

DSC Study of the Polyurethane Formation from Poly(ethylene Adipate) and Toluene Diisocyanate*

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Synopsis

The reaction of poly(ethylene adipate) (PEA) and toluene diisocyanate (TDI) is studied by means of isothermal DSC. The reaction has the stoichiometry of PEA/TDI = 0.5 and a reaction enthalpy of $\Delta H = -65.0$ kJ/mol hydroxyl group. The kinetic order is unity over a wide range of temperature and composition of the reaction mixture. The temperature dependence of the first-order rate constant yields an apparent activation energy of 61.1 kJ/mol. The kinetic data are accommodated by the following rate law:

$$\text{rate} = k_1 \frac{[\text{PEA}][\text{TDI}]}{2[\text{PEA}] + [\text{TDI}]}$$

A mechanism involving a mobile preequilibrium to accommodate the experimental results is proposed.

INTRODUCTION

The polyaddition of diisocyanates to diols to form polyurethanes is of immense practical importance. Hence, the chemistry of this reaction has been investigated quite thoroughly.¹ On the other hand, thermodynamics and kinetics associated with the alcohol–diisocyanate reaction have been studied to a lesser extent. Most reports deal with low molecular weight reactants and reactions in dilute solutions.^{2–6} However, data obtained from solution studies are difficult to extrapolate to reaction conditions encountered during the practical process, i.e., for the reaction of the neat components without the presence of the solvent.

Only recently, several investigations of the polyurethane reaction have been carried out in the absence of a solvent. Most of this work has been prompted by the need to arrive at a better understanding of the reaction rates and heats encountered in the commercially important reaction injection molding (RIM) process.⁷ Polyurethane formation from (ϵ -caprolactone triol) and 1,6-hexane diisocyanate catalyzed by dibutyl–tin dilaurate has been investigated, using adiabatic calorimetry.^{8,9}

The reaction kinetics and the heats of formation for polyurethanes from polyester polyol, butanediol, and 4,4-diphenylmethane diisocyanate have been monitored by the same adiabatic method. Three different catalysts, as well as the noncatalyzed reaction, have been investigated.¹⁰

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The present study is concerned with the noncatalyzed reaction of poly(ethylene adipate) (PEA) with an 80/20 isomeric mixture of 2,4- and 2,6-toluene diisocyanate.

The reaction is monitored by differential scanning calorimetry (DSC) in an isothermal mode. Using the DSC method in the isothermal mode affords a more comprehensive picture of the kinetics of the polyurethane reaction. This is superior to the numerical fitting of adiabatic data used in earlier reports, since a deeper insight into the reaction mechanism is gained by an isothermal kinetic study.

EXPERIMENTAL

Materials

The following materials were used: poly(ethylene adipate) (PEA), ME = 1000: American Cyanamid Company; 2,4-toluene diisocyanate, 2,4-TDI: HYLENE® T brand, DuPont; 80/20 isomeric mixture of 2,4- and 2,6-TDI: HYLENE™ brand, DuPont.

Experiments were carried out with 100% 2,4-TDI as well as with the 80/20 isomeric mixture of 2,4- and 2,6-TDI. Most of the experimental data shown in the Results and Discussion section pertain to the isomeric mixture of 2,4- and 2,6-TDI, which is referred to hereafter as TDI.

Procedures

A DuPont 990 Thermal Analyzer equipped with a standard DSC cell was used in this study. The temperature and heat flow calibrations were carried out using high purity indium, according to the manufacturer's specifications.

Samples were prepared by mixing appropriate amounts of PEA and TDI at low temperature in a dry nitrogen atmosphere. Encapsulation in the DSC sample pans was done in the same atmosphere.

The DSC apparatus was purged with dry nitrogen (flow rate ~ 25 mL/min). Dynamic DSC thermal curves were generated by scanning at $10^\circ\text{C}/\text{min}$. Isothermal DSC thermal curves were generated by scanning rapidly to the desired temperature, allowing the PEA to melt, and then holding the sample isothermally at that desired temperature until reaction was complete. Integration of the thermal curves was done manually.

RESULTS AND DISCUSSION

Temperature-Programmed and Isothermal DSC

The temperature-programmed DSC traces for PEA and TDI (80/20 isomeric mixture of 2,4- and 2,6-toluene diisocyanate) are shown in Figure 1. PEA exhibits a melt endotherm at its melting point of 43°C , while the TDI mixture shows no appreciable thermal events from 25°C to $\sim 250^\circ\text{C}$. The large exotherm between $\sim 50^\circ\text{C}$ and $\sim 180^\circ\text{C}$ for mixtures of PEA and TDI has to be associated, therefore, with the reaction between hydroxyl and isocyanate groups. The curve in Figure 1 shows that the reaction exotherm is composed of two different pro-

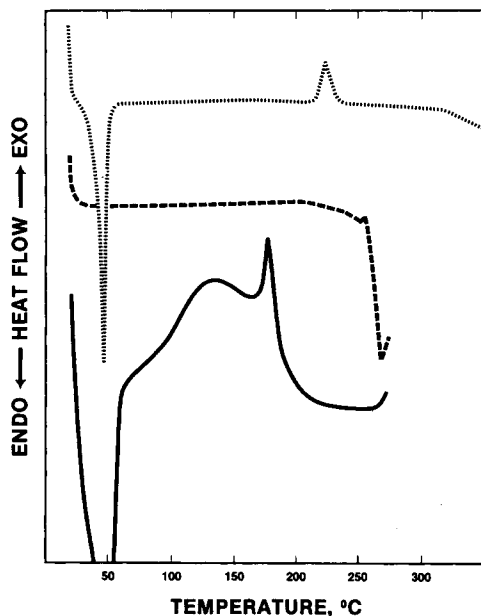


Fig. 1. Temperature programmed DSC: (···) PEA; (---) 2,4-2,6-TDI; (—) PEA, 33 mol % + 2,4-2,6-TDI, 67 mol %; scan rate 10°C/min; atmosphere N₂.

cesses. The lower temperature exotherm is ascribed to urethane formation according to



To promote the low temperature reaction only, the DSC experiments were run in the isothermal mode at temperatures not exceeding 110°C. A typical isothermal DSC trace is shown in Figure 2.

Stoichiometry of the Reaction

The heat of reaction is proportional to the area under the isothermal DSC curve. If normalized to heat per mass unit of reaction mixture, a maximum will be observed if the molar fractions of the reactants are present in stoichiometric ratios. Such a plot of specific heats of reaction as a function of composition is shown in Figure 3. The maximum occurs for compositions containing 33 mol % PEA and 67 mol % TDI, or at a 1:2 molar ratio. This stoichiometry is satisfied by



This means that only the most reactive isocyanate group in TDI has reacted. This selectivity has been observed by others.⁶ The fact that the isocyanate group in the para position of 2,4-TDI is about eight times as reactive as the ortho group renders further support to this explanation.¹¹ Although an 80/20 isomeric mixture of 2,4- and 2,6-TDI was used instead of pure 2,4-TDI, this did not significantly influence our results. The less reactive 2,6-TDI only reacted toward

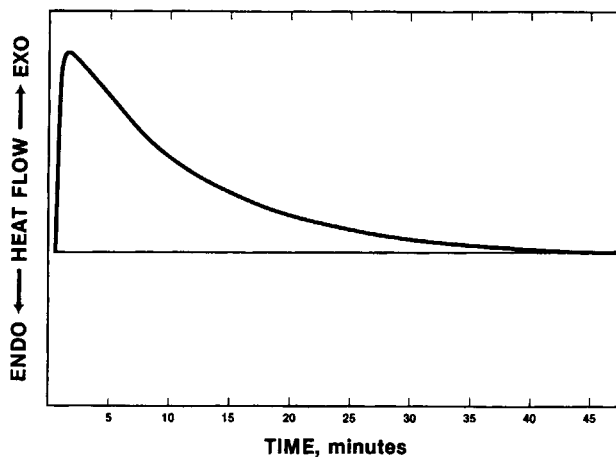


Fig. 2. Isothermal DSC: PEA, 20 mol % + 2,4-2,6-TDI, 80 mol %; $T = 75^{\circ}\text{C}$; atmosphere N_2 .

the end of the rate experiments, after the 2,4-TDI component had been consumed completely. Its effect on the determination of reaction stoichiometry and kinetic measurements remained negligible.

Enthalpies of Reaction

From the specific enthalpies of reaction, one calculates the enthalpies per mole PEA. These molar enthalpies of reaction as a function of composition are depicted in Figure 4. As expected from the stoichiometry, the enthalpies of reaction are constant up to 0.33 mol PEA. For higher mole fractions of PEA, insufficient isocyanate groups are available and the molar enthalpy of reaction appears to be smaller. The branch with negative slope in Figure 4 is drawn to give a zero heat of reaction for pure PEA. The enthalpy of the urethane reaction was found to be $\Delta H = -130 \text{ kJ/mol PEA}$ or $-65 \text{ kJ/mol hydroxyl group}$. This is in good agreement with the value of $\Delta H = -60.3 \text{ kJ/mol isocyanate group}$ reported for the urethane formation from poly(ϵ -caprolactone triol) and chain extended

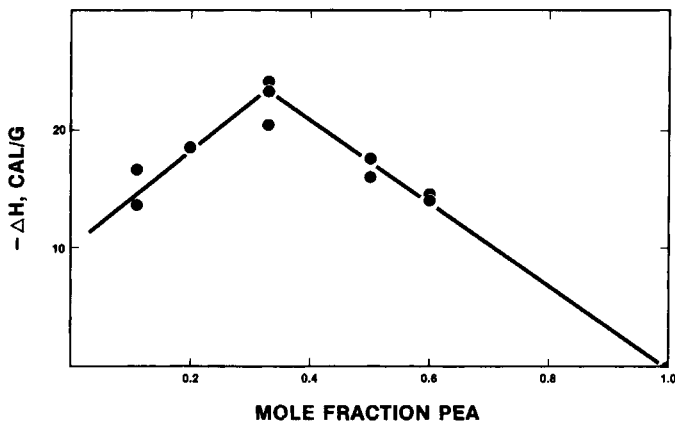


Fig. 3. Plot of specific heat of reaction vs. composition.

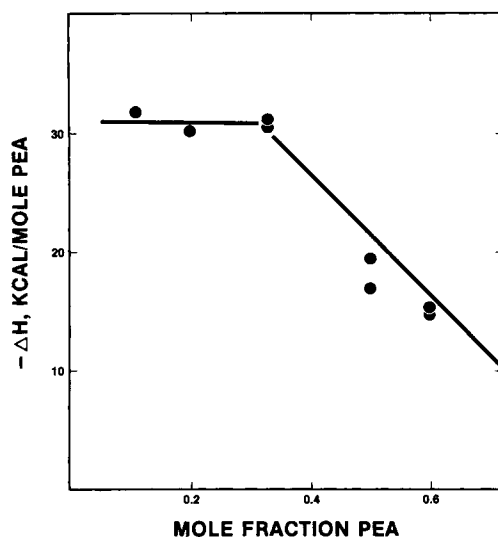


Fig. 4. Molar heat of reaction as a function of composition.

1,6-hexane diisocyanate.⁸ Enthalpies of reaction measured in dilute solution for reaction of low molecular weight alcohols with aromatic isocyanates are reported to be in the range of -77.5 to -104.7 kJ/mol isocyanate group.² This large range emphasizes the difficulties involved when extrapolating from dilute solutions to pure components.

Reaction Kinetics

As shown in Figure 5, the isothermal DSC curves for mixtures containing 20 mol % PEA and 80 mol % TDI decrease exponentially up to at least 90% conversion, suggesting that the reaction obeys a first-order rate law. The first-order

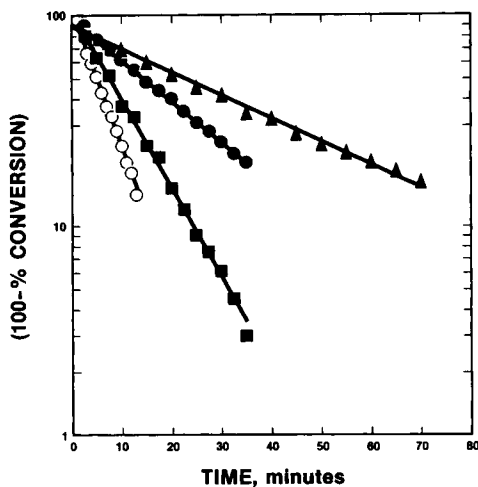


Fig. 5. First order kinetic plots from isothermal DSC experiments. Conditions as in Figure 2.

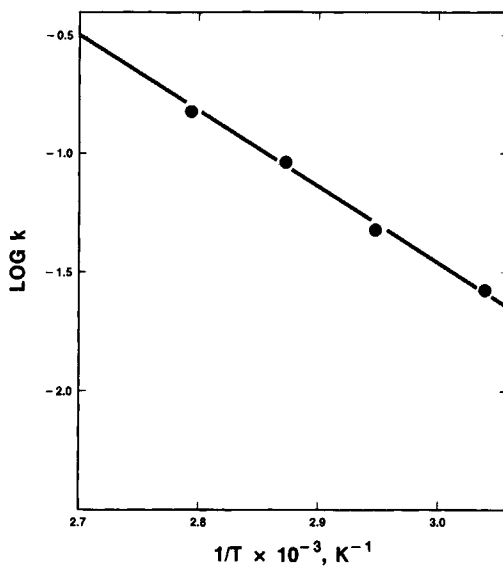


Fig. 6. Arrhenius plot of first-order rate constants obtained from Figure 5.

rate constants can be accommodated by an Arrhenius equation with an apparent activation energy of $E = 61.1$ kJ/mol for the range of $55^{\circ}\text{C} < T < 95^{\circ}\text{C}$ as shown in Figure 6. If the composition of the reaction mixture is varied in the limits of 11 mol % < PEA < 67 mol %, the kinetics of the reaction remain of clean first order over the entire range of compositions, as shown in Figure 7. The experimental first-order rate constants as a function of composition are summarized in Table I. The fact that the reaction exhibits first order kinetics implies that the true rate expression must be complex. The initial concentrations of the two reactants are comparable over the whole range of compositions; therefore, conditions are not met for which pseudo first-order kinetics would be applicable. Therefore, the urethane formation is expected to follow second-order kinetics with the true rate expression given by

$$\text{rate} = k_2[\text{PEA}][\text{TDI}] \quad (3)$$

By plotting the first-order rate constants from Table I vs. the sum of initial

TABLE I
First-Order Rate Constants for Different PEA/TDI Compositions

Composition (mol %)		Concn (mol/kg)		k (min^{-1}) ^a
PEA	TDI	PEA	TDI	
11	89	0.43	3.46	15.4
				16.1
20	80	0.61	2.46	15.1
33	67	0.78	1.58	11.2
				10.5
50	50	0.93	0.93	8.7
60	40	0.97	0.62	8.1
				7.7

^a $T = 85^{\circ}\text{C}$.

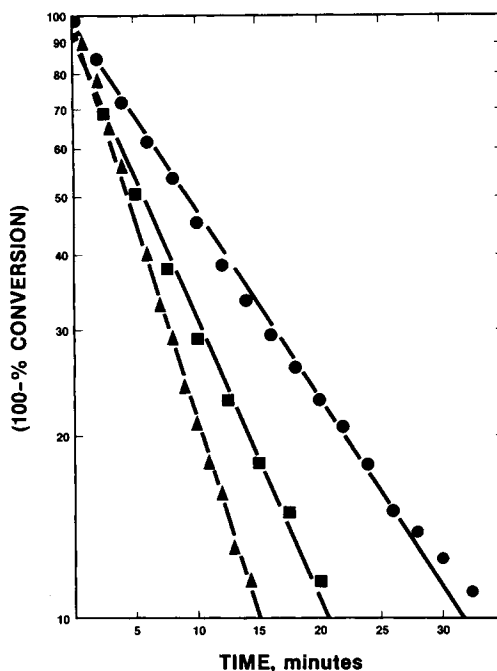


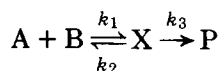
Fig. 7. First-order plots at $T = 85^{\circ}\text{C}$: (●) 60 mol % PEA, 40 mol % TDI; (■) 33 mol % PEA, 67 mol % TDI; (▲) 11 mol % PEA, 89 mol % TDI.

concentrations of hydroxyl and reactive isocyanate groups in the reaction mixture (Fig. 8) one obtains a straight line with an intercept close to zero. If the straight line is forced through the origin, the slope affords a concentration independent second-order rate constant of $k_2 = k_1/([\text{TDI}] + 2[\text{PEA}])$ with a value of $(5.47 \pm 0.24) \times 10^{-2} \text{ min}^{-1} \cdot \text{kg} \cdot \text{mol}^{-1}$. Therefore, for the conditions employed, the reaction of TDI and PEA is characterized by the rate expression given by

$$\text{rate} = k_1 \frac{[\text{PEA}][\text{TDI}]}{2[\text{PEA}] + [\text{TDI}]} \quad (4)$$

Reaction Mechanism

The observed kinetics can be most easily explained in terms of a reaction mechanism according to Scheme 1, where A represents the hydroxyl, B the reactive isocyanate group, X an intermediate complex, and P the urethane linkage formed in the reaction:



Scheme 1

If the complex X is formed by a rapid preequilibrium which is characterized by $K = k_1/k_2$, the overall reaction rate is determined by the rate of decomposition of X, provided that the value of the formation constant K is large enough.

The equilibrium expression is defined by eq. (5). In terms of the analytical

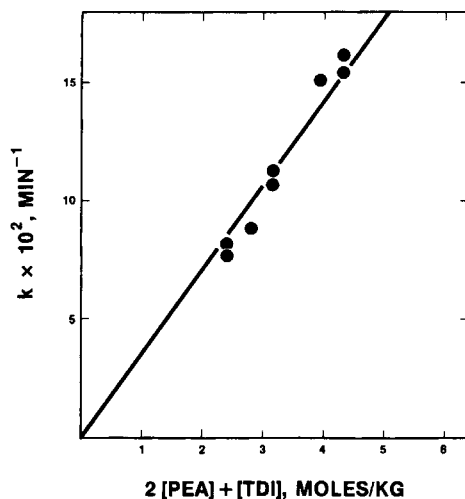


Fig. 8. Dependence of first-order rate constant on composition of reaction mixture.

concentrations, $C_a = [A] + [X]$ and $C_b = [B] + [X]$, the equilibrium is given by eq. (6):

$$K = [X]/[A][B] \quad (5)$$

$$K = [X]/(C_a - [X])(C_b - [X]) \quad (6)$$

The positive root of the quadratic eq. (6) is given by eq. (7), which can be simplified to eq. (8)¹²:

$$[X] = \frac{1}{2} \left[\frac{1}{K} + C_a + C_b + \sqrt{\left(\frac{1}{K} + C_a + C_b \right)^2 - 4C_a C_b} \right] \quad (7)$$

$$[X] \cong \frac{1}{K} + C_a + C_b \quad (8)$$

Comparison with eq. (3) yields the complete rate expression, eq. (9), required by the kinetic model:

$$\text{rate} = \frac{k_1 C_a C_b}{1/K + C_a + C_b} \quad (9)$$

One sees that for $1/K \gg (C_a + C_b)$, that is for low concentrations or small values of K , the model predicts a transition to second order kinetics with $k_2 = k_1 K$. For $1/K \ll (C_a + C_b)$, the overall kinetic order changes to one. In the present study with $(C_a + C_b) \geq 2.4$ mol/kg, first order kinetics are obeyed to at least 90% conversion; at this point, the sum of the reactant concentrations is $(C_a + C_b) \geq 0.24$ mol/kg. For $1/K \ll C_a + C_b$ to hold, $1/K \leq 0.02$ mol/kg or $K \geq 50$ kg/mol can be estimated.

The fact that the reaction of isocyanates with alcohols proceeds via an intermediate complex is well established, and the results of this study strongly support the validity of this kinetic model.^{13,14}

CONCLUSIONS

A simple and accurate method was developed for the determination of heats of reaction and kinetics for the reaction of PEA and TDI in the absence of solvent,

using isothermal DSC experiments. The stoichiometry of the reaction was found to be $\text{PEA} + 2\text{TDI} \rightarrow \text{product}$. This indicates that the hindered isocyanate groups in TDI do not participate in the reaction. The heat of reaction was found to be $\Delta H = -65$ kJ/mol hydroxyl group. The reaction shows first-order kinetics with an apparent activation energy of $E = 61.1$ kJ/mol. The kinetic data are accommodated by the following rate law:

$$\text{rate} = k_1 \frac{[\text{PEA}][\text{TDI}]}{2[\text{PEA}] + [\text{TDI}]}$$

The observed kinetic behavior can be reconciled by assuming the reversible formation of an intermediate complex between PEA and TDI.

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