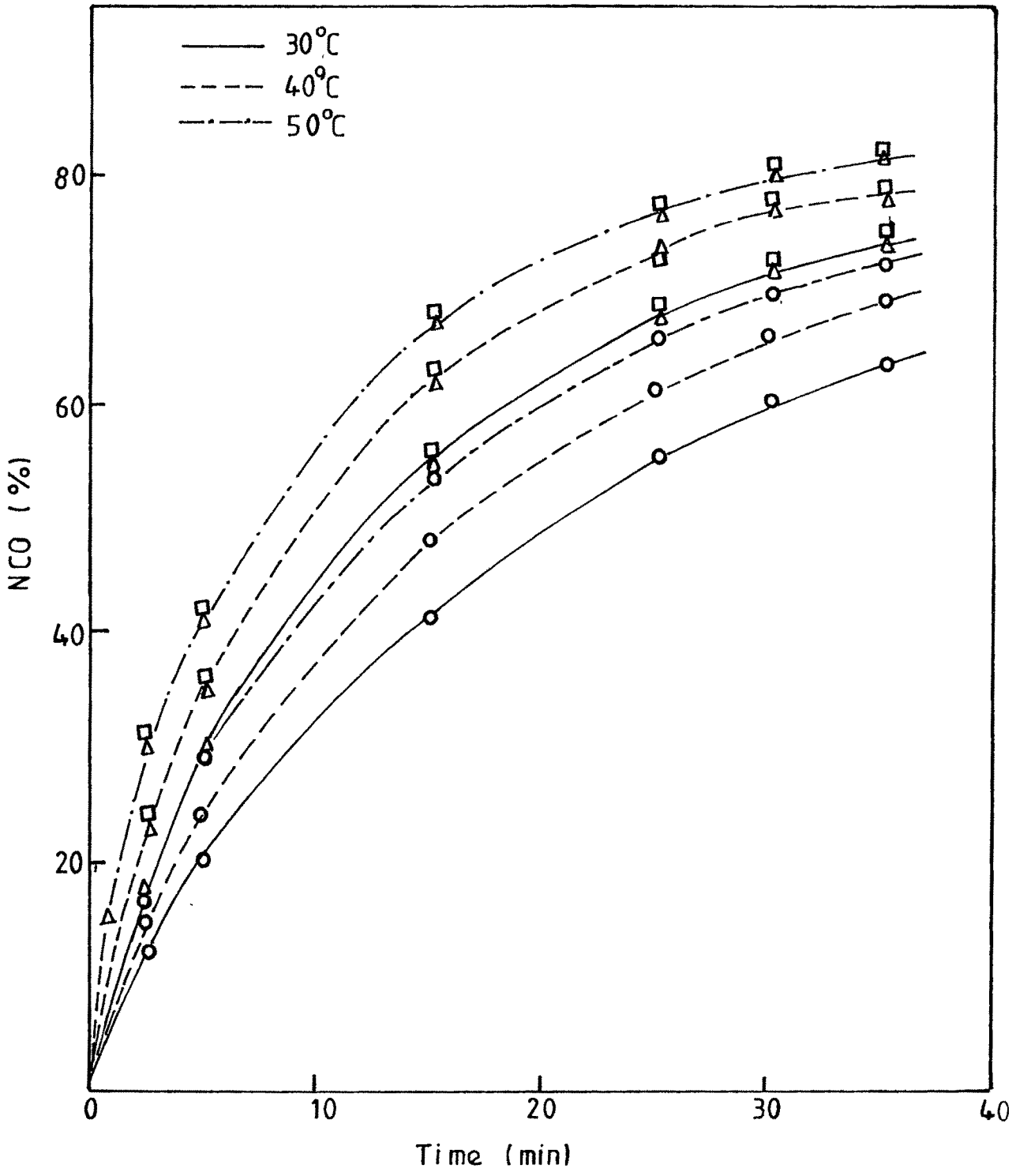

Fig 3.4 Percentage conversion of NCO for the TDI-R92 reaction at different catalyst concentrations of 0 85x10^{-3}M (O), 1 7x10^{-3}M (Δ) and 3 4x10^{-3}M (□) at three different temperatures

studied At a given time, the percentage conversion in the case of R92 was found to be maximum and followed by R60 and CO at a particular temperature and catalyst concentration.

From the above studies it was clear that, the polymerization kinetics of TDI with polyols and CO, in uncatalyzed system may be described by two independent second order equations representing the consumption of each of the distinguishable ortho and para NCO groups The activation energy for the reaction of o-NCO group is slightly higher due to steric hindrance provoked by the neighboring methyl group. For the uncatalyzed system, o-NCO reacts almost three times slower than p-NCO in the temperature range of 30-50°C The rate of polyol -TDI reaction increases with increase in catalyst concentration up to 1.7×10^{-3} M Further increase in catalyst concentration has no profound effect on the conversion The primary hydroxyl groups as well as the amount of hydroxyl groups are responsible for higher reactivities of R60 and R92 compared to CO as evidenced by higher rate constants of former, both in catalyzed and uncatalyzed systems

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