

Kinetics of Isocyanate Amine Reactions

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Synopsis

Development of polyurea-urethane and polyurea reaction injection molding (RIM) systems has created a need for kinetics of polyurea formation. Adiabatic batch reactions in solution were used to determine heats of reaction and relative reactivity of several aromatic amines and *n*-butanol with phenyl isocyanate (PI). In addition to comparing times required to reach 25, 50 and 75% conversion for both catalyzed and uncatalyzed reactions, *n*-th order models with Arrhenius rate constants were used to fit some of the exotherms. The reaction of 3,5-diethyl toluene (2,4 and 2,6)-diamine and PI could not be modeled due to unequal reactivity of the two amine groups. This unequal reactivity was studied using high performance liquid chromatography (HPLC) separation of the reaction products. The reactions of primary aliphatic amines and aromatic isocyanates were too rapid to be monitored in the batch apparatus. With a flow apparatus the reaction half time was estimated to be ~ 0.002 s.

INTRODUCTION

Since the mid 1970s, the reaction injection molding (RIM) process has grown from infancy into a 100 million lb/year process (U.S. production in 1985). Original chemical systems for RIM were three-component polyurethanes composed of an aromatic diisocyanate, a short-chain diol (chain extender), and a polyether polyol (soft segment). Recently, polyurethane systems have been largely replaced by polyurea-urethanes, in which the chain extender is an aromatic diamine such as 3,5-diethyltoluenediamine. The next major step in RIM system evolution, aimed at improving productivity and properties, is in progress.^{1,2} Three-component polyurea systems, where the polyether polyol in a polyurea-urethane system is replaced with an amine-terminated polyether, are being considered for automotive body panels and nonautomotive applications.

Polyurethane and polyurea systems used commercially in RIM are (AB)_n block copolymers. The chain extender and diisocyanate sequences separate from the soft segment due to thermodynamic incompatibility. The degree of phase separation controls both high and low temperature properties. Since the chain extender and soft segment react competitively with the diisocyanate, it is imperative that the relative rates of the two reactions be controlled to optimize the dynamics of phase separation and produce the desired properties.

Kinetic information provides a basis for modeling and controlling the RIM process. Kinetics are necessary for development of new chemical systems and

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catalysts and optimizing phase separation through manipulation of the competing reaction rates. Although the kinetics of urethane RIM systems have been studied by several researchers,³⁻⁵ there have not been many studies of polyurea RIM.⁶ It is clear from this study that further research into rates of urea formation from compounds relevant to the RIM process is needed due to differences in both reaction rates and mechanisms from urethane RIM.

Urethane and urea formation in solution have been studied extensively. However, most studies did not involve compounds used in RIM. The research of Baker and co-workers was a breakthrough in the areas of kinetics and mechanisms of urethane formation.⁷⁻⁹ They used a titration method to measure unreacted isocyanate (see ASTM D1638). This technique was later used by many researchers to examine the effects of catalysts and solvents on reaction rates, and to study mechanisms. This work has been reviewed by several authors.¹⁰⁻¹³

Urea formation has not been characterized as thoroughly as urethane formation, due to the extremely high reaction rates. Experimental techniques applied to ureas range from analysis of product composition from competitive reactions to ultraviolet (UV) spectroscopy. Of all previous studies, one included primary aliphatic amines. Davis and Ebersole¹⁴ conducted reactions where *n*-butylamine and aniline reacted competitively with phenyl isocyanate (PI). Based on the composition of the product mixture, relative overall reaction rates were calculated. Titration techniques, both for isocyanate and potentiometric titration for amine, were used by several authors to study mechanisms of urea formation, the effects of steric hindrance and substituents on aromatic rings, and some work on solvents and catalysts.^{7-9, 15-20} Most of these reactions were run under extremely dilute conditions, or with slow reacting highly substituted aromatic amines. Borkent²¹ studied the faster reaction of sec-butylamine and 4,4'-diphenylmethane diisocyanate (MDI). Systems with sufficient concentration to reduce the half time to < 60 seconds were studied in a stopped flow UV spectrophotometer.

Axelrood et al.²² published the only solution study involving a direct comparison of urea and urethane formation. The reactants were 3,3'-dichloro-4,4'-diaminodiphenylmethane, a polypropylene oxide and PI. Both the amine and the polyol were considerably slower than components in current RIM systems. However, the study did reveal the relative effects of 1,4-diazabicyclo[2.2.2]octane (DABCO) and several organometallic catalysts on the ratio of reaction half times.

Adiabatic temperature rise methods were applied to urea formation in solution by Nissen and Markovs.²³ They ranked reactivity of potential aromatic amine chain extenders for RIM based on the initial slope of the reaction exotherms. No comparisons were made at higher conversion levels.

Casey et al.²⁴ used viscosity rise to examine the cure of urethane-urea elastomers. These elastomers comprise a toluene diisocyanate-terminated prepolymer, a polycaprolactone diol, and various diamine chain extenders. Reactivities are discussed using structure-activity relationships such as the Hammett correlation.

The objectives for this study were to determine relative reactivity of compounds with an active hydrogen (i.e., a hydrogen that is replaceable by sodium) having commercial RIM significance; to study the effects of RIM

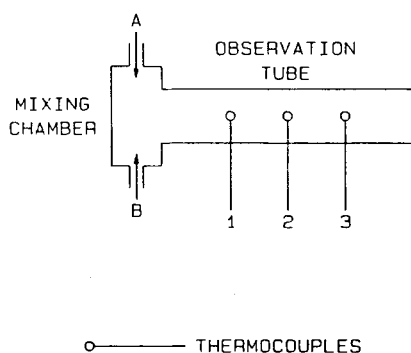


Fig. 1. Schematic of a continuous flow reactor using temperature measurement to determine conversion.

catalysts on relative reactivity and to measure heats of reaction. The method used was measurement of reaction exotherms under adiabatic conditions. Heats of reaction were required for calculation of conversion from temperature data. They were determined by generating temperature rise vs. concentration calibration curves. All reactions were run in solution to minimize errors due to incomplete mixing, diffusion control, and high reaction rates encountered under RIM conditions. At least one reactant was monofunctional to prevent molecular weight build-up and precipitation. Results from this study, especially heats of reaction and the rate of reaction between an aliphatic amine and an aromatic isocyanate provided direct input into the RIM phase of our work.²⁵

Initial work proved that the reaction between an aliphatic amine and an aromatic isocyanate was too rapid to be studied in a batch apparatus. Fast reactions in solution have frequently been studied in continuous flow reactors. Figure 1 is a schematic of a reactor with thermocouples monitoring the reaction exotherm as the material flows down the observation tube. During flow, the temperature at any position reaches steady state. The average time to reach the thermocouple is calculated by dividing the distance from the mixing chamber by the average velocity of the stream. For further information on continuous flow techniques, see the reviews by Roughton²⁶ and Roughton and Chance.²⁷

In addition, high performance liquid chromatography (HPLC) was used to study the relative reactivity of unreacted and monosubstituted 3,5-diethyl-toluene-2,6-diamine (2,6 DETDA) with PI, since it was not possible to fit the overall exotherms for the reaction of 2,6 DETDA and PI with kinetic models based on a single rate constant.

ADIABATIC TEMPERATURE RISE

To determine kinetic parameters from an adiabatic experiment, the temperature rise must be related to the extent of reaction. The assumptions used for this study were:

Constant heat capacity, density and heat of reaction over the temperature range.

Homogeneous reaction mixture after an initial mixing period.

No heat sources other than reaction.

No diffusion restrictions on the reaction rate.

The energy balance for a single irreversible reaction, including heat loss is:

$$\rho C_p dT/dt = (-\Delta H_r) r_a - U(T - T_{amb}) \quad (1)$$

where U is the heat transfer coefficient per unit volume, and r_a is the reaction rate. Other notation is defined at the end of the paper. The rate can be expressed in terms of the initial concentration of the limiting reagent, C_o , and the extent of reaction ($\alpha = (C_o - C)/C_o$).

$$\rho C_p dT/dt = (-\Delta H_r) C_o d\alpha/dt - U(T - T_{amb}) \quad (2)$$

To simplify data analysis, the temperature values were corrected for heat loss prior to calculating conversion. The heat transfer coefficient was determined using a non-reactive system. Without reaction, the energy balance simplifies to:

$$\rho C_p dT/dt = -U(T - T_{amb}) \quad (3)$$

With the assumption of constant ρ and C_p , Eq. (3) integrates to:

$$\ln(T - T_{amb}) = \ln(T_o - T_{amb}) - (U/\rho C_p)(t - t_o) \quad (4)$$

The value of U was calculated from the slope of a plot of $\ln(T - T_{amb})$ vs $(t - t_o)$. All temperature data were corrected by addition of the following factor through Simpson's rule integration.

$$(U/\rho C_p) \int_{t_o}^t (T(t) - T_{amb}) dt \quad (5)$$

Once heat loss has been compensated for, temperature and fractional conversion are directly related.

$$\alpha = \frac{\rho C_p (T - T_o)}{(-\Delta H_r) C_o} \quad (6)$$

The heat of reaction is calculated from the maximum temperature attained, T_{ad} .

$$-\Delta H_r = \frac{\rho C_p (T_{ad} - T_o)}{C_o} \quad (7)$$

Combining Eqs. (6) and (7), the final expression for α is:

$$\alpha = \frac{T - T_o}{T_{ad} - T_o} \quad (8)$$

The lengths of time required for the reactions to reach 25, 50, and 75% conversion were compared. These "reaction times" had to be compared at several conversions to get an accurate measure of relative reactivity under adiabatic conditions. For isothermal reactions, the half time alone can be used to calculate the rate constant if the reaction order is known. However, under adiabatic conditions two systems may have the same half time but very different overall kinetics. A reaction may begin quickly and require a long time to reach completion. Another system may react slowly at the beginning but accelerate to completion. These two types of behavior are representative of low and high activation energies, respectively.

For more in-depth analysis, the data can be fit with a kinetic model. N -th order models with Arrhenius temperature dependence of the rate constants are typically chosen for urethane polymerizations.

$$r_a = A \exp(-E_a/RT) C_I^n C_H^m \quad (9)$$

Equation (9) can be expressed in terms of conversion only.

$$\frac{d\alpha}{dt} = A \exp\left[\frac{-E_a}{R(\Delta T_{ad} \cdot \alpha + T_o)}\right] C_{Io}^{n-1} C_{Ho}^m (1 - \alpha)^n (1 - \alpha/r)^m \quad (10)$$

where r is the ratio of initial concentrations of reactive groups (alcohol or amine to isocyanate). The isocyanate was always the limiting reagent. At each experimental value of α , time was calculated from the integral form of Eq. (10), and kinetic parameters were determined by minimizing the sum of differences between calculated and experimental times over all values of α . One of the orders or the sum of the orders as well as the pre-exponential factor and the activation energy could be used as regression variables.

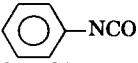
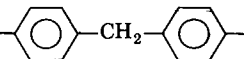
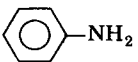
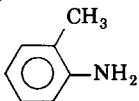
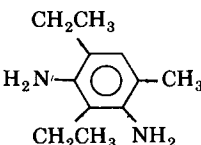
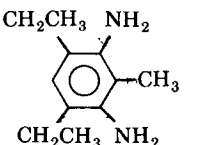
EXPERIMENTAL

Materials

Reactants are listed in Table I. Three classes of active hydrogen compounds, aliphatic and aromatic amines and alcohols were included. PI was used for all reactions run in the batch apparatus and uretonimine-modified 4,4'-diphenylmethane diisocyanate (u-MDI) was used in the continuous flow reactor. All reactants and catalysts were chosen because of their application in RIM systems. DETDA (the isomeric blend), the catalysts, DABCO and dibutyltin dilaurate (DBTDL) and u-MDI are all used extensively in RIM. PI was chosen as a monofunctional analog to MDI. The amine-terminated polyethers differed only in molecular weight and functionality from the soft segment components of polyurea RIM systems. Finally, n -butanol was substituted for butanediol, a common component of polyurethane systems.

Dimethylacetamide (DMAc) was the primary solvent, since all reactants and products were soluble in it. Diethylene glycol dimethyl ether (diglyme) was also used, since its chemical structure resembles that of the polyethylene oxide portion of polyols used in polyurethane and polyurea-urethane RIM systems. Some of the disubstituted ureas produced precipitated in diglyme.

TABLE I
Chemical Systems

| Isocyanates | | Alcohol |
|--|--|---|
|  phenyl isocyanate [PI] | $\text{OCN}-\text{R}-\text{NCO} + \begin{array}{c} \text{OCN}-\text{R} \quad \text{N}-\text{R}-\text{NCO} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{C} \\ \quad \\ \text{C} \quad \text{N} \\ \quad \\ \text{O} \quad \text{R}-\text{NCO} \end{array}$ Uretonimine modified 4,4' diphenylmethane diisocyanate [u-MDI] where R =  | $\text{CH}_3(\text{CH}_2)_3\text{OH}$ <i>n</i> -butanol |
| Aromatic amines | | Aliphatic amines |
|  aniline |  <i>o</i> -toluidine | $\text{CH}_3(\text{CH}_2)_3 \text{NH}_2$ <i>n</i> -butylamine |
|  77% 3,5 diethyltoluene-2,4-diamine 18% 3,5 diethyltoluene-2,6-diamine [2,4 and 2,6 DETDA] + 5% other amines |  | $\text{H}_2\text{N}-\underset{\text{CH}_3}{\text{CH}}\text{CH}_2-(\text{OCH}_2-\underset{\text{CH}_3}{\text{CH}})_a-\text{NH}_2$ difunctional amine-terminated polypropylene oxide |
| | | $\text{H}_2\text{N}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-(\text{OCHCH}_2)_a-\text{OCH}_2\text{CH}_2\text{OCH}_3$ monofunctional amine-terminated polypropylene oxide |

The isocyanates were phenyl isocyanate (99%, Aldrich Chemicals Corp.) for batch reactions and u-MDI (LF168, Rubicon Chemicals Corp.) for the flow apparatus. Isocyanate purity was verified by titration (ASTM D1638). The solvents, DMAc and diglyme, (99% pure, Aldrich Chemicals Corp.) were dried over molecular sieves (Davidson 8-12 mesh, 4A pore size, Fisher Scientific). The catalysts, DABCO and DBTDL were commercial grades from Air Products and Chemicals Co. and M & T Chemicals Inc., respectively. Other reagents: aniline, *n*-butylamine, and *o*-toluidine were obtained from Aldrich Chemicals Corp. (99% + purity). *N*-butanol was reagent grade from Fisher Scientific. D230, M600 and D2000 were commercial samples from Texaco Chemicals Corp. (Jeffamine D230, M600, and D2000). The isomeric mixture of 2,4 and 2,6 DETDA was supplied by Ethyl Corp. The 2,6 DETDA was produced by Lonza Inc. Aromatic amines were stored under dry nitrogen.

Equipment and Procedures

Batch reactions were run in 220 cc polypropylene cups insulated by a block of polystyrene foam wrapped in fiberglass tape. An impeller mixer (Talboy's Eng. Corp. model no. 7163-2883) with a 37 mm propeller blade was used for mixing. Two 75 μ m diameter T-type thermocouples were placed in the center of the cup 12 mm from the bottom using a stiff wire running down the side of the cup. The cup could not be tightly sealed around the impeller so dry nitrogen was fed into the reactor with a syringe needle. Data was collected by an A/D converter (California Data Systems Model AD-100-2) mounted in a Zenith 100 series microcomputer.

Solutions of the alcohol or amine and catalyst (as needed) were prepared in advance and stored over molecular sieves prior to use. When a reaction was run, the solvent and isocyanate were added to the cup first and data collection and stirring started. The active hydrogen solution was added and stirring continued for 10 seconds when the impeller was removed. The actual concentrations of the reactants for each run were determined by weighing the delivery syringes for the solvent, isocyanate, and alcohol or amine solution. Standard conditions for comparing reaction times were an initial isocyanate concentration of 5×10^{-4} eq/g (based on the average specific gravity, 5.0×10^{-4} eq/g = .474*M*) and mole ratio of amine or alcohol to isocyanate of 1.01. These conditions were used for all the data reported unless otherwise noted.

To further study the reaction of DETDA and PI, products of the reaction of one mole each of PI and DETDA were analyzed with HPLC. The components of the instrument were a Beckman 100b solvent delivery module, a Beckman 340 organizer, an Altex Ultrasphere ODS column and a Beckman 163 variable wavelength UV detector. The mobile phase was 65% methanol/35% water, and the detector was set to 290 nm. Flow rate was .8 mL/min with 5 μ L injection. Peak area was determined by cutting and weighing.

A mini-RIM machine was used as the impingement mixer for the flow studies. The machine and its operation are described in detail elsewhere.²⁸ The mixhead was based on the design of McIntyre and Macosko²⁹ with a mixing chamber diameter of 4.76 mm. The mixing chamber cleaning rod was solid, so there was no recycle of the reactants prior to the shot. All tests were started at room temperature, thus thermal equilibration of the apparatus was not necessary. The entire mixhead was operated in a vertical position to minimize air entrapment in the flow. A stainless steel compression fitting at the end of the mixing chamber was used to hold a polypropylene observation tube in place (4.76 mm I.D.). T-type thermocouples (250 μ m diameter) were located in the center of the flow in the compression fitting and along the length of the observation tube and held in place with epoxy. The distances of the thermocouples from the impingement point were determined after the wires were fixed in place. The overall adiabatic temperature rise of the system was measured by delivering the stream to an insulated polypropylene cup. Temperature data was collected with the A/D converter and microcomputer described above.

Solutions of the aliphatic amine M600 and u-MDI were prepared so concentrations and mole ratio were .5eq/L and 1.0 after mixing. The solutions were stored under dry nitrogen before use.

Data Analysis

To analyze the data from the two types of experiments, several initial experiments and calculations were required. These experiments included determining heat capacities, heats of reaction, the mixing time and heat loss (for the batch apparatus) and Reynolds numbers for the flow apparatus.

Heat capacities for all the reagents were determined from literature, the chemical suppliers or experimentally using a differential scanning calorimeter (DSC, Mettler Model TA3000). Both solvents were tested with the DSC and results were within 1% of those reported in the literature. Heat capacities were assumed to be independent of temperature and for mixtures equal to the weight average of individual component values. Heat capacities used in the calculations of conversion were those of the chemical systems only, the apparatus was not included. This was verified by mixing known amounts of solvent at different temperatures in the apparatus. The final temperatures were within 1.5% of the expected values.

Heat loss compensation is described by Eqs. (3) to (5). The linearity of the relationship between $\ln(T - T_{amb})$ and $(t - t_o)$ was established by monitoring heat loss from DMAc for 75 minutes over a range of 18°C. To determine the value of U to use in correcting kinetic data for heat loss, data collection was continued for 15 minutes for the rapid reactions of the aliphatic amines with PI. The average value of $U/\rho C_p$ was $2.8 \times 10^{-4} \text{ s}^{-1}$ for both DMAc and diglyme (Fig. 2 is an example). The only exception was the reaction of DETDA and PI in diglyme, because the product precipitated at 40% conversion. For this reaction, $U/\rho C_p$ was determined after 25 min to be $6 \times 10^{-5} \text{ s}^{-1}$. The kinetic runs were typically stopped after 10 min.

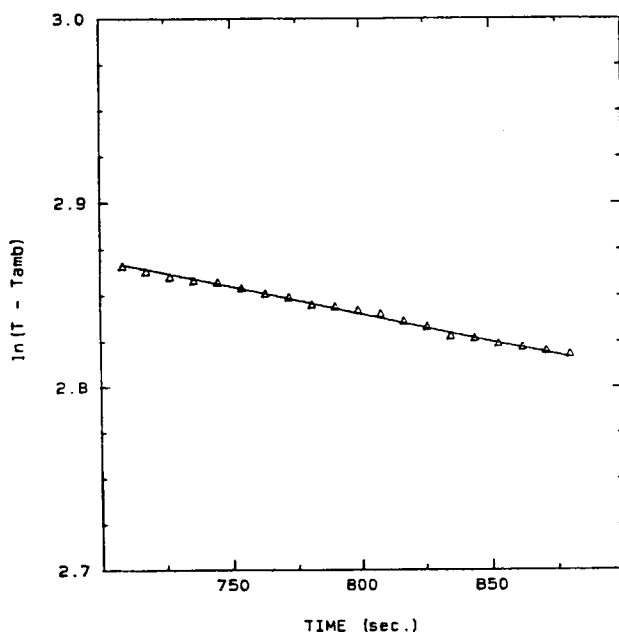


Fig. 2. Determination of the heat transfer coefficient for the batch apparatus [Eq. (4)].
Slope = $U/\rho C_p = .000292 \text{ s}^{-1}$.

The fast reactions of several aliphatic amines (*n*-butylamine, D230, M600, and D2000) and PI were used to characterize the mixing time of the batch apparatus. Large variations in temperature between the thermocouples and sharp temperature peaks during the first few seconds of the reactions were indicative of poor mixing. In 21 reactions, the average time until the thermocouples readings converged and/or the temperature stabilized after a sharp peak was 3.2 s. No kinetic data was analyzed before 3.5 s after injection.

Quality of mixing in a flow apparatus is normally determined by studying a reaction known to be complete in less than the minimum measurement time of the apparatus (e.g., acid-base). These blank mixing tests could not be used in the mini-RIM due to possible degradation of seals. Quality of impingement mixing can also be related to the Reynolds number of the mixhead orifice.³⁰

$$\text{Re} = \frac{4\rho Q}{\pi D_m \mu} \quad (11)$$

where Q is the volume flow rate, ρ the density, D_m the diameter of the orifice and μ the viscosity. For this work, the typical Reynolds number was 32,000. This value is significantly higher than is currently used in RIM.

Deviations from plug flow also lead to inaccurate results, and turbulent flow is necessary to minimize these deviations.^{26,27} The critical Reynolds number for transition from laminar to turbulent flow in a tube is 2100 and the calculated value for this study was 12,000.

RESULTS

Heats of Reaction

Since kinetic data was not analyzed after 10 min, it was necessary to determine temperature rise at 100% conversion in a separate study. Aniline, D230, and *n*-butanol were chosen as representative of the three classes of reactants. Calibration curves of $C_p \Delta T_{ad}$ vs. C_o (eq/g) were generated for the reactions of these three compounds with PI in DMAc. To insure rapid and complete reactions, a 40% excess of alcohol or amine was used, and *n*-butanol reactions were catalyzed with 2 mol% DBTDL. The calibration curves are shown in Figure 3 and the results are in Table II.

Several other reactions of aliphatic amines and highly catalyzed reactions of aromatic amines were run at the standard conditions of 5.0×10^{-4} eq/g and $r = 1.01$ to verify the heats of reaction [Table II(b)]. For the aliphatic amines, *n*-butyl amine, D230, M600, and D2000 reacting with the isocyanates, PI and u-MDI, in DMAc or diglyme, all heats of reaction were within the range of the slope of the calibration curve for D230.

The aromatic amines, aniline, DETDA (isomeric blend), and *o*-toluidine were tested in both solvents with PI. A high catalyst level of 5 mol% DABCO was used to insure rapid reaction. The values from the two solvents compare favorably, and the aniline results are within confidence limits of the slope of the calibration curve. The ranking of heats of reaction is DETDA > *o*-toluidine > aniline, which is the reverse of reactivity.

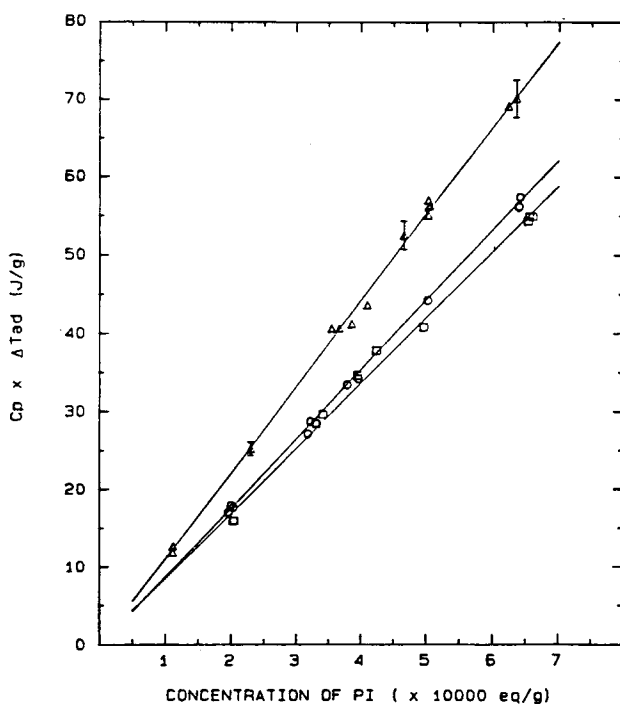


Fig. 3. Calibration curves for heats of reaction with PI in DMAc. (○) aniline; (□) *n*-butanol; (Δ) D230.

TABLE II
Heats of Reaction

| Active hydrogen compound | Isocyanate | Solvent | Average ($-\Delta H_r$) (kJ/eq) |
|--|------------|---------|-----------------------------------|
| (a) Based on several concentrations (slopes in Fig. 3; 95% confidence) | | | |
| Aniline | PI | DMAc | 89.1 ± 5.1 |
| D230 | PI | DMAc | 111 ± 4.4 |
| <i>n</i> -Butanol | PI | DMAc | 83.9 ± 4.4 |
| (b) Based on data at 5×10^{-4} eq/g (average of three runs) | | | |
| <i>n</i> -Butylamine | PI | diglyme | 114 |
| <i>n</i> -Butylamine | PI | DMAc | 112 |
| D230 | PI | diglyme | 112 |
| D2000 | PI | diglyme | 113 |
| M600 | PI | diglyme | 114 |
| M600 | u-MDI | diglyme | 115 |
| Aniline | PI | diglyme | 91.3 |
| Aniline | PI | DMAc | 88.4 |
| DETDA | PI | diglyme | 93.6 |
| DETDA | PI | DMAc | 95.9 |
| <i>o</i> -Toluidine | PI | diglyme | 93.0 |
| <i>o</i> -Toluidine | PI | DMAc | 92.3 |

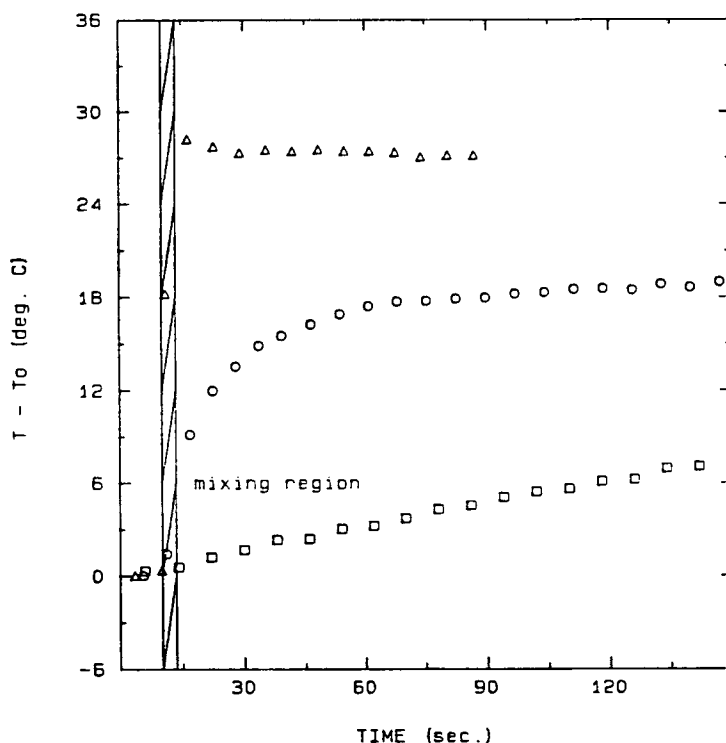


Fig. 4. Relative reactivity of an alcohol, an aromatic amine and an aliphatic amine with PI in DMAc at standard conditions. (○) aniline; (□) *n*-butanol; (Δ) D230.

For kinetic analysis, the temperature rise at 100% conversion of the limiting reagent was predicted based on the heats of reaction from the calibration curves for *n*-butanol and aniline [Table II(a)] or the DABCO-catalyzed reactions for DETDA and *o*-toluidine [Table II(b)].

Uncatalyzed Reactions

Each reaction was repeated from three to six times. All reported reaction times are average values. Reaction times were reproducible to within 5–10%.

Uncatalyzed reactions in DMAc were the main test of relative reactivity. The wide range of reactivity among the three classes of reactants is illustrated in Figure 4. Reaction times for 25, 50, and 75% conversion are listed in Table III.

The importance of comparing times to several levels of conversion is seen by the change in the *n*-butanol/*o*-toluidine ratio over the conversion range of 25 to 75%. *N*-butanol took five times longer to reach 25% conversion, but only two times longer to reach 75%. The comparison could not be carried to higher conversions because of the long times required. In contrast, the relative ratio for aniline and *o*-toluidine remained essentially constant over the conversion range. This illustrates that *n*-butanol and *o*-toluidine reactions have different activation energies and/or reaction orders, while the kinetic models for aniline and *o*-toluidine would differ mainly in pre-exponential factor.

TABLE III
 Uncatalyzed Reactions with PI in DMAc

| Active hydrogen compound | Time to: | | | A (L/mol s ¹) | Ea kJ/mol |
|--------------------------|-----------|---------------------------|-----------|--------------------------------|--------------|
| | 25% Conv. | 50% Conv. (in seconds) | 75% Conv. | | |
| Aniline | < 3.5 | 10.0 | 40.0 | 543 ($x = 2$) | 17.2 |
| <i>o</i> -Toluidine | 19.0 | 59.0 | 271 | 72.6 ($x = 2$) | 16.8 |
| <i>n</i> -Butanol | 92.0 | 242 | 510 | 3.16×10^8 ($x = 1$) | 61.1 |
| DETDA | 11.0 | 56.0 | 470 | | |
| (2,6) | | | | | |
| DETDA | 13.0 | 63.0 | 490 | | |
| (2,4 and 2,6) | | | | | |

The comparison between 2,6 and the isomeric mixture of 2,4 and 2,6 DETDA shows the negative effect of steric hindrance. The 4 position of DETDA is the most hindered, and in the isomeric mixture the 4 position represents 40% of the reactive groups. The higher concentration of more reactive groups in the pure 2,6 accounts for its higher initial reaction rate. Above 50% conversion the rates converge to within the limits of reproducibility.

The data of Table III also indicate that unreacted and monosubstituted DETDA should react at very different rates. This is apparent from the fact that both 2,6 DETDA and the 2,4-2,6 mixture reach 25% conversion before *o*-toluidine, which is less sterically hindered, but require 1.75 times longer to reach 75% conversion.

This conclusion is consistent with expectations based on the substituents present on the aromatic ring of DETDA. Both alkyl and amine groups increase the electron density of an aromatic ring, which would activate the aryl amine toward reaction with isocyanates. Steric hindrance from the substituents opposes this electronic activation. However, DETDA does have higher initial reactivity than *o*-toluidine, so the electronic effect is clearly dominant.

The urea formed from the reaction of the first amine group on DETDA will withdraw electrons from the ring and deactivate the second amine. The net result is a large difference in reactivity between monosubstituted and unreacted DETDA. Since isomeric and 2,6 DETDA have equivalent reaction times above 50% conversion, this substitution effect masks differences between the two types of DETDA due to steric hindrance in the 4 position.

Further quantification of the unequal reactivity of DETDA will be presented later. An analogous situation exists for aromatic diisocyanates such as 2,4 or 2,6 toluene diisocyanate (TDI).¹³ The reaction of the first isocyanate group replaces a strongly activating isocyanate with a weakly activating urethane, leading to decreased reactivity for monosubstituted TDI.

Kinetic Modeling

To facilitate kinetic modeling, the aniline/PI reaction was run at several mole ratios to determine reaction order. Previous researchers have proposed

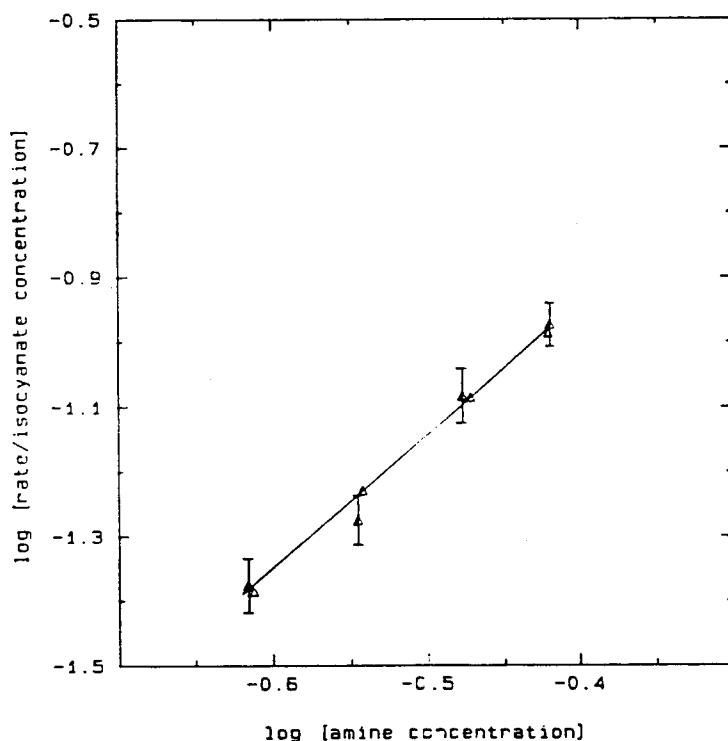


Fig. 5. Determination of the reaction order in amine at 50% conversion for the reaction of aniline with PI in DMAc. Slope = $m = 2.05 \pm 0.19$.

between second and third order overall, with first order in isocyanate.^{7-9,15,20} Craven supported his mechanism by determining order in amine at 0 and 50% conversion from the slope of a logarithmic plot of r_a/C_{I_0} vs C_{H_0} (assuming first order in isocyanate). For this study, 50% conversion was convenient for order determination, so reaction rate was calculated by fitting a line to the temperature vs. time data between 45 and 55% conversion. This slope is simply related to rate for constant heat capacity.

$$r_a = C_{I_0} d\alpha/dt = (C_{I_0}/\Delta T_{ad}) dT/dt \quad (12)$$

The order in aniline was found to be $2.05 \pm .19$ (Fig. 5).

On the same set of aniline reactions, activation energy and pre-exponential factor were calculated from the integral form of Eq. (10) as described earlier. All mole ratios were used simultaneously. In one fit, the orders were fixed at one for PI and two for aniline, and the pre-exponential factor and activation energy were calculated to be $542.6 \text{ (L/mol)}^2 \text{ s}^{-1}$ and 17.2 kJ/mol . In a second fit, the aniline order, m , was included as a regression variable. The calculated value of m was 2.02, which supports the use of a third-order model. Pre-exponential factor and activation energy for the variable order model were $654.6 \text{ (L/mol)}^{2.02} \text{ s}^{-1}$ and 17.6 kJ/mol . Kinetic parameters were in good agreement and the fit to the data was excellent (Fig. 6).

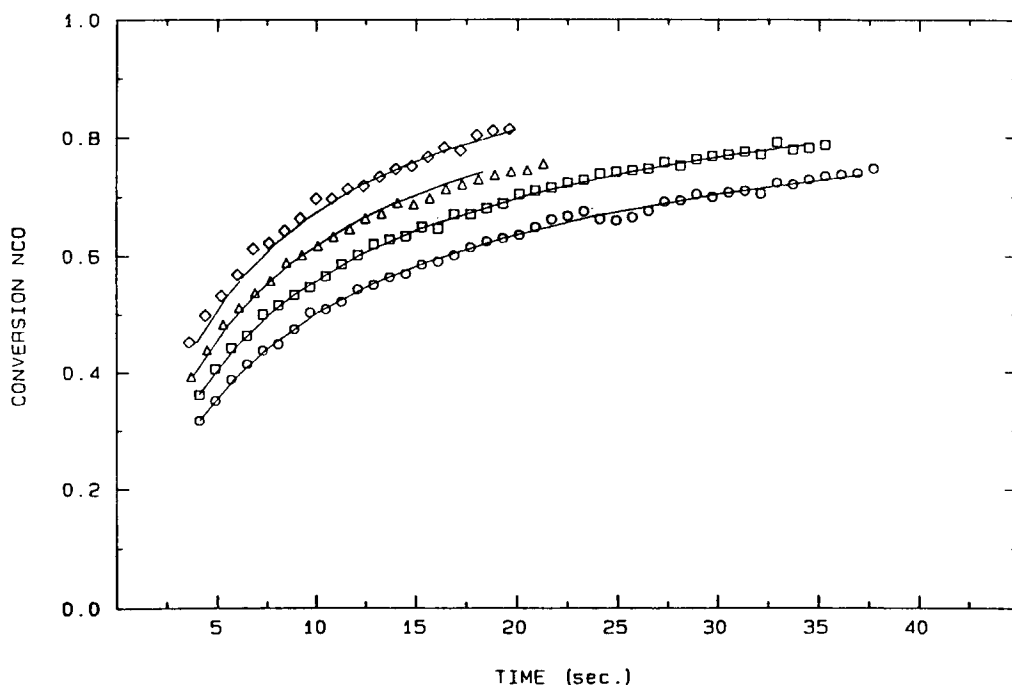


Fig. 6. Reaction of aniline with PI in DMAc at several mole ratios. Symbols are data, and lines are predictions from the variable order model ($m = 2.02$, $A = 654.6 \text{ (L/mol)}^{2.02} \text{ s}^{-1}$, $E_a = 17.6 \text{ kJ/mol}$). (\circ , r) 1.02; (\square , r) 1.11; (\triangle , r) 1.20; (\diamond , r) 1.30.

The activation energy is significantly lower than previously reported for alcohol/isocyanate reactions. The high order and low activation energy account for the high initial reactivity.

O-toluidine and DETDA reactions could not be modeled using the two regression variables, A and E_a . With the assumptions of first order in PI, second order in amine and $E_a = 16.8 \text{ kJ/mol}$, pre-exponential factors were estimated, and the values were 455.6 and $72.6 \text{ (L/mol)}^2 \text{ s}^{-1}$ for aniline and *o*-toluidine, respectively. As seen in Figure 7, the DETDA exotherm could not be described with a model containing one Arrhenius rate constant. The reason could be substitution effects or order changing with conversion.

Unequal Reactivity in DETDA

Since substitution effects were implicated by the reaction times and modeling attempts, HPLC was used to further investigate the competitive, consecutive reaction of DETDA and PI.



where Un, M, and D are unsubstituted, monosubstituted, and disubstituted DETDA. Once reaction orders are selected, rate equations can be written.

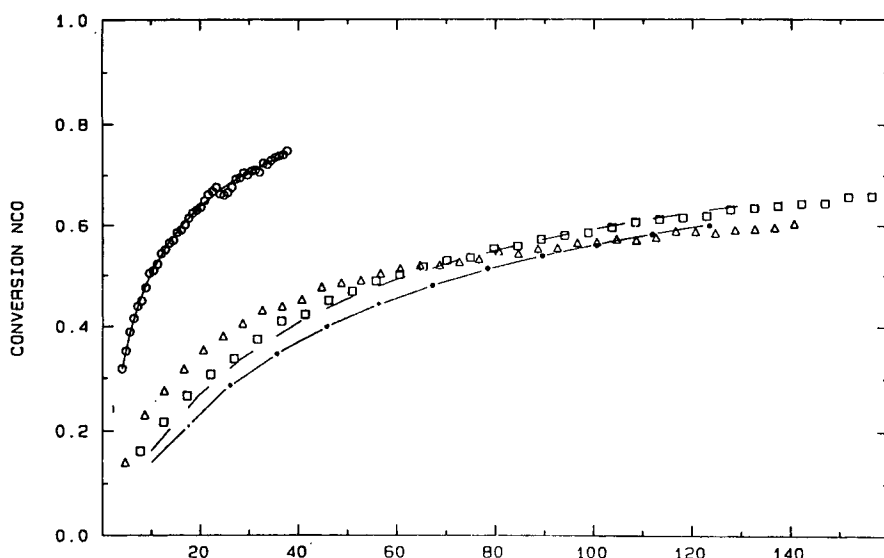


Fig. 7. Reaction of aromatic amines with PI in DMAC. Symbols are data and lines are predictions from third-order models with assumed activation energy of 16.8 kJ/mol. (°—) aniline; (□—) *o*-toluidine; (△—) (2,6) DETDA.

Based on the aniline experiments, first order in PI and second order in amine was assumed.

$$\begin{aligned}
 d[\text{Un}]/dt &= -K_1[\text{PI}][\text{Un}]^2 \\
 d[\text{M}]/dt &= K_1[\text{PI}][\text{Un}]^2 - K_2[\text{PI}][\text{M}]^2 \\
 d[\text{D}]/dt &= K_2[\text{PI}][\text{M}]^2
 \end{aligned} \tag{14}$$

To determine relative concentrations, a mole balance is made for DETDA.

$$\frac{[\text{Un}]_0}{[\text{Un}]} = 1 + \frac{[\text{M}]}{[\text{Un}]} + \frac{[\text{D}]}{[\text{Un}]} \tag{15}$$

The concentration of unreacted DETDA in a reaction mixture was found by running standard solutions of unreacted DETDA. The concentration in the reaction mixture is then calculated from the relative area of the peaks in the reaction mixture and a standard.

To obtain $[\text{D}]/[\text{Un}]$ for a reaction mixture, a standard was run in which a large excess of PI was reacted with DETDA, so that only the disubstituted form of DETDA would remain. The excess PI was quenched with water and a known amount of unreacted DETDA was added. From the relative concentrations and areas, a proportionality constant was calculated and used on reaction mixtures. Approximately 2% of the DETDA remained monosubstituted, indicating that quenching of the PI was either too early or incomplete at the time that the unreacted DETDA was added.

TABLE IV
 Catalyzed Reactions with PI in DMAc

| Catalyst | Catalyst level (mol %) | Time to: | | |
|---------------------|---------------------------|-----------|---------------------------|-----------|
| | | 25% Conv. | 50% Conv. (in seconds) | 75% Conv. |
| <i>n</i> -Butanol | — | 92.0 | 242 | 510 |
| | DBTDL | 0.01 | 61.0 | 329 |
| | DBTDL | 0.1 | 25.0 | 96.0 |
| | DBTDL | 2.0 | 6.5 | 30.0 |
| | DABCO | 2.0 | 56.0 | 342 |
| <i>o</i> -Toluidine | — | 19.0 | 59.0 | 271 |
| | DBTDL | 0.1 | 18.0 | 260 |
| | DBTDL | 2.0 | 17.0 | 263 |
| | DABCO | 0.1 | 19.0 | 265 |
| | DABCO | 2.0 | 7.5 | 87.0 |

Once the distribution was calculated from Eq. (15), a Runge-Kutta integration method with a Newton-Raphson loop was used to solve the differential rate equations for the ratio of rate constants, K_1/K_2 , that best fit the experimental product distribution.

Two reactions were run with one mole each of DETDA and PI, and K_1/K_2 was found to be $3.2 \pm .8$. The large uncertainty margin was due to the error introduced in $[D]/[Un]$ by the monosubstituted DETDA and the cut and weigh method of area determination. However, these results make it obvious why a model with a single rate constant could not be found to fit the exotherms.

The reactions were repeated at double the initial concentrations, but the same ratio of reactants. The $[M]/[D]$ ratios at the two concentration levels were within the experimental uncertainty, so the orders of the two reactions appear to be equal.

Catalyzed Reactions

The effects of DBTDL and DABCO on the reaction times for the *o*-toluidine/PI and *n*-butanol/PI reactions are summarized in Table IV.

Up to 2 mol%, DBTDL had no measurable effect on the *o*-toluidine/PI reaction. In contrast, 2 mol% DBTDL reduced reaction times for *n*-butanol/PI by an order of magnitude. DBTDL has been reported to be very specific for urethane formation. However, some catalytic effect has also been reported for reactions of aromatic amines and isocyanates that are much slower than those used here.^{18,22} Based on the results in Table IV, it is doubtful that DBTDL catalyzes the fast amine/isocyanate reactions in commercial RIM systems.

DABCO had a more significant effect on the *o*-toluidine reaction than the *n*-butanol reaction. At 2.0 mol%, DABCO reduced reaction times for *o*-toluidine to 30 to 40% of the uncatalyzed values, while times for *n*-butanol remained at 60 to 70% of their original values. This high catalyst level was needed to achieve measurable increases in rate.

Kinetic parameters, E_a and A were calculated for the reactions of *n*-butanol and PI at several levels of DBTDL. Orders were fixed at one for both

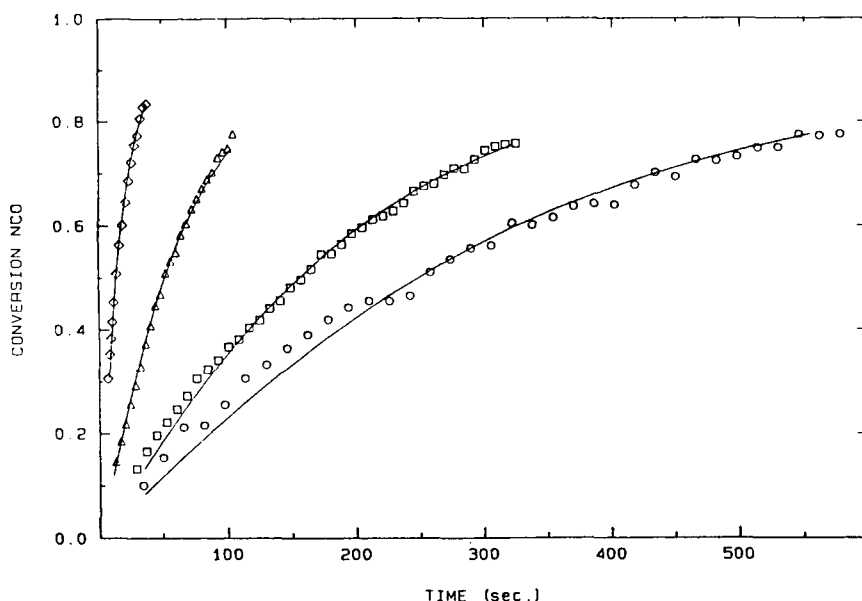


Fig. 8. Comparison of second order models with data for DBTDL-catalyzed reactions of *n*-butanol with PI in DMAc (Table V). (○) uncatalyzed; (□) 0.01 mol % DBTDL; (Δ) 0.1 mol % DBTDL; (◇) 2.0 mol % DBTDL.

TABLE V
Kinetic Parameters for *n*-Butanol in DMAc

| DBTDL level (mol %) | E_a (kJ/mol) | A (L/mol · s) |
|---------------------------|-------------------|-----------------------|
| — | 61.1 | 3.16×10^8 |
| .01 | 62.8 | 7.97×10^8 |
| .1 | 68.3 | 1.82×10^{10} |
| 2.0 | 71.6 | 2.52×10^{11} |

reactants. The results are shown in Figure 8 and listed in Table V. The activation energies increased with catalyst level and are higher than reported from isothermal reactions.¹³ The values presented here are parameters used to model the exotherms. Temperature, concentrations, and mole ratios would have to be varied systematically to get a universal set of kinetic constants.

Influence of Solvent

To more closely simulate RIM conditions, diglyme was also used as a solvent. One negative factor was the precipitation in the DETDA/PI reaction. Conducting the reaction in a clear vessel, the onset of turbidity was observed at 40% conversion. The final solutions for reactions of aniline and *o*-toluidine with PI in diglyme were slightly cloudy.

The results are presented in Table VI and Figures 9 and 10. The change in solvent decreased the initial reaction rates for the aromatic amines. Above

TABLE VI
Effects of Solvents

| Active hydrogen compound | Solvent | Time to: | | |
|---|---------|-----------|---------------------------|-----------|
| | | 25% Conv. | 50% Conv. (in seconds) | 75% Conv. |
| Aniline | DMAc | < 3.5 | 10.0 | 40.0 |
| | diglyme | 16.0 | 47.0 | 124 |
| <i>n</i> -Butanol (catalyzed with 0.1mol % DBTDL) | DMAc | 25.0 | 51.0 | 96.0 |
| | diglyme | 21.0 | 47.0 | 105 |
| DETDA (2,4 and 2,6) | DMAc | 13.0 | 63.0 | 490 |
| | diglyme | 39.0 | 89.0 | 296 |

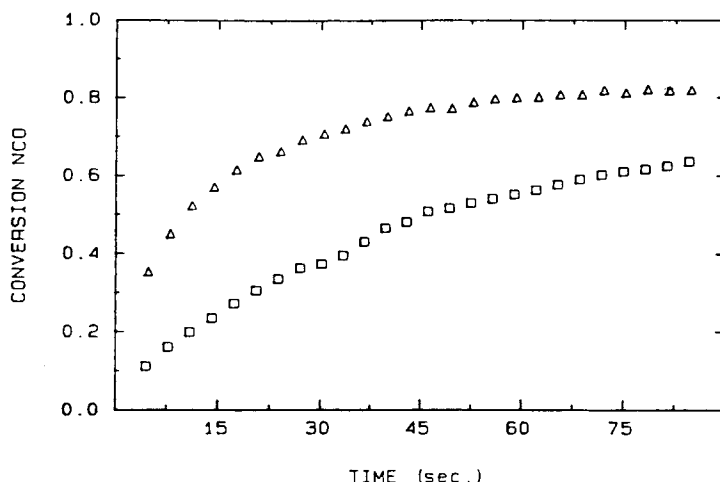


Fig. 9. Effect of changing solvent on the rate of the reaction of aniline with PI. (□) Diglyme; (Δ) DMAc.

50% conversion, the reaction times for the two solvents became closer for aniline. In the DETDA/PI reaction, times were actually shorter in diglyme than DMAc at high conversions, despite the slow initial rate in diglyme.

The catalyzed reaction of *n*-butanol and PI was virtually unaffected by the solvent change. Over a significant conversion range, reaction times from the two solvents were within experimental uncertainty. Since the dominant reaction path for this catalyzed reaction is the one involving the DBTDL, changes in reactant, product or solvent catalysis between DMAc and diglyme would not lead to large changes in reaction times.

Flow Experiments

The temperature traces for three thermocouples spaced along the length of the observation tube for a flow reaction of M600 and u-MDI are shown in Figure 11. The initial jump in temperature signals the start of injection. A variable length of time was required for the thermocouples to reach steady

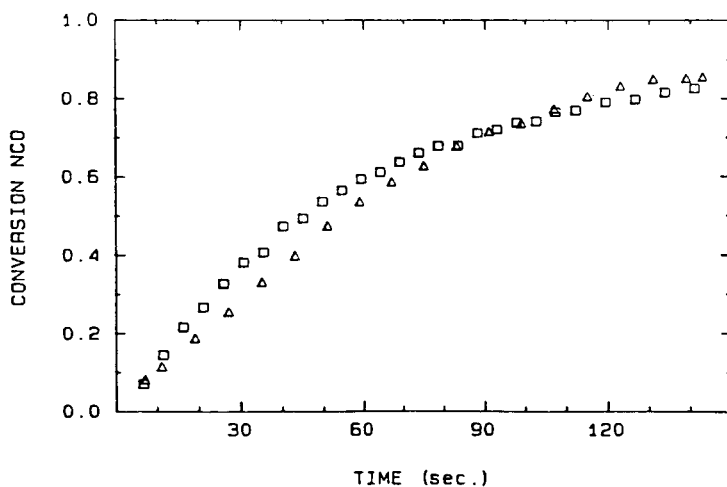


Fig. 10. Effect of changing solvent on the rate of the reaction of *n*-butanol with PI, catalyzed by 0.1 mol % DBTDL. (□) Diglyme; (△) DMAC.

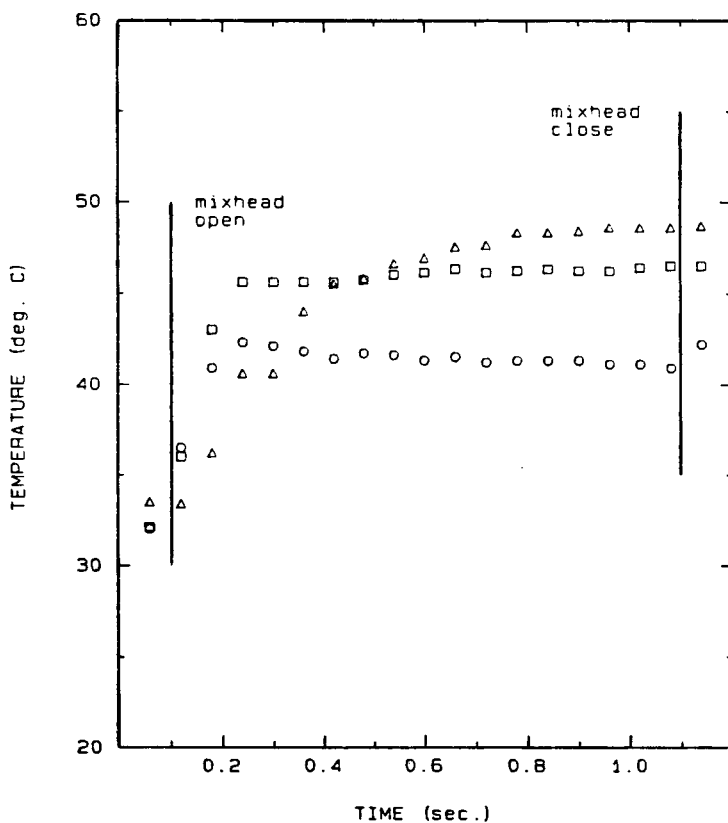


Fig. 11. Temperature vs. time data from one trial of the flow apparatus for the reaction of a polyether amine with u-MDI in diglyme. The thermocouples were located 1.11 (○), 2.89 (□) and 7.95 (△) cm from the impingement nozzles. Volume flow rate = 101.6 cc/s.

state. This variability may have been due to disturbances in the flow around the thermocouples or inconsistency in the thermocouple junctions themselves. Temperature was averaged over the second half of the shot only. In achieving maximum flow rates and minimizing the time to reach the first measurement point, shot times were restricted to 1.0-1.2 s.

The reaction exotherms were generated by plotting steady-state temperature vs. the time required to reach the thermocouples assuming plug flow in the tube. Uncertainty in time values was approximately 6% from the velocity and thermocouple position measurements. The overall exotherm predicted from the heats of reaction measured in the batch apparatus was $28.3 \pm .4^\circ\text{C}$. In two sets of runs conducted over a range of flow rates from 89 to 103 cc/s, the average exotherms were 28.4 and 27.0°C .

A slight dependence on flow rate was noted. The maximum conversion at any measurement point corresponded to the maximum flow rate even though the times to those points decreased with increasing flow rate. Since it is clear that a flow apparatus is needed to monitor these extremely rapid reactions, a more accurate apparatus is recommended to study mechanisms and generate models for polyurea RIM.

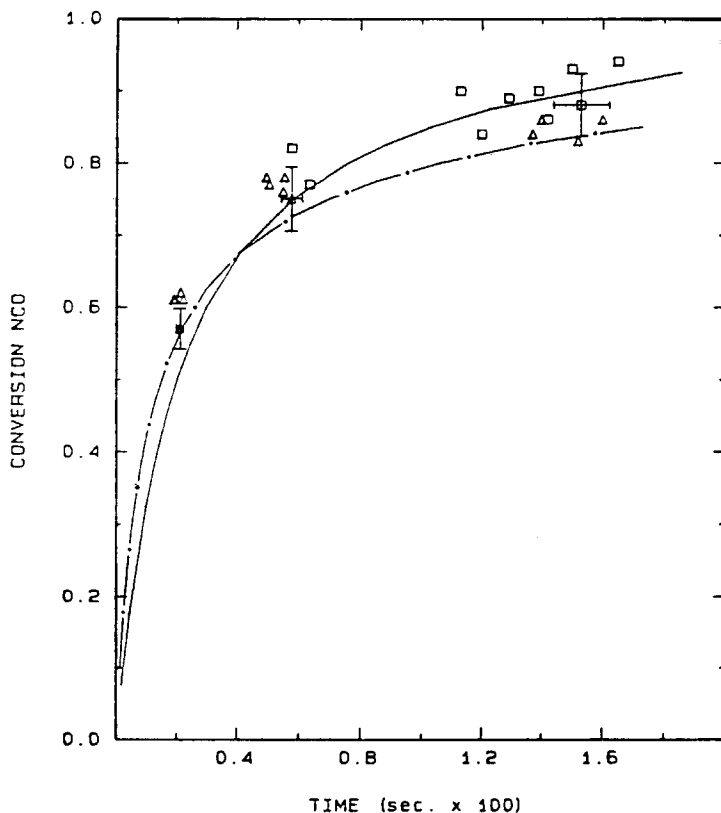


Fig. 12. Composite conversion curve, for the reaction of u-MDI with a polyether amine. Second- (---) and third-order (—) models included for reference. Each set of runs spanned several flow rates. The sets differed in location of the first thermocouple: (Δ) First set; (□) Second set.

Conversion vs. time data from the two sets of reactions, which differed in the position of the first thermocouple are shown in Figure 12. The minimum time that could be achieved was 1.92×10^{-3} s, and the conversion at that time was already 57%. Since all the data was confined to a narrow conversion range, it could not be used to generate a model. Sample exotherms for second and third order models that closely simulate the data are included in the figure.

The reaction rates for the aromatic amines used in this study were too low to be measured effectively in the flow apparatus. The difference in reactivity between the aliphatic and aromatic amines is so high that, when combined into a single system to react competitively with an isocyanate such as in polyurea RIM, the polymerization would be essentially sequential with the aliphatic amine reacting first, assuming good mixing.²⁵

CONCLUSION

Adiabatic solution reactions were proven to be applicable to comparing reactivity of alcohols and amines important to the RIM process and testing the effects of catalysts used in RIM. Relative reactivity can be compared simply in terms of reaction times, or using kinetic models when a range of conditions is included in the work.

Using calibration curves of adiabatic temperature rise vs. concentration, heats of reaction were found to have the ranking of aliphatic amine > aromatic amine > alcohol.

The batch reactions in solution showed that steric hindrance in the 4 position of DETDA slowed the reaction of the isomeric mixture of 2,4 and 2,6 DETDA used in commercial RIM systems relative to 2,6 DETDA before 50% conversion. The batch reactions also showed that the reaction rate for DETDA and PI decreased with conversion indicating that the urea formed by the reaction of the first amine group deactivates the aromatic ring toward further reaction. HPLC analysis of the product distribution from 2,6 DETDA/PI reactions with 2,6 DETDA in excess was used to determine the ratio of rate constants for the reactions of unsubstituted and monosubstituted DETDA. A value of $3.2 \pm .8$ was found.

As expected, DBTDL had a strong effect on the reaction rate for *n*-butanol and PI. Reaction times were reduced by an order of magnitude at 2 mol% DBTDL. However, DBTDL had no effect on the *o*-toluidine/PI reaction even at 2 mol%. DABCO had a much stronger influence on urea formation than on urethane, but only above 0.1 mol%. In hybrid urea-urethane RIM systems, catalysts are added to speed reaction relative to phase separation. Using DBTDL alone will greatly accelerate the urethane reaction and make its rate more competitive with urea formation. Since the second amine in DETDA is much slower than the first, the cure time itself could be limited by the chain extender, which can be catalyzed by the tertiary amine DABCO.

It is obvious that the use of these catalysts can dramatically change the order in which the components react in polyurea-urethane RIM systems. This will affect the phase separation and ultimate physical properties.

Initial reaction rates for uncatalyzed urea formation were decreased by changing the solvent from DMAc to diglyme. Catalyzed urethane formation

was unaffected by the solvent change. Diglyme should more closely simulate RIM process conditions.

It was necessary to use a flow apparatus to study the kinetics of the reaction of an aliphatic amine with an aromatic diisocyanate. The minimum conversion that could be measured was 57% at 1.92×10^{-3} seconds after mixing. Further work is needed to design an apparatus in which reaction mechanisms, kinetic models and the effects of diffusion on reaction rates can be determined. The capability of studying the whole range of reaction rates presented here in a single apparatus is also needed.

Under the competitive reaction conditions in three-component polyurea RIM systems, the aliphatic amine groups can be expected to react completely before appreciable reaction of the aromatic amine chain extender. It is doubtful whether a high enough level of catalyst could be used to produce the same situation (of the soft segment component reacting at a rate which is several times faster than the chain extender) in polyurea-urethane systems.

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NOTATION

| | |
|-------|--|
| D230 | 230 molecular weight amine-terminated polyether |
| M600 | 600 molecular weight amine-terminated polyether |
| D2000 | 2000 molecular weight amine-terminated polyether |
| DABCO | 1,4-diazabicyclo[2.2.2]octane |
| DBTDL | dibutyltin dilaurate |
| DETD | 3,5 diethyltoluene (2,4 and 2,6)-diamine |
| DMAc | dimethylacetamide |
| MDI | 4,4'-diphenylmethane diisocyanate |
| PI | phenyl isocyanate |
| u-MDI | uretonimine modified MDI |

General

| | |
|--------------|-----------------------------------|
| A | pre-exponential factor |
| C_i | concentration |
| C_p | heat capacity (J/g°C) |
| D | disubstituted DETDA |
| D_m | mixhead orifice diameter |
| E_a | activation energy |
| ΔH_r | heat of reaction |
| K_1, K_2 | rate constants |
| m | reaction order in active hydrogen |
| M | monosubstituted DETDA |
| n | reaction order in isocyanate |
| Q | volume flow rate |

| | |
|-----------------|---|
| r | mole ratio ($C_{\text{Ho}}/C_{\text{Io}}$) |
| r_a | reaction rate |
| R | universal gas constant |
| Re | Reynolds Number |
| t | time |
| T | temperature |
| T_{ad} | maximum temperature |
| ΔT_{ad} | overall temperature rise ($T_{ad} - T_o$) |
| T_{amb} | ambient temperature |
| U | heat transfer coefficient [$\text{J}/(\text{cc}^\circ\text{Cs})$] |
| Un | unsubstituted DETDA |
| α | fractional conversion of the limiting reagent |
| ρ | density |
| μ | viscosity |

Subscripts

| | |
|---|-----------------|
| I | isocyanate |
| H | active hydrogen |
| o | initial value |

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