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**Gel Permeation Chromatographic Analysis of  
Polyurethane Prepolymer Synthesis Kinetics.**

**I. The Effect of Catalyst**

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# Gel Permeation Chromatographic Analysis of Polyurethane Prepolymer Synthesis Kinetics.

## I. The Effect of Catalyst

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### Synopsis

Polyurethane prepolymers are a complex mixture of oligomers. The proportion of the various species in this mixture determines the handling properties of the prepolymer as well as the physical properties of the final polyurethane. An analytical method has been developed that gives a clear and sensitive picture of both the reaction kinetics and the concentrations of the oligomeric species in the prepolymer mixture. The analytical method is applied to the polypropylene glycol/tolylene diisocyanate/catalyst system. The expected changes in reaction rates and in the formation of higher oligomers in the prepolymer were observed when catalyst was added at three different polyol molecular weights. An alternative equation for predicting the number average degree of polymerization is developed for the cases where reactant ratios are significantly less than one. An empirical equation is derived that permits expressing the reaction kinetic data in a linear plot. This equation is used to express the results of this work.

### INTRODUCTION

The preparation of polyurethanes with specific properties requires starting materials with well-defined composition. A great deal of lore has built up around the issue of how to prepare polyurethane prepolymers with the most convenient handling properties and with the potential to produce final products with the most attractive physical properties. Certainly the literature contains a theoretical basis for understanding how the properties of prepolymers might depend on the reaction parameters, but there has not been a practical analytical procedure for determining the concentrations of the individual species that are present. Indeed, in large part the analysis of the polyurethane prepolymers has been limited to titrations and physical tests which give only averages of end-group concentrations or molecular weights. Furthermore, the data available in the literature contains few details about the functionality or oligomer distribution of the prepolymer. Thus this research effort was intended to develop analytical techniques that would give a detailed description of the species present in a polyurethane prepolymer. This paper reports the application of these techniques to a study of the effect of a catalyst on the distribution of oligomer species. Other work in progress is

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addressing the application of these analytical techniques to the effects of reactant ratios and molecular weights.

The potential of size exclusion chromatography or gel permeation chromatography (GPC) as an analytical tool to be applied to oligomers has been recognized in the literature.<sup>1,2</sup> Cazes et al.<sup>3</sup> applied HPLC to a study of the kinetics of polyurethane polymerization. Alfredson<sup>4</sup> demonstrated that liquid chromatography could be used to separate the polyols and diisocyanates used in preparing polyurethanes. Recently, Furukawa and Yokoyama<sup>5</sup> also described the analysis of polyurethane prepolymers by gel permeation chromatography after derivatization. Their study did not succeed in separating the various oligomers in the prepolymer. Furthermore they used methanol as the derivatizing reagent and thus their reaction required several hours to complete. They addressed the analysis of reaction mixtures with several different stoichiometries, but the principal thrust of their work was the analysis of the products from amine degradation of the cured polyurethane. Papazian<sup>6</sup> demonstrated the use of gel permeation chromatography by applying it to the reaction products of excess aliphatic diisocyanate with trimethylol propane. The latter study achieved moderate separation of the oligomer species, but did not draw any conclusions regarding the polyurethane reaction conditions. In none of these studies was a capping agent selected so as to enhance the sensitivity of the detection.

## EXPERIMENTAL

### Preparation of Quenching Reagent

A reagent to be used to react with and to stabilize the isocyanate groups should have the properties of ease of handling, rapidity of reaction with the isocyanate, and contribution to the detectivity of the analyzed species. *N*-4-nitrobenzyl-*n*-propylamine (PNBP) has been used to derivatize hazardous diisocyanates prior to their colorimetric analysis.<sup>7</sup> PNBP has the properties desired in that it imparts a relatively high molar absorptivity when it reacts with an isocyanate. PNBP reacts rapidly and quantitatively with isocyanate and it is readily purified for laboratory use. PNBP was acquired from Aldrich Chem. Co. (No. 22, 191-0) and was purified before use as follows. Approximately 1 g of the reagent was dissolved in 45 mL of 0.08M HCl. This solution was washed twice with 75 mL of chloroform and the wash was discarded. The aqueous solution was made basic with 20 mL of 1M NaOH and was washed twice with 75 mL of chloroform. The chloroform solutions, which contain the PNBP, were combined and dried by passing them through a funnel fitted with Whatman 1PS filter paper containing anhydrous sodium sulfate. This solution was stored in the dark at 10°C until use.

### Preparation of Prepolymer Samples

The prepolymer samples were prepared from Dow Chemical Co. Voranol brand poly(propylene ether) glycol (abbreviated PPG or polyol) with a variety of molecular weights as specified. An 80 : 20 isomer ratio mixture of 2,4- and 2,6-tolylene diisocyanate (abbreviated TDI, Polysciences, Inc. No. 3934, as received) was used. Where a catalyst was specified, ferric acetylacetonate

(FAA, as received from Aldrich Chemical Co.) was used. The prepolymers were made by mixing a weighed quantity of the TDI with a weighed, preheated 3 g sample of the PPG polyol. Where a catalyst was required, FAA was dissolved in the PPG in a concentration equal to 0.1% by weight of the PPG. All weighings were made to an accuracy of  $\pm 0.0001$  g. After the TDI and the polyol were mixed, they were placed in a desiccator in an oven maintained at  $50 \pm 1^\circ\text{C}$ . After the stated reaction time, a small portion (ca. 0.015 g) was transferred from the reaction flask to a small test tube. The sample was weighed and 3–5 mL of the PNB solution was added and diluted to 10.0 mL with chloroform. PNB was always seen to be present in significant excess as evidenced by the appearance of a peak in the chromatogram that corresponds to unreacted PNB. Mixing of the sample of prepolymer with PNB was completed within 0.5 min. Reaction of the isocyanate with the PNB was very fast. Analysis showed the reaction to be complete in less than 2 min in every case.

### Gel Permeation Chromatography

GPC was used to separate and measure the concentrations of the species in the prepolymer. A Waters Associates Model 510 pump was used with a Valco Model 7125 manual injector fitted with a 25  $\mu\text{L}$  injection loop. UV-grade tetrahydrofuran was used as the mobile phase at a flow rate of 1.3 mL/min. PL-Gel 5- $\mu\text{m}$  particle size GPC columns of nominal pore sizes 50, 100, 500, and 1000 Å were used. The absorbance maximum of the stabilized prepolymer was found to be 269 nm, very near the absorbance maximum of the unreacted PNB (267 nm) and of a sample of PNB-stabilized TDI (275 nm). The variable-wavelength UV detector (Beckman Model 165) was set at 269 nm. The absorbance versus concentration was determined for a series of PNB-stabilized prepolymers. They were seen to follow Beer's Law over the range of interest in this study. Central to the calculations made in this work is the assumption that the absorptivity per mole of capped oligomeric species is constant. This is equivalent to saying that all of the absorbance at 269 nm results from the nitrobenzylamine (or nitrobenzylurea) chromophore. This assumption was tested by determining the molar absorptivity for TDI capped with both PNB and with methanol. The methanol-capped TDI is considered to be a model for the absorbance of the TDI moieties that are not at the ends of the oligomers. The molar absorptivity of the nitrobenzylurea-capped TDI was calculated to be  $6000 \text{ L m}^{-1} \text{ cm}^{-1}$ . The methanol-capped TDI gave a molar absorptivity of  $800 \text{ L m}^{-1} \text{ cm}^{-1}$ . The remainder of the oligomer is seen to contribute relatively little to the absorbance compared with the terminal nitrobenzylurea chromophore. The assumption of the independence of molar absorptivity from the size of the species is thus demonstrated to be reasonable.

### Calibration of the GPC System

Prepolymers were prepared from narrow-molecular-weight PPG standards (American Polymer Standards Corp.) according to the procedures given above. These prepolymers were quenched and analyzed by the same GPC procedure as used for the test samples. The data were collected and analyzed using an



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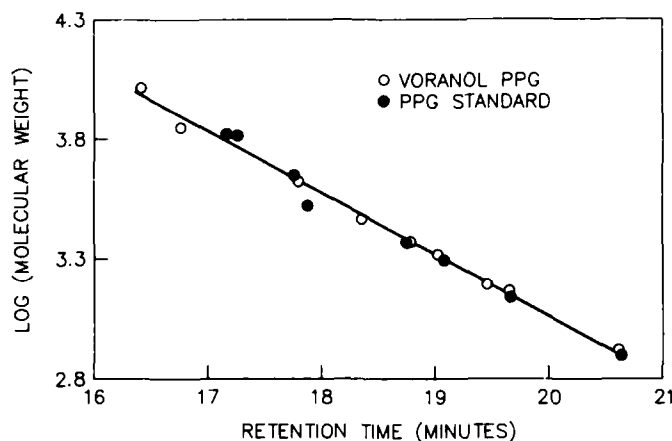


Fig. 1. Calibration curve for the gel permeation chromatograph system. From each PPG reaction, several different molecular weight peaks elute and are included in this calibration curve. The line is a linear least squares fit to all of the data. The coefficient of correlation of this line is 0.997.

IBM PC-XT computer with Nelson Analytical Co. #3000 chromatography software. The structure of the eluting peaks was assigned according to the assumptions explained in "Results and Discussion." The molecular weight of each eluting species was calculated from the molecular weight furnished with the PPG standard and the assumed structure. A calibration curve was plotted from these data. A second calibration curve was plotted from the data on the Voranol PPG samples using their assumed structure and the number-average molecular weight calculated from their "hydroxyl numbers." Both of these plots are given in Figure 1.

The excellent agreement between the curve from the standard, narrow distribution PPG and the curve from the Voranol brand PPG is additional evidence that the assumptions made about the structure of the species are valid.

## RESULTS AND DISCUSSION

The experiments were designed to investigate the effect of a catalyst on the kinetics of formation and on the composition of polyurethane prepolymers. The most significant effect is obviously expected to be to greatly speed up the reaction. Also important, however, might be a modification of the proportion of the species in the prepolymer that contain multiple monomer units. There is no simple, unambiguous nomenclature for these species. They will be referred to henceforth as "multi-segment" species. A further abbreviation to simplify the discussion is the use of "A" to represent the TDI or the TDI portion of the oligomer and the use of "B" to represent the polyol or the polyol portion of the oligomer.

In prepolymer formation reactions, there is always present an excess of the diisocyanate. Thus the species present after the reaction is complete must be terminated by isocyanate groups. In the chromatograms of these reaction mixtures, there is a large peak present at a molecular weight greater than the

TDI peak. This peak has been assigned as a mono-segment isocyanate-capped PPG polyol, or A-B-A. The progression of peaks of higher molecular weights occurs at retention times consistent with their identification as progressive multisegment species. Specifically, the next peak above the A-B-A peak is A-B-A-B-A and the next higher peak is A-B-A-B-A-B-A. These peak identities are consistent with those reported in the literature.<sup>5</sup> The other assumption about peak identity is in the TDI peak area. There is a peak that occurs at a slightly higher molecular weight than the principal peak from TDI. This second peak is at a retention time that is consistent with its identity being a TDI dimer, possibly a carbodiimide dimer.

At a given molar ratio of diisocyanate-to-polyol, the degree of polymerization in the resulting prepolymer might be expected to be predictable from a modified form of the Carothers' equation<sup>8</sup>

$$\bar{x}_n = \frac{1 + r}{1 + r - 2rp} \quad (1)$$

where  $\bar{x}_n$  is the number average degree of polymerization,  $p$  is the extent of completion of the reaction, and  $r$  is the ratio of reactants (expressed as a number less than 1). As the reaction approaches completion (i.e.,  $p \rightarrow 1$ ) this becomes

$$\bar{x}_n = \frac{1 + r}{1 - r} \quad (2)$$

In the classical derivation of the modified Carothers' equation, the assumption is made that the number of moles of "A-B" groups in the final polymer is equal to one half the sum of the number of moles of "A" and "B,"

$$N_{AB} = \frac{1}{2}(N_A + N_B) \quad (3)$$

This definition implies that the degree of polymerization of an oligomer like "A-B-A" is 1.5. In the synthesis of prepolymers, the mole ratios of the reactants is typically 0.55 or less. When the reactant ratio is this small there is a significant amount of unreacted monomer present and eq. (3) is no longer valid. When one monomer is present in significant excess, the other then becomes a limiting reagent. The number of moles of "A-B" then can be no larger than the number of moles of the limiting reagent in the starting mixture, or in equation form

$$N_{AB} = N_B \quad (4)$$

where "B" is the limiting reagent. This leads to a different form of the equation for the number-average degree of polymerization for this case,

$$\bar{x}_n = \frac{2r}{1 + r - 2rp} \quad (5)$$

When the reaction approaches completion, this reduces to

$$\bar{x}_n = \frac{2r}{1-r} \quad (6)$$

For a reactant ratio,  $r$ , of 0.5 this form of the equation predicts an average degree of polymerization of 2 when the reaction nears completion. The usual Carothers' equation would predict a value of 3. As even smaller reactant ratios are considered, the usual Carothers' equation converges to a value of 1, whereas eq. (6) converges to zero. This latter is more realistic for mixtures wherein there is significant content of unreacted monomer after the reaction is complete. The average degree of polymerization for the mixture must account for this component—which has a degree of polymerization of zero.

For eq. (4) to be valid, it is necessary to redefine the term "degree of polymerization" for small oligomers. For this case, degree of polymerization may be defined as the number of molecular segments corresponding to the limiting reagent. It is simpler to consider this as the number of complete monomer groups in a molecule. For polyurethane prepolymer synthesis, a complete monomer group consists of one diisocyanate reacted with one polyol, or "A-B." The species "A-B-A," or an isocyanate-terminated prepolymer, contains only one complete monomer unit and thus should be viewed as having a degree of polymerization of one.

Another important factor in the kinetics of the formation of prepolymers is the relative reactivities of the two isocyanate groups on the 2,4-isomer of the diisocyanate. Of even more importance, however, is the reactivity of the second isocyanate after the first has already been converted into a urethane group. Measurements and modeling have shown that the presence of one urethane group on the tolylene molecule quenches the reaction rate of the remaining isocyanate as much as ten fold.<sup>9</sup> The implication of this for prepolymer formation is that there must be a greater proportion of single-segment (A-B-A) species than might be predicted, since the formation of higher-segment species must involve the occurrence of the quenched reaction. Stated in another way, this decrease in reaction rate when the first of the isocyanate groups in a diisocyanate reacts assures that the formation of multi-segment species will be reduced and that the average degree of polymerization will be less than predicted by either eqs. (2) or (6).

The effect of a catalyst on the synthesis of a polyurethane prepolymer extends beyond a simple increasing of the reaction rate. The effect is not entirely consistent, but, in general, catalysts serve to promote the slower reactions more than the faster ones.<sup>10</sup> This would imply that for the preparation of polyurethane prepolymers, a catalyst might serve to equalize the reaction rates between the first and the second isocyanate groups to react in a diisocyanate. This rate equalization will serve to produce a greater relative amount of the multisegment molecules, with a concomitant increase in viscosity. Production of the multisegment species also leaves behind additional unreacted diisocyanate and thus increases the handling hazards of the prepolymer.

The progress of the reaction between TDI and polypropylene glycol was followed by periodically removing samples from the reaction mix and immedi-

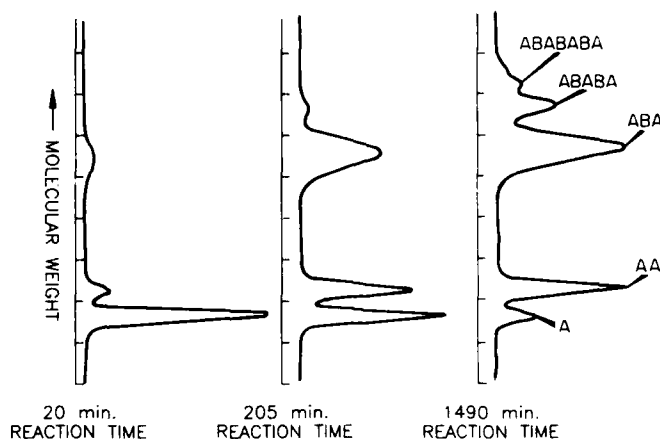


Fig. 2. Gel permeation chromatograms for the reaction between PPG of molecular weight 1968 and 2.09 mol ratio of TDI after 20, 205, and 1490 min. "A" represents TDI and "B" represents PPG polyol portions of the molecule.

ately derivatizing them. The GPC chromatogram of these is used to indicate the progress of the reaction as well as the distribution of the oligomers. An illustrative set of chromatograms is shown in Figure 2.

The peak areas in these chromatograms are proportional to the molar concentration of the species. Although the polyol is the limiting reagent it is not easily determined by this analytical method. Consequently, a percent conversion based on the amount of TDI that has reacted to form "ABA" or "ABABA" or higher oligomers was calculated at each sampling time. Percentage conversion of the diisocyanate was calculated by dividing the sum of the areas of the oligomers by the sum of the areas of all of the analyzed peaks, with each peak area multiplied by the number of moles of TDI that the assumed species contains. As an example, for one reaction mixture containing a 2.09 ratio of TDI to PPG (molecular weight 1968), the molar ratios of A : AA : ABA : ABABA : ABABABA were 1.000 : 3.508 : 8.140 : 2.447 : 1.017. This gives a calculated percent conversion of 77.55% for this reaction mixture.

The reaction between a diisocyanate and a polyol might be expected to show second-order kinetics. However, the data generated in the present work do not follow a typical second-order kinetics plot. Such non-linearity has been observed frequently in the literature and is ascribed both to the difference in reactivity between the 2- and the 4- position isocyanates in the 2,4-tolylene diisocyanate<sup>11</sup> and to a combination of this effect and the lower reactivity of the second isocyanate caused by the urethane group.<sup>12</sup> Figure 3 shows a typical plot of the fractional conversion data produced in the present work.

The kinetics literature suggests no simple way of plotting these data so as to show them in linear form. However, on inspection it was found that these data can be expressed in an alternative, empirical way that simplifies inspection of the reaction systems. The equation for this alternative form is:

$$\% \text{ Conversion} = \frac{at}{b + t} \quad (7)$$

where  $t$  is time.



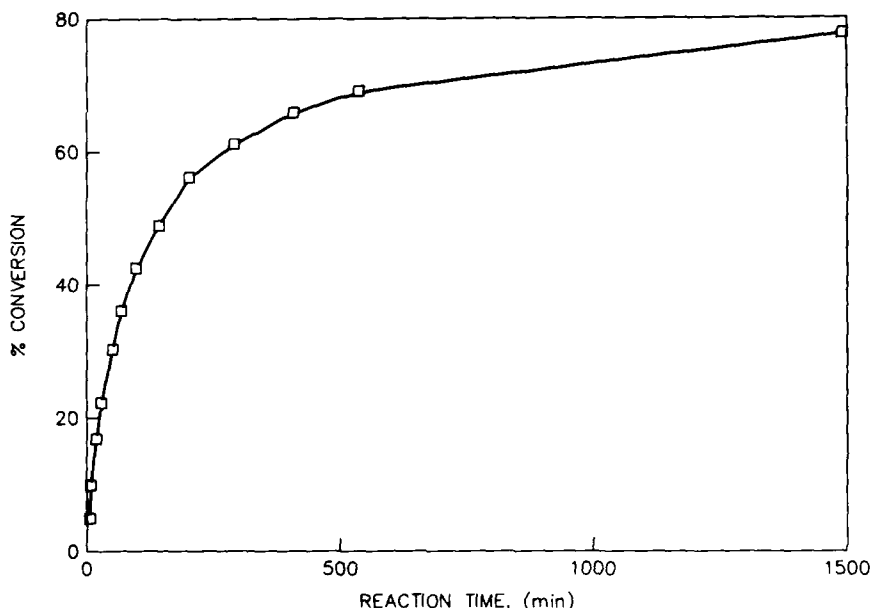


Fig. 3. Fractional conversion of isocyanate into polyurethane prepolymer as a function of time for a PPG polyol of molecular weight 1968 reacted with 2.09 mole ratio of TDI.

Examination of eq. (7) shows that at very long times the conversion approaches " $a$ ", and thus this term can be viewed as a limiting fractional conversion. The " $b$ " term is a characteristic time and can be seen to be the time at which the conversion reaches half the limiting value. This is, of course, not a true half life, although a similar parameter has been so described in the literature.<sup>13,14</sup>

The data are conveniently plotted in an alternative form of Eq. (7):

$$\frac{t}{\% \text{ Conversion}} = \frac{t}{a} + \frac{b}{a} \quad (8)$$

The values for the  $a$  and  $b$  terms are determined from the slope and intercept of a plot of eq. (8). The data from Figure 3 are replotted into this form in Figure 4.

The utility of this type of plot is that it is much easier to follow the progress of the reaction under study, and particularly to observe changes in the reaction rate as the conditions are changed.

The effect of catalyst on the TDI/PPG prepolymer system was studied at several different reaction stoichiometries and polyol molecular weights. For some of these conditions, samples were removed periodically as the reaction progressed. These samples were stabilized and analyzed by the procedure discussed above and thus provided more detailed reaction rate data. For other of the reaction conditions, samples were only taken after reaction completion. The data from all of these tests were reduced as discussed above and are presented in Table I.

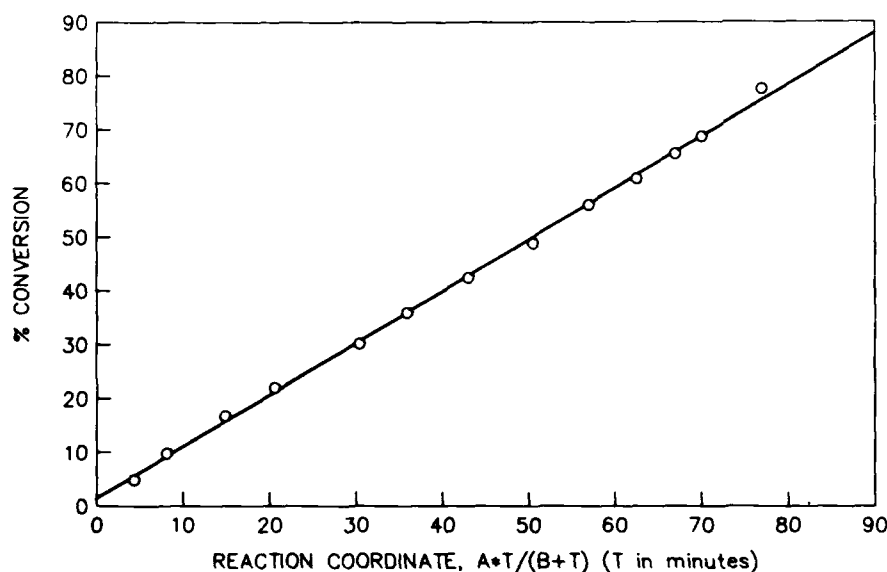


Fig. 4. Alternative plot of conversion data. The line shown is from a least squares fit of the calculated points. The value of  $a$  was calculated to be 81.6% and  $b$  to be 88.7 min from this plot. The correlation coefficient was 0.9997.

Also given in Table I are the measured ratios of the multi-segment components in the prepolymers. The concentrations of these components were monitored throughout the course of the reaction in the more-extensive kinetic studies above. However, the values reported in the table are those taken at the end of the reaction time.

The  $a$  term in the table is from a least-squares fit of the data to eq. (8) and is a measure of the extent of completion of the reaction that was run. There was always free TDI present in the reaction mixture and therefore these  $a$  values are all less than 100%.

The presence of catalyst has a large effect on the reaction rate as illustrated by the "half life" data in the table under the  $b$  term. The prepolymer formation reaction is accelerated from 13 to 22 times by the FAA catalyst.

The effect of catalyst on the ratios of the higher oligomers is as was predicted in the discussion above. This is seen by comparing the ABABA/ABA and ABABABA/ABABA ratios of each of the pairs of data in Table I. The consistent increase in the amount of higher segment chains when catalyst is present doubtlessly results from the equalization of the reaction rates of the 2- and 4-positions on the 2,4-TDI. With this equalization a much higher proportion of the initial AB groups are terminated by the much more reactive 4-isocyanate groups. This increases the rate of the chain extension reaction.

The number-average degree of polymerization may also be calculated for this data set from the peak areas of all species multiplied by the degree of polymerization of that species, divided by the peak areas of all species. In Table II are the results of this calculation, along with the degree of polymerization predicted from the reactant stoichiometry and eq. (6).

It was discussed above that the measured degree of polymerization should always be less than is predicted by eq. (6) but that the presence of catalyst

TABLE I  
Polyurethane Prepolymer Samples Prepared and Their Oligomer Ratios and Reaction Rate Parameters

| Sample number | Polyol MW | NCO:OH ratio <sup>a</sup> | Catalyst concentration (%) | a (%) | b min | ABABA ABA ratio | ABABABA ABABA ratio |
|---------------|-----------|---------------------------|----------------------------|-------|-------|-----------------|---------------------|
| 101           | 443       | 1.90                      | 0                          | —     | —     | 0.32            | 0.38                |
| 111           | 443       | 1.89                      | 0.1                        | —     | —     | .44             | .51                 |
| 203           | 1190      | 2.16                      | 0                          | 92.7  | 72.8  | .31             | .52                 |
| 213           | 1190      | 2.17                      | 0.1                        | 85.4  | 3.3   | .37             | .63                 |
| 303           | 1968      | 2.09                      | 0                          | 81.6  | 88.7  | .30             | .42                 |
| 313           | 1968      | 2.13                      | 0.1                        | 86.9  | 7.0   | .44             | .89                 |

<sup>a</sup> NCO:OH is the ratio of diisocyanate to diol in the reaction mixture.

TABLE II  
Number-Average Degrees of Polymerization Measured by GPC Compared  
with Values Predicted by Equation (6)

| Sample number | Polyol MW | NCO: OH ratio | Catalyst concentration (%) | Number-average degree of polymerization |           |
|---------------|-----------|---------------|----------------------------|-----------------------------------------|-----------|
|               |           |               |                            | Measured                                | Predicted |
| 101           | 443       | 1.90          | 0                          | 1.10                                    | 2.22      |
| 111           | 443       | 1.89          | 0.1                        | 1.11                                    | 2.25      |
| 203           | 1190      | 2.16          | 0                          | 1.18                                    | 1.72      |
| 213           | 1190      | 2.17          | 0.1                        | 1.16                                    | 1.71      |
| 303           | 1968      | 2.09          | 0                          | 1.00                                    | 1.83      |
| 313           | 1968      | 2.13          | 1.0                        | 1.26                                    | 1.77      |

may cause the degree of polymerization to increase. Table II shows that the measured degree of polymerization is always much less than the predicted value. Number-average degree of polymerization is not a sensitive indicator of the extent to which the polyurethane prepolymer reaction has proceeded beyond single-segment species. The formation of multi-segment species always leaves behind unreacted TDI which keeps the average degree of polymerization virtually constant. This is reflected in the values reported in Table II.

### CONCLUSIONS

The analytical procedure consisting of derivatizing the polyurethane prepolymer's isocyanate groups and separating and measuring the individual species gives a clear and sensitive picture of the progress of the reaction. The presence of a reaction catalyst is shown to increase the proportion of the higher-segment oligomers in the prepolymer. An alternative form of the Carothers' equation was derived and shown to be more useful at reaction stoichiometries significantly less than one. An empirical equation that gives a linear plot of reaction kinetics is presented, discussed, and used to express rates.

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## 13. ABSTRACT (Maximum 200 words)

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