# KINETICS OF POLYURETHANE FORMING REACTIONS GELLING SYSTEMS

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## ABSTRACT

An important polymer having wide industrial applications across the industry is polyurethane. The *use of this polymer extends from simple foams to rigid panels and components of various tools and finished products prepared by reaction injection moulding.* Kinetic studies in $RA_2$ and $RB_3$ polymerisations reveal equal reactivity of functional groups during network-forming reactions of polyurethane gelling systems, both before and after the gel point. The importance of intramolecular reaction in such polymeric systems is further confirmed and analyzed in relation to catalyst addition and / or dilution of the initial reactants.

*Keywords: Triol characteristics, Gel interaction, Intermolecular reaction.*

## INTRODUCTION

The present study formed part of an overall investigation into the rheology of polyurethane gelling systems [1].

Kinetic studies and its relation to the gelation phenomena in non-linear network-forming reaction systems of the present type have been extensively discussed in relation to both polyesters and polyurethanes by various researchers [2-15]. The aim of the present work is to supplement the kinetics and gelation studies on aliphatic polyurethane-forming networks, and extend the kinetic studies well beyond the gel point. Thus, the molecular growth of the network chains from the kinetics and gelation studies can be related to the measured physical properties in rheological details, prior to the gelation and past the gel point.

## EXPERIMENTAL

Polyoxypropylene triols of various molar masses (supplied by Union Carbide) were reacted with hexamethylene diisocyanate (Aldrich chemicals) at 70° C, both in bulk and in solution with nitrobenzene (BDH Chemicals). Some of the reactions were also catalyzed with DABCO, chemically known as 1,4 diazobiscyclo [2,2,2] octane (BDH Chemicals), and the consequent effects on the reaction kinetics and gelation phenomena analyzed.

The Niax triols used in the present work consisted of both the higher molar mass, LHT 112 and the lower molar mass, LHT 240. Their respective equivalent weights along with the purification and analytical details are given in Table (1). The hexamethylene diisocyanate, HDI used had acceptable equivalent weights in the range of 83.80-84.45, compared with the theoretical value of 84.10. The experimental details for determining the above parameters, along with the relevant kinetic and gelation equations are described Elsewhere [1].

Combining all the rate expressions, the rate of formation of urethane may be expressed as:

$$dx/dt = k_1 k_3 (a-x)(b-x)^2 / [k_2 + k_3(b-x)]$$
$$+ k_1' k_3' (a-x)(b-x)^2 / [k_2' + k_3'(b-x)]$$
$$+ k_1'' k_3'' (a-x)(b-x)^2 / [k_2'' + k_3''(b-x)] \qquad (1)$$

Table 1. Triol characterization data.

| Triol | Expt | % w/w | Equivalent of $H_2O$ | % unsaturation= | Equivalent weight |
|---|---|---|---|---|---|
| | Nos. | of water | /Equivalent of OH | 1 Equivalent of triol | /g mol$^{-1}$ |
| LHT 240 | $R_1$-$R_6$ | 0.044 | 0.0018 | 0.0452 | $260.9 \pm 0.40$ |
| LHT 112 | $C_5$-$C_7$ | 0.025 | 0.0017 | 0.0694 | $398.7 \pm 4.0$ |
| | $R_7$ | 0.017 | 0.0046 | * | $478.0 \pm 2.0$ |

* Unsaturation present in this sample was checked only by IR spectra (peak at $5.9\mu$ or 630 cm$^{-1}$)

where the first term in the right hand side is for the OH catalysis, the second term for autocatalysis, and the last term for the added catalyst. Hopkins [3] simplified the expression in equation (1) for added catalyst, and obtained:

$$dx/dt = k'' \text{ (catalyst) } (a-x)(b-x) \qquad (2)$$

where $k''$ is the second order rate constant, $k_2$, divided by the initial catalyst concentration, while $(a-x)$ and $(b-x)$ are the usual concentrations of isocyanate and hydroxyl groups, respectively.

## RESULTS AND DISCUSSION

### Kinetic Studies

The kinetic plots of Figure (1) show that in the absence of catalysts, both bulk and nitrobenzene diluted reaction tend to follow a rate of reaction between first and second order. This behaviour persists even with small additions of DABCO catalyst, less than 3% [DABCO]/[NCO]$_o$. However, addition of more than 3% of the catalyst to the initial isocyanate concentration, results in second order kinetics as is evident from $R_3$ Figure (1) and experiments $C_5$, $C_6$ Figure (2) using LTH 112 and HDI. This agrees well with the results of Hopkins [3], who showed that for bulk catalyzed reactions of LHT 240 and LHT 112 with HDI separately, second order kinetics were obtained, provided DABCO concentration 5% (mole) of the initial

isocyanate concentration, [NCO]$_o$.

In order to investigate the effect of catalyst on the third order rate constant $k''$, Table (2) was compiled for the reaction of LHT 112 and HDI at 70°C, containing varying amounts of DABCO. $k''$ was determined using equation (2) above. Table (2) shows $k''$ is independent of the catalyst concentration within the errors involved in the evaluation of $k_2$. It also shows that the second order rate constant, $k_2$ is an increasing function of the initial catalyst concentration.

Table 2. Effect of catalyst on the third order rate constant, $k''$.

| Experiment | [DABCO]/[NCO]$_o$ mol% | $k_2$/kg mol$^{-1}$ *10 $^3$/min$^{-1}$ | $k''$/kg$^2$ mol$^{-2}$ min$^{-1}$ |
|---|---|---|---|
| $C_5$ | 3.652 | 6.500 | 1.78 |
| $C_6$ | 3.200 | 5.500 | 1.72 |
| $C_7$ | 1.874 | 5.200 | 1.80 |

### Gelation studies

For the range of dilutions (Bulk to 40% of monomers by weight) and DABCO catalyzed reactions studied in the present work, gelation was found to occur at reaction extents higher than those predicted by the Flory and Stockmayer theory of Gelation [5], according to which

$$\alpha^{-1}_c = (P_A P_B)_c^{-1} = (f——1) \qquad (3)$$

## Table 3. Intramolecular branching parameter data.

| Experiment No. | | Catalyst concent. [DABCO]/[NCO]$_0$/% | monomer conc. / w/w % | Reciprocal initial conc. [OH]+[NCO]$^{-1}_0$ | Reciproc conc. at gel | $\lambda'_{ab}$ |
|---|---|---|---|---|---|---|
| LHT 112 | C$_5$ | 3.652 | 100 | 0.2424 | 0.9184 | 0.0409 |
| & | C$_6$ | 3.200 | 100 | 0.2422 | 0.8903 | 0.0296 |
| HDI | C$_7$ | 2.874 | 100 | 0.2421 | 0.8271 | 0.0003 |
| LHT 240 | R$_1$ | 0 | 100 | 0.1728 | 0.9361 | 0.1532 |
| & | R$_2$ | 1.359 | 100 | 0.1728 | 1.1656 | 0.2030 |
| HDI | R$_3$ | 3.982 | 100 | 0.1742 | 1.2968 | 0.2242 |
| | R$_4$ | 0 | 70.0 | 0.2243 | 1.2952 | 0.1693 |
| | R$_5$ | 0 | 60.7 | 0.2398 | 1.4174 | 0.1749 |
| | R$_6$ | 0 | 40.0 | 0.2760 | 1.6567 | 0.1786 |
| LHT 112 & HDI R$_7$ | | 0 | 100 | 0.2810 | 1.2583 | 0.0984 |
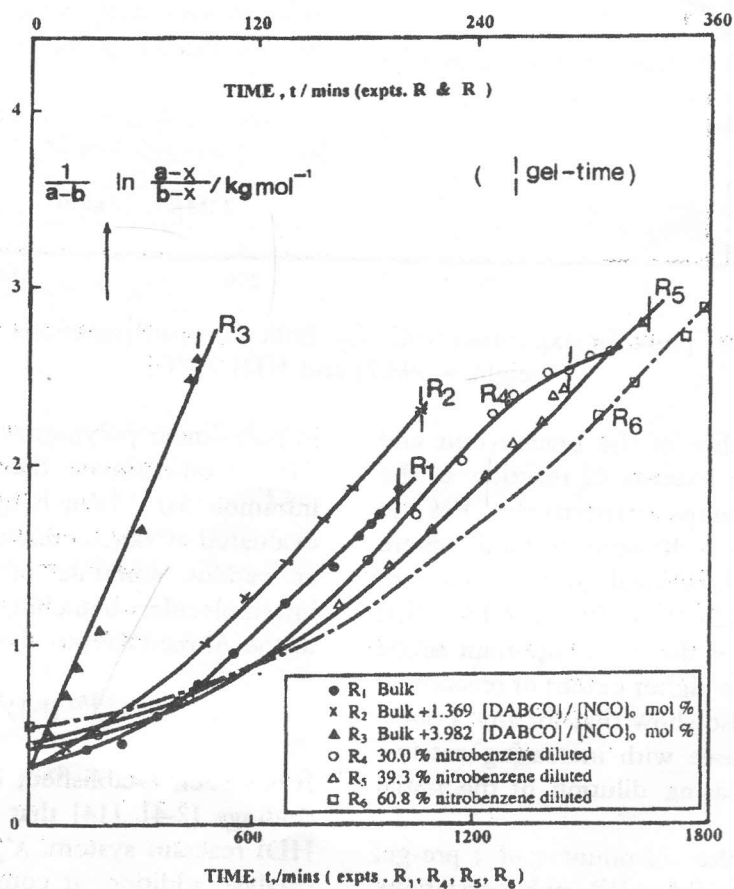


Figure 1. Second order plots for experiments R$_1$-R$_6$ LET 240 (equivalent weight = 260.9) and HDI at 70°C.
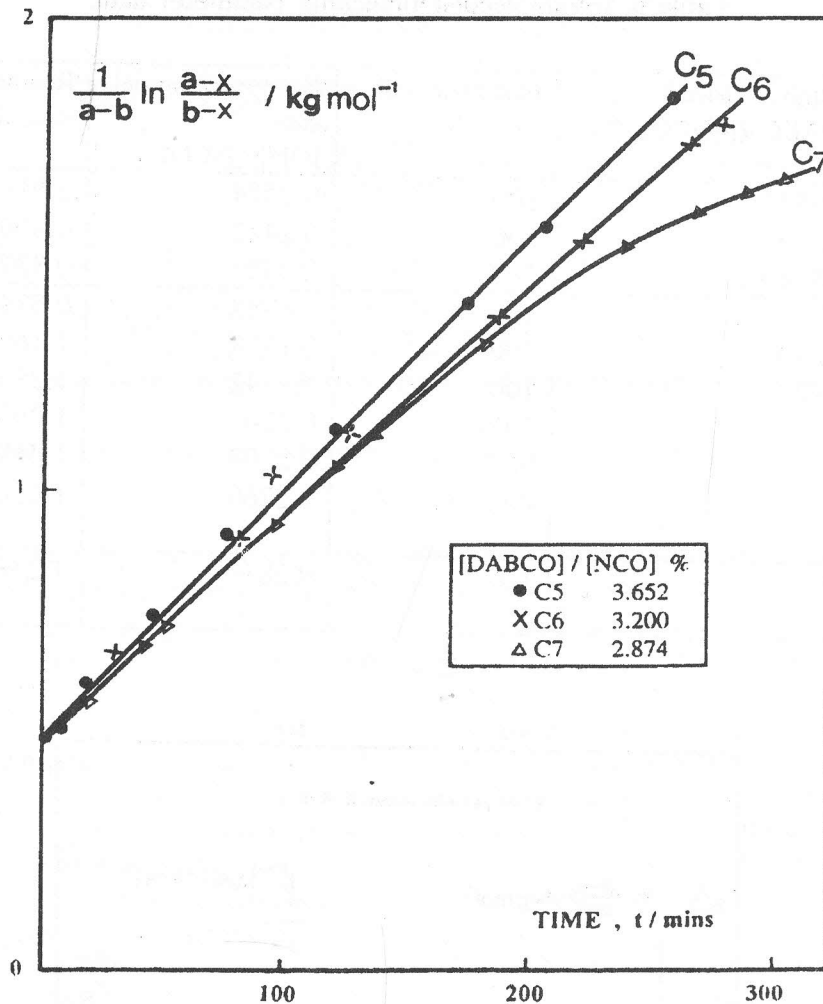
Figure 2. Second order plots for experiments $C_5$-$C_7$. Bulk catalysed reactions of LET 112 (equivalent weight = 398.7) and HDI 70°C.

Here, f is the functionality of the branch unit and $(P_A)_c$ and $(P_B)_c$ are the extents of reaction at the gel–point of A and B groups, respectively. For the experimental systems which were studied, where equal reactivity of like functional groups is assured, it was established [2-4], [6-9], [12-13] that intra-molecular reaction is the most important single factor responsible for the higher extent of reaction at gelation. The results also show that for any Triol – HDI reaction, $\alpha_c$ increases with increasing catalyst concentration and increasing dilution of the initial reactants.

Measurement of the amount of pre-gel intramolecular reaction in $RA_2$+ $RB_3$ polymerizations [9] showed that such reaction can rarely be neglected in non–linear polymerization, even in bulk.

Using approximate theories of gelation [10-13], the intramolcular branching parameter, $\lambda'_{ab}$ was evaluated at various dilutions with nitrobenzene and at various amounts of catalyst Table (3). The intramolecular branching parameter, $\lambda'_{ab}$ according to the Ahmed-Stepto theory [13] is given by:

$$\alpha_c^{1/2} (f-1)^{1/2} - 1 = \lambda'_{ab} \qquad (4)$$

It has been established, in confirmation with earlier findings [2-4], [14] that for a particular polyol and HDI reactant system, $\lambda'_{ab}$ increases with increasing catalyst addition at constant dilution. The $\lambda'_{ab}$ is found to increase with increasing catalyst addition in

all of the triol-HDI systems. Catalyst addition, hence, results in an increasing amount of intramolecular reaction in the present systems similar to the findings of Hopkins [3] and Hunt and co—workers [16].

Hunt and co—workers [16] explained this increasing $\lambda'_{ab}$ with catalyst as perhaps due to increasing side reactions causing non-branching reactions. Allophanate formation is probably insignificant as a side reaction as indicated from earlier IR studies [1]. As observed by Ahmed [2] for polyester systems and systems and Hopkins [3] for polyurethane systems, a higher molar triol, containing more oxypropylene units produces less intramolecular reaction in the polyurethane—forming reactions of the present type. The $\lambda'_{ab}$ values are thus lower for experiments $C_5 - C_7$ of reaction between LHT112 and HDI, when compared with experiments $R_1 - R_3$ of reactions between LHT 240 and HDI. A smaller molar mass of triol means that fewer bonds on the average separate a pair of unreacted groups on a chain. These groups are therefore more proximate to each other, resulting in an increasing intramolecular reaction.

As for the effect of dilution on the gelation data, it is evident from earlier work [2,3] and this study, that the probability of intramolecular reaction increases with dilution. Similar to Ahmed's result, $\lambda'_{ab}$ was found to show a linear dependence on initial dilution and a slight curvature for dilution at gel.

*Post-gel studies*

After the gel, the reaction mixture consists of two pairs, the gel fraction and the sol fraction. The reaction continues until only the gel remains. The post-gel reaction is difficult to investigate because of the extremely high viscosity and structural complexity of the reactant mixture.

Figures (3) and (4) for experiments $R_2$-$R_5$ and Figure (5) for experiment $R_7$ show typical post—gel kinetics as well as conversion plots, for experiments involving both a low and a high molecular weight triol and HDI.
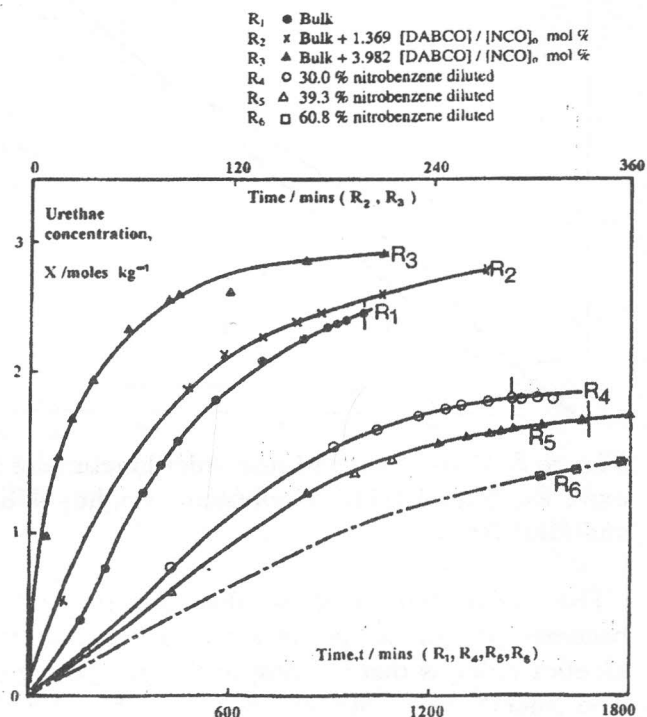
$R_1$ ● Bulk
$R_2$ ✕ Bulk + 1.369 [DABCO] / [NCO]$_0$ mol %
$R_3$ ▲ Bulk + 3.982 [DABCO] / [NCO]$_0$ mol %
$R_4$ ○ 30.0 % nitrobenzene diluted
$R_5$ △ 39.3 % nitrobenzene diluted
$R_6$ □ 60.8 % nitrobenzene diluted



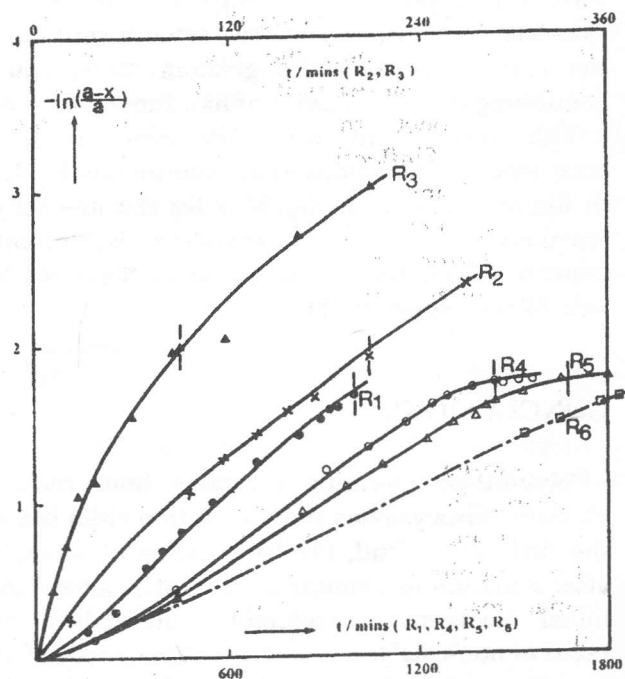Figure 3. Conversion curves for expts $R_1$-$R_5$, LHT 240 (Equivalent weight = 260.9) and HDI at 70°C.



Figure 4. First order kinetic plots for expts. $R_1$-$R_6$, (LET 240, Equivalent weight = 260.9 and HDI at 70°C).
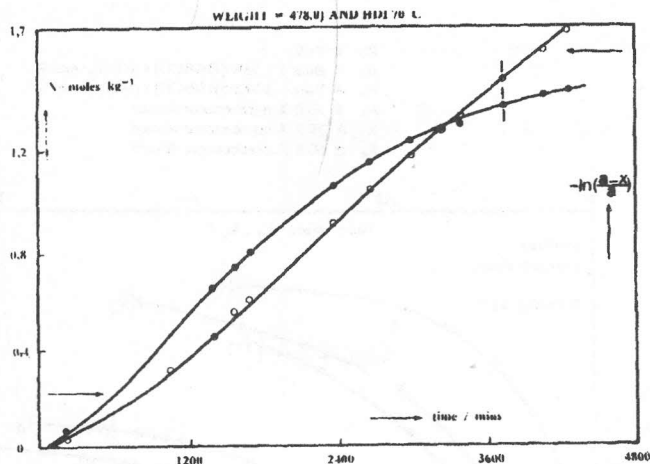
Figure 5. Conversion and first order kinetic plot for expt. $R_7$, Bulk LH112 (Equivalent weight - 478.0) and HDI 70°C.

The above figures show that the sol friction becomes part of the gel in more or less the same kinetics order as that existing in the pre-gel region. The smooth conversion curves, given the difficulty and errors involved in the measurement of the urethane content in the post-gel period due to swelling of the gel by the di—n—butyl amine/toluene solvent and possible trapping of some unreacted isocyanate groups, indicate the smooth continuity of the reaction beyond the gelatoin stage, and the continuing equal reactivity of like functional groups.

With respect to the conversion plots, the occurrence of inflections as in experiments $R_1$, $R_4$-$R_6$ in figure 3 and $R_7$ In figure 5 for the un-catalysed reactions, shows that autocatalysis is present as expected from the second term in the right hand side of the equation (1).

## CONCLUSIONS

Polyurethane—forming reactions from triols and aliphatic diisocyanates show a reaction order between the first and second, the latter being obtained only after a minimum amount of catalyst is added to the initial reactants. Considerable autocatalysis takes place in non-catalyzed reactions. The reactions show an increased intramolecular reaction with catalyst addition and/or dilution of the initial reactants. Equal reactivity of like functional groups seems plausible well beyond the gel point.

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