# Mixing Effects During Polymerization by the Adiabatic Temperature Rise Technique

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## Introduction

The most common method used for obtaining kinetic data for polyurethane polymerizations is the adiabatic temperature rise (ATR) experiment. The temperature of an adiabatic polymerizing mixture can be related directly to monomer conversion, thus providing simple conversion vs. time measurements.

Lipshitz and Macosko (1977) and Richter and Macosko (1978) performed ATR measurements on cross-linking polyurethanes with the goal of fitting kinetic schemes to their data. Lee et al. (1980) and Kolodziej et al. (1982) also used ATR experiments, but for another purpose, which was to quantify the quality of mixing for reaction injection molding (RIM) materials in an impingement mixhead.

In this note we present new experimental data comparing linear and cross-linking polymerizations. The effect of catalyst location, which had not been examined before, is also studied.

## Experimental

### *Materials*

The cross-linking system consists of a trifunctional polyol (TONE 0305, Union Carbide) and a diisocyanate (143-L, Upjohn). The trifunctional polyol is a polyester-based material with a molecular weight of 540 kg/kmol. The diisocyanate is a liquid form of diphenylmethane diisocyanate (MDI) with an isocyanate equivalent of 143.7 kg/kmol NCO. The linear system consists of two diols and a diisocyanate. The diols are 1,4 butane diol (BDO) for the chain extender and ethylene oxide end-capped polypropylene oxide (NIAX 12-56, Union Carbide) (PPO) for the long chain flexible diol. Pure MDI (Mondur-M, Upjohn) was used in these experiments. The diols and trifunctional polyol were degassed before use. The liquid form of MDI (143-L, Upjohn) was used as received. The solid form (Mondur-M, Mobay) was melted and filtered at 60°C.

### *Apparatus*

A small batch stirred tank reactor (BSTR) was chosen to perform the ATR experiments; the apparatus is pictured in Figure 1. Since the bulk polymerization produces a polyurethane block in the reactor, the beakers and impellers in the BSTR were discarded after each run. The impellers were four-bladed turbines handmade from 0.00083 m thick aluminum sheet and 0.0079 m wooden dowels; their dimensions are shown in Figure 1.

An iron-constantan (type J) thermocouple was hooked directly to a Cole Parmer model 8373-20 two-pen chart recorder. The constant-speed motor and controller system used was a model HST20N made by G. K. Heller Corp. with a speed range of 0 to 2,000 rpm.

### *Procedure*

The experimental procedure is simple, and experiments may be performed quickly and reproducibly. The basic concept is due to Fisher (1974), who studied acid-base reactions in a BSTR. He separated the reactants initially using a rubber membrane formed by pouring a rubber solution onto the acid phase and allowing the solvent to evaporate. The base was then added on top of the membrane. This configuration was used so that he had a well-defined initial condition for the rapid reaction. An experiment was started by energizing an impeller that ruptured the membrane and allowed mixing of the reactants.

A similar procedure is employed in our ATR experiments. A rubber membrane is not required, however, because the monomers react to form an impervious polymer skin when layered, which effectively shuts off the polymerization. Thus, if the monomers are layered carefully, a reproducible initial condition is guaranteed.

## Conditions

### *Cross-linking system*

The cross-linking system was used to examine the bulk polymerization behavior as a function of mixing level (impeller

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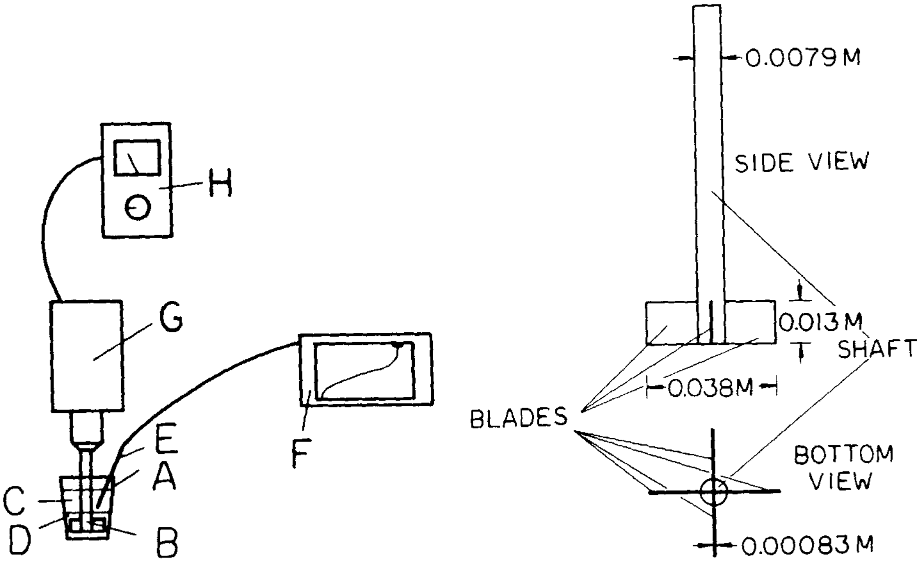

**Figure 1. Experimental apparatus.**

A. Insulated 100 mL plastic beaker
B. Disposable impeller
C. Diol or triol phase
D. Diisocyanate phase
E. Thermocouple
F. Chart recorder
G. Constant-speed motor
H. Motor controller

speed) and catalyst location. A layer of 35.51 g of 143-L diisocyanate was placed in a 100 mL plastic beaker and 44.49 g of degassed TONE 0305 trifunctional polyol were added on top of this. An impeller was placed so that it was nearly in contact with the bottom of the beaker. The impeller was energized for 10 s in all experiments. Dibutyltin dilurate catalyst was added in either phase at a level of 0.1 wt. % based on the polyol weight. The initial temperature for all the runs was room temperature (~25°C).

*Mixing Level.* Experiments were performed with the catalyst in the trifunctional polyol phase at four rotational speeds, 250, 375, 500, and 750 rpm (an equivalent experimental procedure is to keep the rpm constant and to change the time of mixing). The tank circulation time under these conditions is approximately $10^{-1}$ s. The experiments gave temperature rises in the range 100 to 140°C, and had durations of approximately 1 min. At the end of the polymerization all samples were yellow in color due to the yellow color of the MDI used, and were transparent. At low mixing speeds striations were visible to the unaided eye and unreacted polyol remained in a thin layer (several millimeters thick) on top of the samples. The experimental curves for the mixing speeds mentioned above are displayed in Figure 2a. As the impeller speed is increased, the initial rate of reaction is enhanced and the total temperature rise increases.

*Catalyst Location.* Experiments were performed at 250 and 750 rpm with the catalyst placed in either phase. The temperature rises obtained ranged from 120 to 140°C and these experiments had an approximate duration of 1 min. The appearance of the samples did not change significantly as a function of catalyst location, and was again yellow and transparent. The experimental curves are shown in Figures 2b and 2c for 250 and 750 rpm, respectively. When the catalyst is placed in the diisocyanate phase, the temperature rises more rapidly than when the catalyst is placed in the polyol phase.

### *Linear system*

The linear system was also used to examine the bulk polymerization behavior as a function of mixing level (impeller speed) and catalyst location. A layer of 27.72 g of diphenylmethane diisocyanate (Mondur-M, Mobay) was placed in a 100 mL plastic beaker and 52.28 g of degassed diol and polyol mixture (BDO/PPO molar ratio = 4/1) were added on top of this. The impeller was placed so that it was nearly in contact with the bottom of the beaker. The impeller was energized for 10 s in all experiments. Dibutyltin dilaurate catalyst was added in either phase at a level of 0.01 wt. % based on the polyol weight. The initial temperature for all the runs was 60°C.

*Mixing Level.* Experiments were performed with the catalyst in the polyol phase at three rotational speeds, 125, 250, and 500 rpm. The tank circulation time under these conditions in approximately $10^{-1}$ s. The experiments gave temperature rises in the range 90 to 125°C, and had durations of approximately 1 min. At the end of the polymerization the samples were white in color and opaque. At low mixing speeds striations were visible to the unaided eye and unreacted polyol remained in a thin layer (several millimeters thick) on top of the samples. The experimental curves for the mixing speeds mentioned above are displayed in Figure 3a. As the impeller speed is increased, the initial rate of reaction is enhanced and the total temperature rise increases.

*Catalyst Location.* Experiments were performed at 250 and 500 rpm, with the catalyst placed in either phase. The temperature rises obtained ranged from 100 to 125°C, and these experiments had an approximate duration of 1 min. The appearance of the samples did not change significantly as a function of catalyst location, and was again white and opaque. The experimental curves are shown in Figure 3b and 3c for 250 and 500 rpm, respectively. There is no significant difference, within experi-

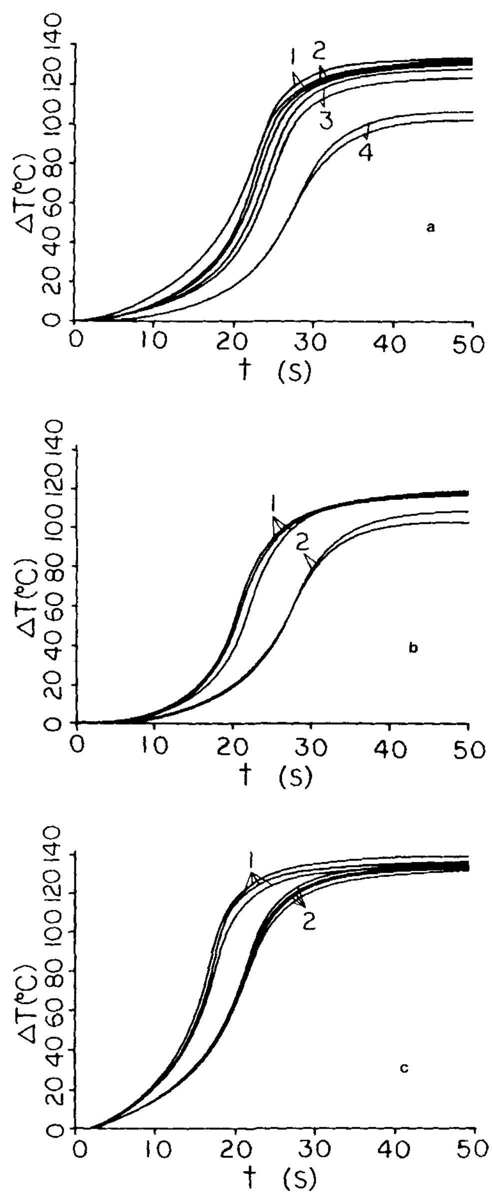

**Figure 2. Cross-linking system.**

a. Effect of mixing. (1) 750 rpm; (2) 500 rpm; (3) 375 rpm; (4) 250 rpm.
b. Effect of catalyst location at 250 rpm. (1) Catalyst in diisocyanate phase; (2) catalyst in polyol phase.
c. Effect of catalyst location at 750 rpm. (1) Catalyst in diisocyanate phase; (2) catalyst in polyol phase.

mental error, between the runs with the catalyst in the polyol phase and those with the catalyst in the diisocyanate phase; this is observed for both impeller speeds.

## Results

### *Effects of mixing level*

Both urethane systems studied are mixing-sensitive. As the rotational speed of the impeller is increased, the initial rate of reaction and the ultimate temperature rise are increased. At high levels of mixing, a limiting curve is approached that corresponds to a mixing scale where diffusion ceases to be the controlling mechanism. Lee et al. (1980) and Kolodziej et al. (1982) reported comparable results. Chella and Ottino (1983) presented a diffusion-reaction model for the cross-linking system that predicted these results.

The cross-linking system was always clear during the experiment. The linear system was cloudy initially, then clear midway through the experiment, and then cloudy at the end. The cross-linking system displayed somewhat larger changes in ATR behavior as a function of mixing level. This may be seen by comparing Figures 2a and 3a. The differences between these systems lies mainly in the polymeric structure formed, which is a network in the cross-linking system and a group of linear chains in the linear system. The end groups in the cross-linking system are probably less mobile, especially at high conversions, than those in the linear system. The behavior of the cross-linking system is therefore more influenced by diffusional resistances, and if significant monomer segregation exists (poor mixing) the cross-linking system is more strongly affected. This conclusion was also noted by Kolodziej et al. (1982), who found that the ATR technique was less sensitive for probing mixing levels in linear systems than in cross-linking systems.

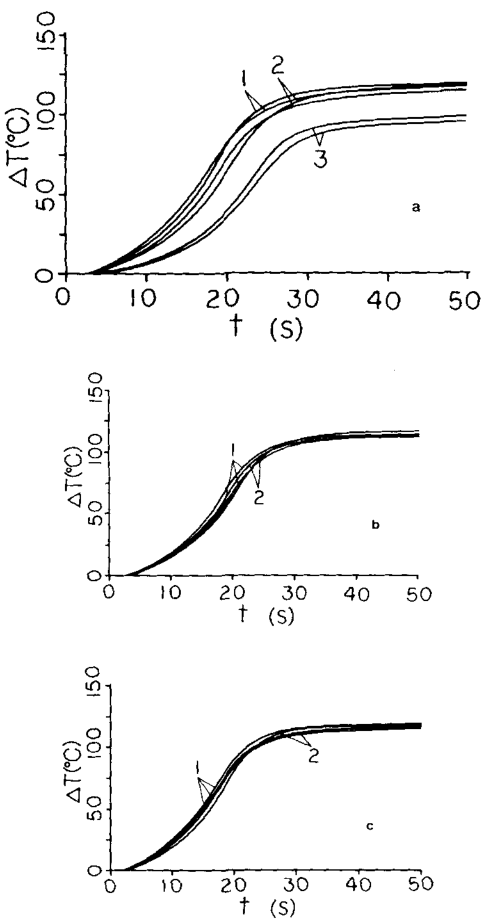

**Figure 3. Linear system.**

a. Effect of mixing. (1) 500 rpm; (2) 250 rpm; (3) 125 rpm.
b. Effect of catalyst location at 250 rpm. (1) Catalyst in diisocyanate phase; (2) catalyst in polyol phase.
c. Effect of catalyst location at 500 rpm. (1) Catalyst in diisocyanate phase; (2) catalyst in polyol phase.

### *Effect of catalyst location*

In industrial applications the catalyst is usually mixed with the diol phase, mostly due to storage considerations. The cross-linking system showed substantial changes in its ATR behavior as the location of the catalyst was changed. When the catalyst was contained in the diisocyanate phase, the polymerization proceeded more quickly than when the catalyst was in the polyol phase (a given temperature, e.g. 80% max., is reached in roughly half the time). Since this effect was more severe at lower mixing levels, as may be noted by comparing Figures 3b and 3c, we believe that this phenomenon is at least partly associated with diffusion-reaction interactions arising from imperfect mixing. Thus, the overlap of the monomer and catalyst concentration profiles is different when the catalyst location is changed, resulting in different ATR behavior. However, since this effect was also noted at relatively high speeds (750 rpm), for which the system may have been kinetically controlled, we cannot rule out chemical effects such as complexation. Also, it might be conjectured that the catalyst location could very well have changed the boundary conditions at the interface of reaction due to surfactant qualities of the catalyst. However, other work in our interfacial microstage reactor similar to that reported by Fields et al. (1986) did not show differences in interfacial stability when the catalyst location was changed.

In contrast, the linear system did not show significant changes in ATR behavior as the catalyst position was changed (even at lower rpm than the cross-linking system). This is probably due to the linear system being less severely diffusion-controlled than the cross-linking system. Also, chemical effects do not seem to be present in this case.

The ability to predict successfully the consequences of catalyst location is a necessary requirement for models of ATR in linear and cross-linking systems. Current models in the literature (Chella and Ottino, 1983) cannot account for this effect. Simulations show that the rather large scatter inherent in ATR data may be the result of striation thickness distribution (Fields and Ottino, 1986) and small variations in the fluid mechanical history (Fields and Ottino, 1986). The experimental scatter is most likely due to these two effects. This scatter may obscure the observation of small changes in behavior, and may be the reason that one does not detect significant changes in the linear system behavior with different catalyst locations.

## Acknowledgment

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