

Honey Bee 230 and Honey Bee 150: Reactivity of Soy Based Polyols

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ABSTRACT

Novel soy based polyols Honey Bee 230 and Honey Bee 150 are studied by FTIR. Polyurethane formation rates are determined and compared to fossil fuel based polyols. The kinetic results are used to improve formulations and lower variation in the reactivity of soy based polyurethane foams and non-cellular elastomers.

INTRODUCTION

Recently MCPU introduced novel natural oil polyols (NOP), the Honey Bees. These polyols were shown to have wide utility in both foams and the CASE markets. In our last paper [1], we suggested that the Honey Bees would have reactivities typical of primary hydroxyl functionalities. It is well known that while all NOPs all have similar sources and applications [2-6], the materials themselves can have wildly different reactivities. For example, compared with propylene oxide polyether polyols, many NOPs, including castor oil, have lower reactivity. Since the addition reaction of polyol + isocyanate to form polyurethane, is under kinetic control, reactivity directly influences the quality and physical properties of the resultant polymer. Thus, evaluation of the NOP's reactivity can be very important in both foam and CASE formulations.

Differences in reactivity can be due to differences in the natural oil, the functional group, or the synthetic route to functionalization. The Honey Bees are based on soybean oil (Figure 1), which is a naturally occurring triglyceride containing, on average, 4.65 sites of unsaturation. As described previously [1], Honey Bee NOPs are produced from soybean oil by inserting guest molecules onto and between oil molecules (Figure 2). As a result of their unique synthetic route, Honey Bees have high purity, low color, low/no odor, and low cost. And unlike some other NOPs, the Honey Bees can be designed to have variable reactivity. The guest molecules can be designed with secondary hydroxyl groups or solubilizing agents as well, thus allowing both the reactivity and solubility of the soy based Honey Bees to be "tuned" for each application.

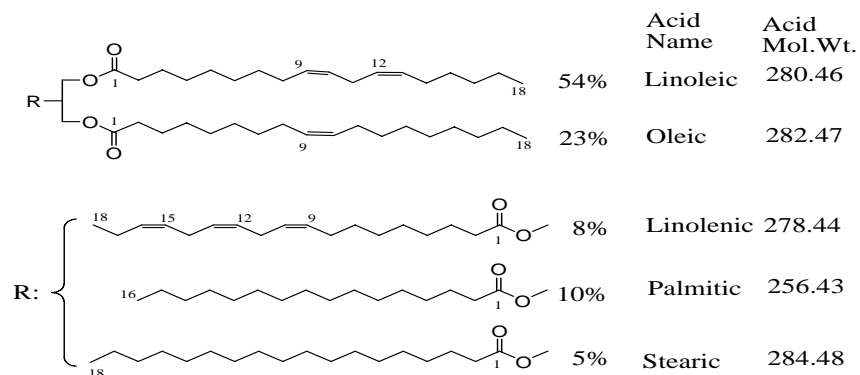
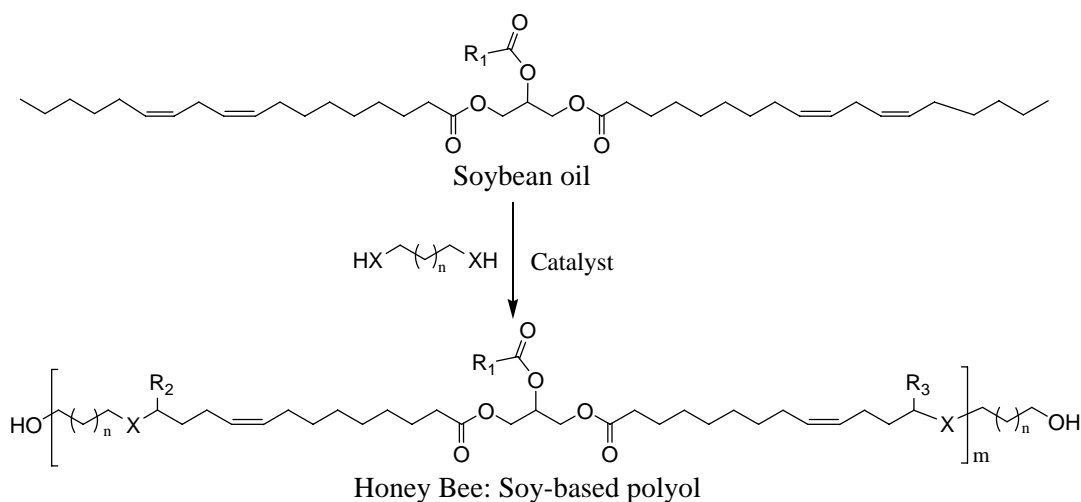


Figure 1. Structure of Soybean Oil.



R1: hydrocarbon chain of linoleic acid, or oleic acid, or palmitic acid, or linolenic acid, or stearic acid.

R2: pentyl, octyl, butyl groups.

R3: octyl, pentyl, butyl groups.

X: N, S, O, ...

Figure 2. Synthetic route of MCP Soy-based Honey Bee polyols

In this work, we wanted to test the hypothesis that Honey Bee reactivity would follow that of typical fossil fuel polyols. If this is the case, primary hydroxyl Honey Bee reaction rates, should be measurably greater than secondary hydroxyl fossil fuel based polyols [7].

EXPERIMENTAL

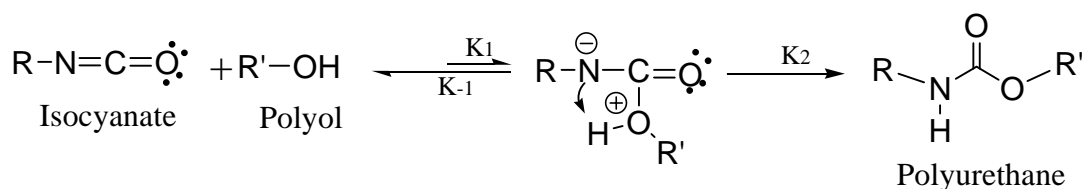
To measure a reaction rate, we can monitor either the appearance of a product or the disappearance of a reactant. Any physical characteristic which can be unambiguously related to the change in concentration can be monitored. Evaluation of these changes by standard kinetic methods [8] yields order and reaction rate. For example, the rate for the reaction of polyether polyol and TDI has been determined by measuring the residual isocyanate content with titration and infrared absorption methods [9]. Fourier Transform Infrared spectroscopy (FTIR) is particularly well suited to study polyurethane reactions [10-13]. In this work, we used FTIR to study the reaction rates of Honey Bee 230 and Honey Bee 150 in comparison to fossil fuel industry benchmarks polyether diols of 1000 and 2000 molecular weight.

Materials. Honey Bee 150, Honey Bee 230, uretonimine modified 4,4'-MDI, 1000 and 2000 PPO diols were used as commercially manufactured and received.

Instrument. Spectra were recorded on a Mattson Genesis II FTIR Spectrometer.

Reaction Conditions. MDI and polyol (Honey Bee 150, Honey Bee 230, 1000 and 2000 PPO diols) were allowed to react at 77°F under nitrogen. No catalyst was used.

In the reaction of isocyanate and polyol



We can simplify the formation of polyurethane as



Then the reaction rate will be given by

$$-\frac{d[\text{MDI}]}{dt} = -\frac{d[\text{Polyol}]}{dt} = k_1[\text{MDI}][\text{Polyol}] - k_{-1}[\text{MDI} \bullet \text{Polyol}] \quad (1)$$

$$\frac{d[\text{PU}]}{dt} = k_2[\text{MDI} \bullet \text{Polyol}] \quad (2)$$

$$\frac{d[\text{PU}]}{dt} = -\frac{d[\text{MDI}]}{dt} = -\frac{d[\text{Polyol}]}{dt} \quad (3)$$

From equation 1, 2 and 3, concentration of transition state will be given by

$$[\text{MDI} \bullet \text{Polyol}] = \frac{k_1[\text{MDI}][\text{Polyol}]}{k_{-1} + k_2} \quad (4)$$

If the starting concentrations of isocyanate and polyol are equal, equations 1 and 2 can be written as

$$-\frac{d[\text{MDI}]}{dt} = k[\text{MDI}]^2 \quad (5)$$

where

$$k = \frac{k_1}{k_{-1} + k_2} \quad (6)$$

Integrating gives a kinetic equation of polyurethane formation reaction

$$\frac{1}{[\text{MDI}]} - \frac{1}{[\text{MDI}]_{\text{initial}}} = kt \quad (7)$$

For this equation, a plot of $1/[\text{MDI}]$ versus reaction time t should produce a straight line with slope k and intercept $1/[\text{MDI}]_{\text{initial}}$ where $[\text{MDI}]_{\text{initial}}$ is the initial concentration of isocyanate and k is the rate constant at a given temperature, pressure and other reaction conditions. The isocyanate concentration $[\text{MDI}]$ can be monitored by, e.g., FTIR at any time t during the reaction.

RESULTS AND DISCUSSION

The FTIR spectra of the reaction mixture for the reaction of Honey Bee 150 and MDI are shown in Figure 3. The spectra were scanned at 12 minutes and 26 minutes at room temperature, respectively. A strong infrared absorption peak at 2273 cm^{-1} is characteristic of the NCO group. As seen in Figure 3, the absorbance at 2273 cm^{-1} has decreased significantly between 12 and 26 minutes, relative to other peaks characteristic of functional groups that are not engaged in the reaction.

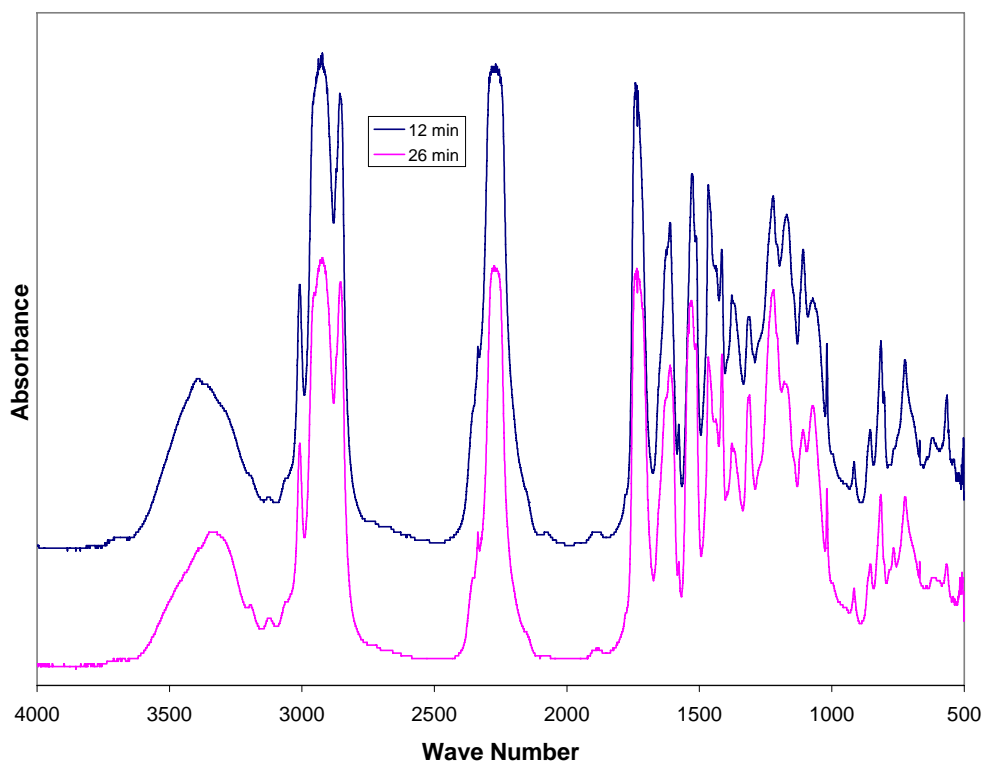


Figure 3. IR Spectra of reaction mixture for the reaction of Honey Bee 150 and MDI at 12 minutes and 26 minutes at 77°F.

The relative concentrations of MDI at the various reaction times have been determined by integrating the absorbance of the NCO peak relative to a reference peak at 1528 cm^{-1} . A plot of this data are shown in Figure 4. Analysis of this data consistent with our kinetic model demonstrates the unusual reactivity of Honey Bee 150.

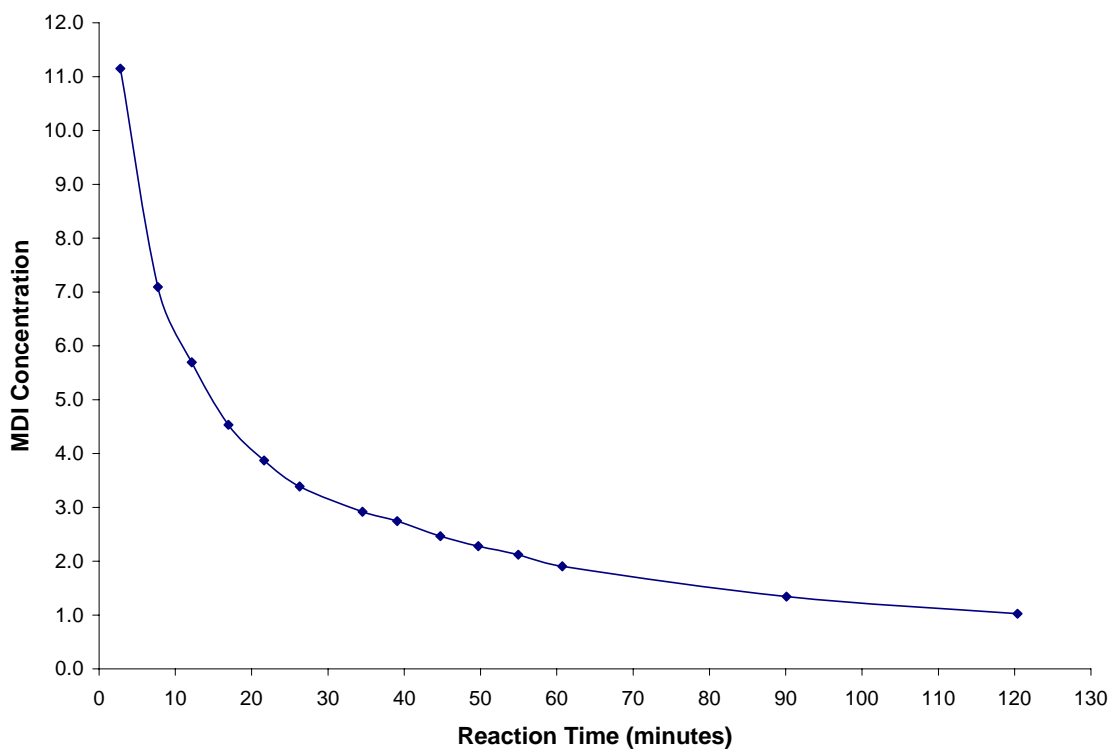


Figure 4. MDI concentration plot for the reaction of Honey Bee 150 and MDI at 77°F.

As seen in Figure 4, reaction between MDI and Honey Bee 150 starts rapidly, begins slowing within 30 minutes, and starts to approach its asymptotic limit within 90 minutes, all without catalyst. The data were analyzed according to our kinetic model by plotting of $1/[MDI]$ versus reaction time t . The slope of this plot, shown in Figure 5, yields a rate constant for the reaction of Honey Bee and MDI at 77°F.

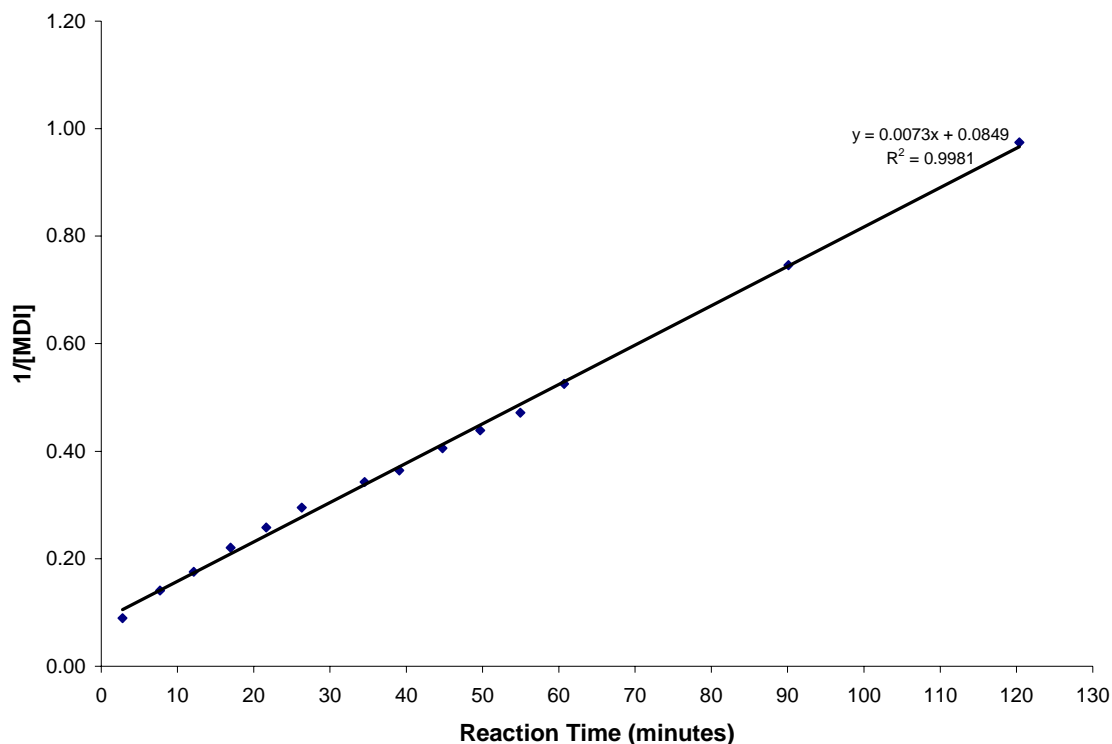


Figure 5. Plot of $1/[MDI]$ versus reaction time t for the reaction of Honey Bee 150 and MDI at 77°F.

Data from the reaction of Honey Bee 150 and MDI gave a good correlation to the model ($R^2 = 0.9981$), yielding a rate constant of 0.0073 for the reaction of Honey Bee 150 and MDI at 77°F.

The reaction rate of Honey Bee 230 was determined in a similar manner, although our results show the reactivity of Honey Bee 230 is higher than that of Honey Bee 150, presumably due to its higher concentration of active hydrogen functionality (OH) per unit volume. Raw data are shown in Figure 6, where the reaction is seen to begin slowing within 20 minutes.

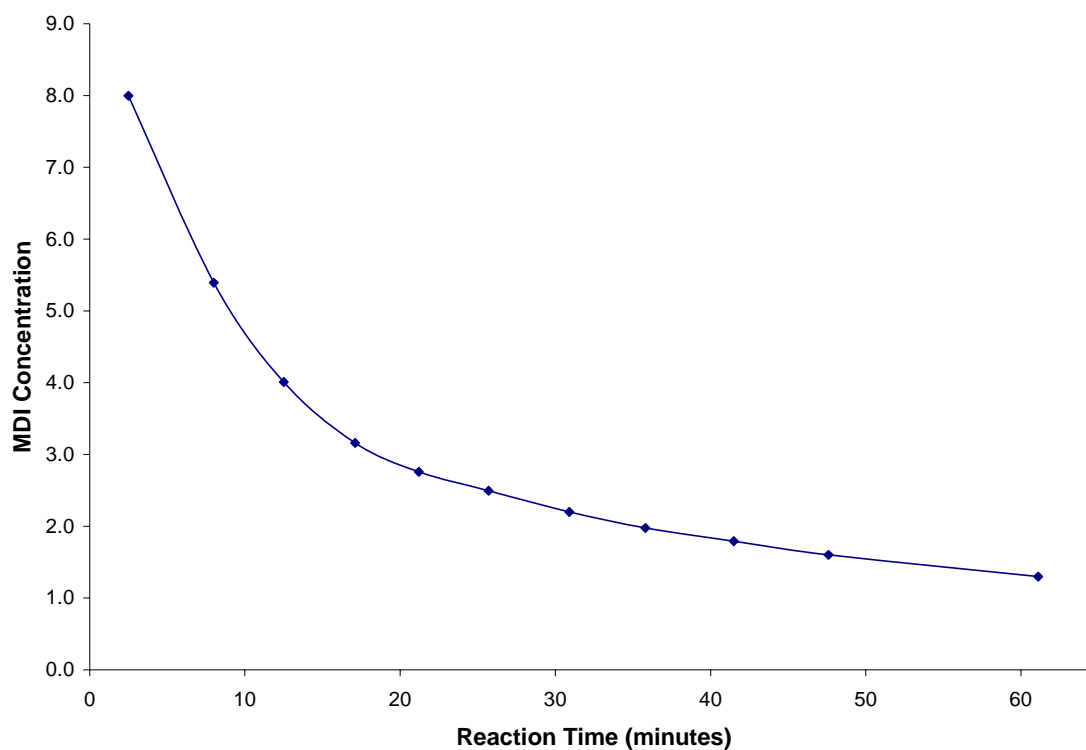


Figure 6. Plot of MDI concentration versus reaction time for the reaction of Honey Bee 230 and MDI at 77°F.

We calculated the rate constant for the reaction of Honey Bee 230 and MDI at 77°F at 0.0109 (Figure 7), again with good correlation to the model ($R^2=0.9964$). Both reactions are consistent with second order kinetics. The higher rate constant for Honey Bee 230 indicates its higher reactivity. A half-life for the reaction of Honey Bee 150 and MDI, and Honey Bee 230 and MDI, can be determined from the rate constants. For Honey Bee 150 the half-life is calculated as 137.0 minutes, for Honey Bee 230 as 91.7 minutes.

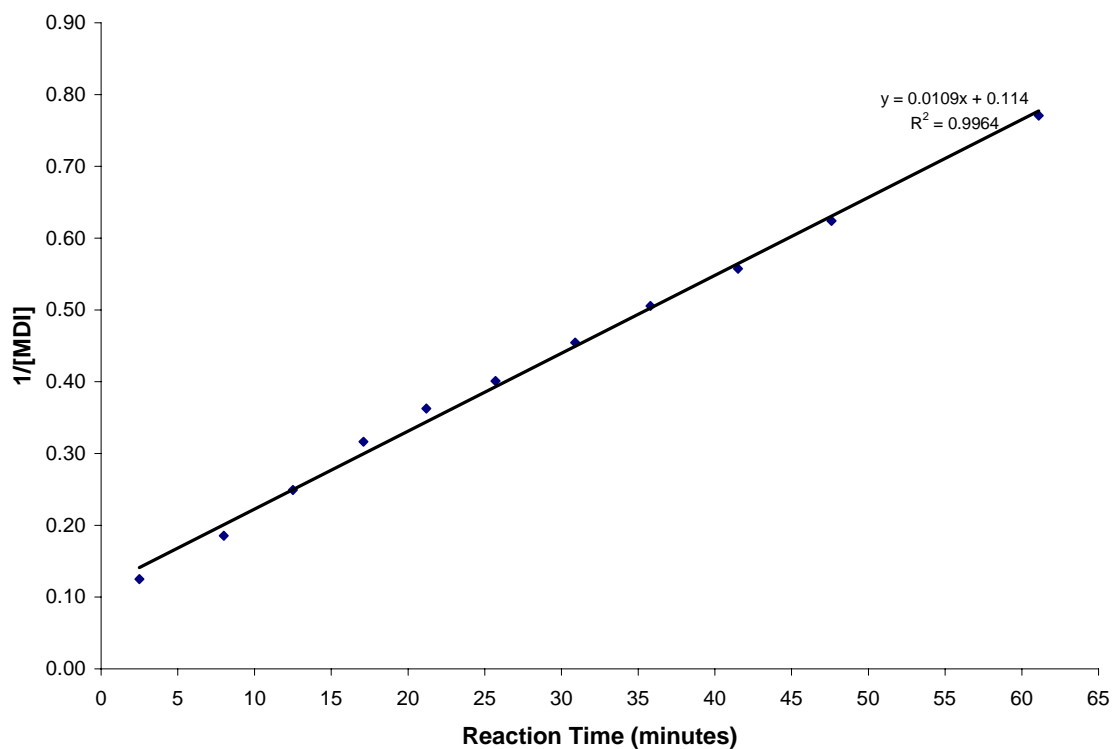


Figure 7. Plot of $1/[MDI]$ versus reaction time t for the reaction of Honey Bee 230 and MDI at 77°F.

To test our hypothesis by contrasting the reactivity of primary hydroxyl soy based Honey Bee polyols with secondary hydroxyl fossil fuel based polyols we also determined the reactivity of propylene oxide polyether diols of 1000 molecular weight and propylene oxide polyether diols of 2000 molecular weight under the same conditions. The FTIR spectra of a reaction mixture scanned at 6.5 minutes and 5.0 hours for the reaction of PPO 1000 diol and uretonimine modified MDI are shown in Figure 8. The NCO absorbance again decreases substantially relative to reference peaks, indicating formation of polyurethane by reaction of polyol and isocyanate.

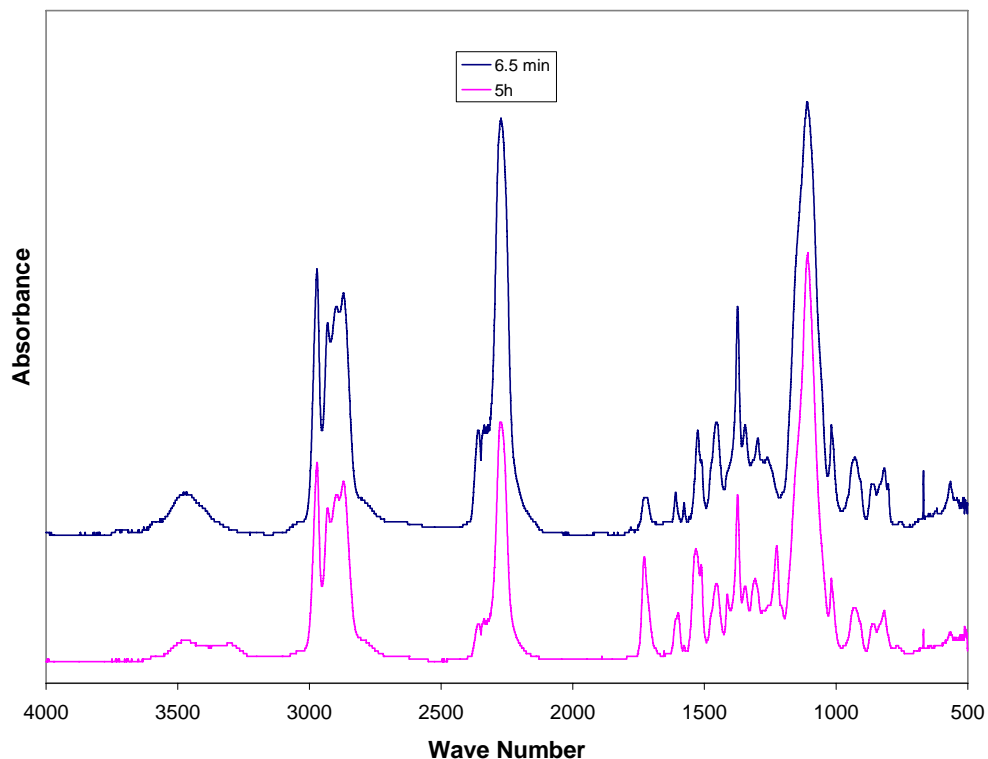


Figure 8. IR spectra of the reaction mixture at 6.5 minutes and 5.0 hours for the reaction of 1000 diol and MDI at 77°F.

As seen in Figure 8, and in contrast with the Honey Bees, the reaction does not begin to slow substantially until 300 minutes.

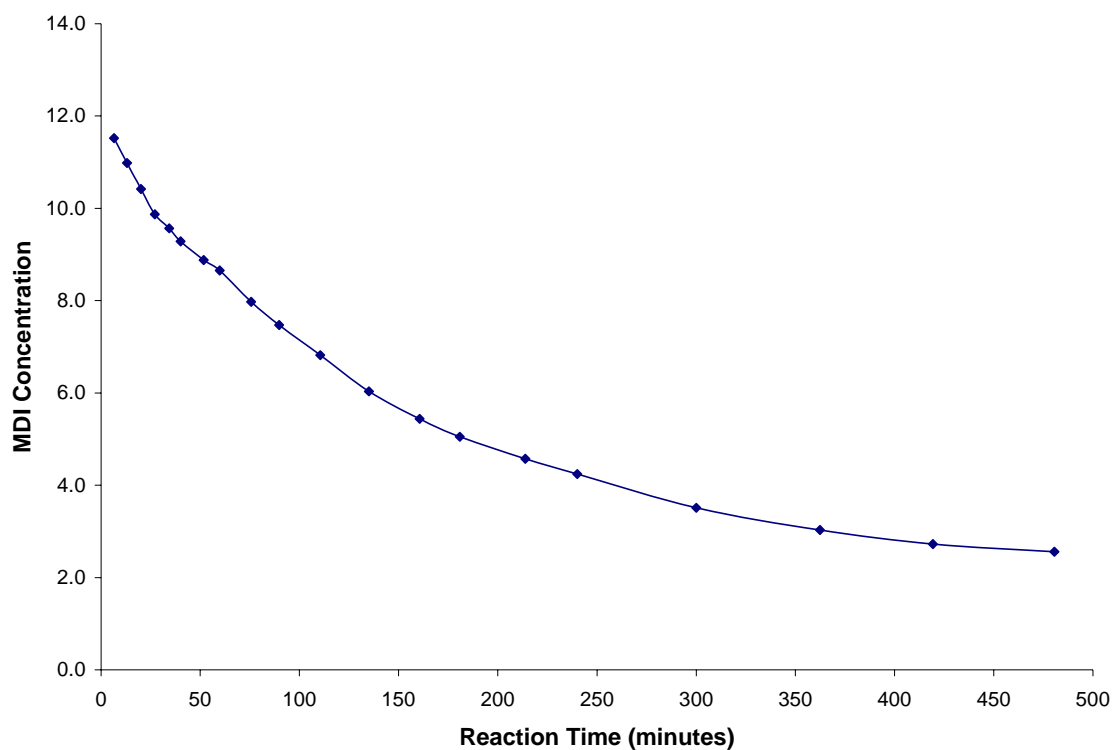


Figure 9. Plot of MDI concentration versus reaction time for the reaction of 1000 polypropanyl ether diol and MDI at 77°F. A rate constant of the reaction of PPO 1000 diol and MDI was determined by plotting 1/[MDI] versus reaction time (Figure 10). This plot yielded a good correlation coefficient ($R^2 = 0.9974$) indicating consistence with the kinetic model. The slope gave a rate constant of 0.0007, corresponding to a half-life of 23.8 hours at 77°F.

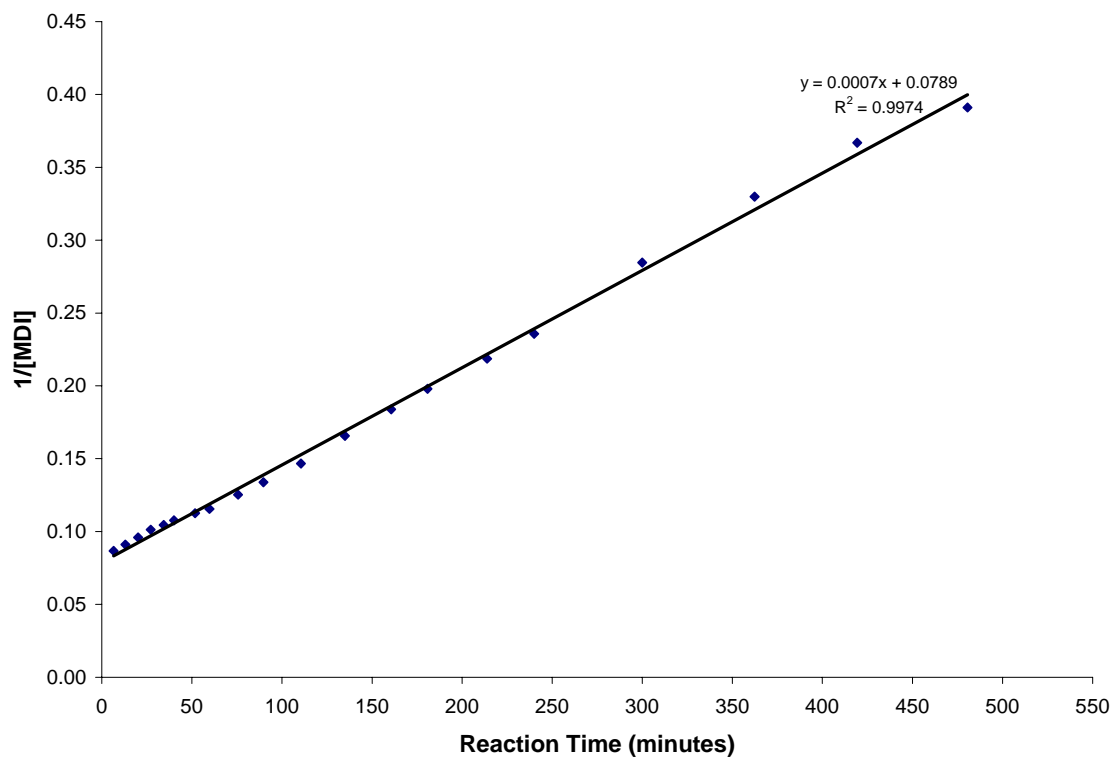


Figure 10. Plot of 1/[MDI] versus reaction time t for the reaction of 1000 polypropanyl polyether diol and MDI at 77°F.

The reactivity of PPO 2000 diol was also determined in the same manner, the relevant data are presented in Figure 11. The reaction begins to slow at around 300 minutes.

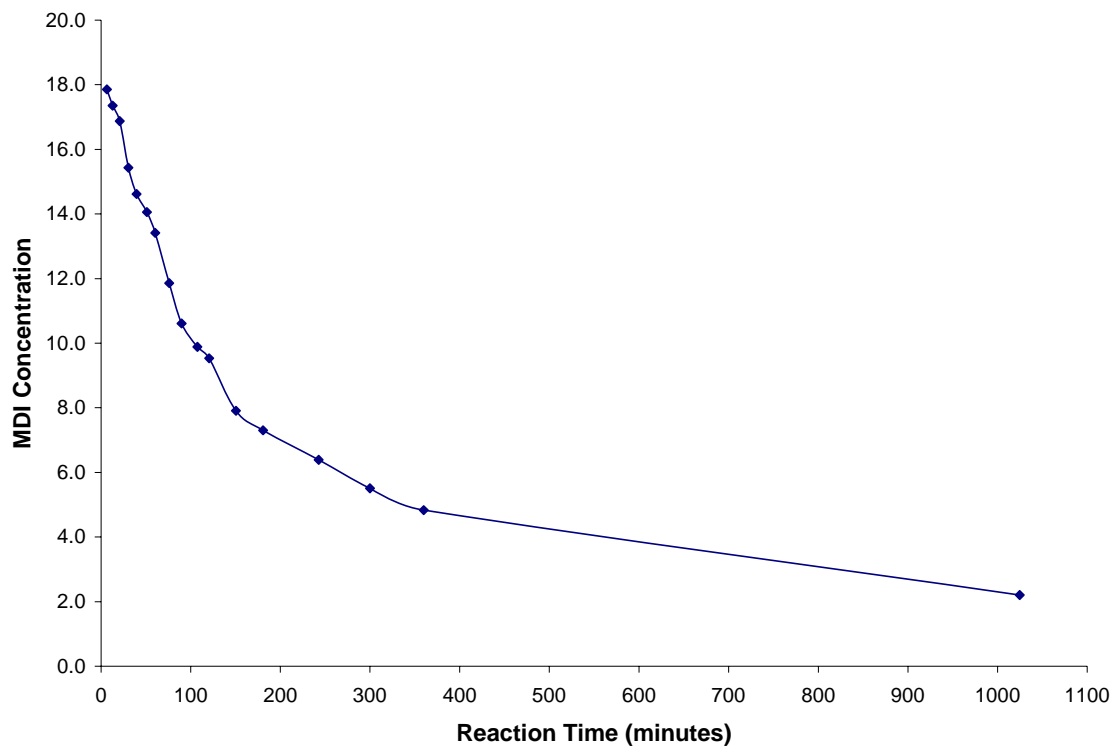


Figure 11. Plot of MDI concentration versus reaction time for the reaction of 2000 polypropanyl ether diol and MDI at 77°F. A plot of $1/[MDI]$ versus reaction time (Figure 12) gives good correlation ($R^2 = 0.9964$) and the slope yields a rate constant of 0.0004 or a half-life of 41.7 hours at 77°F.

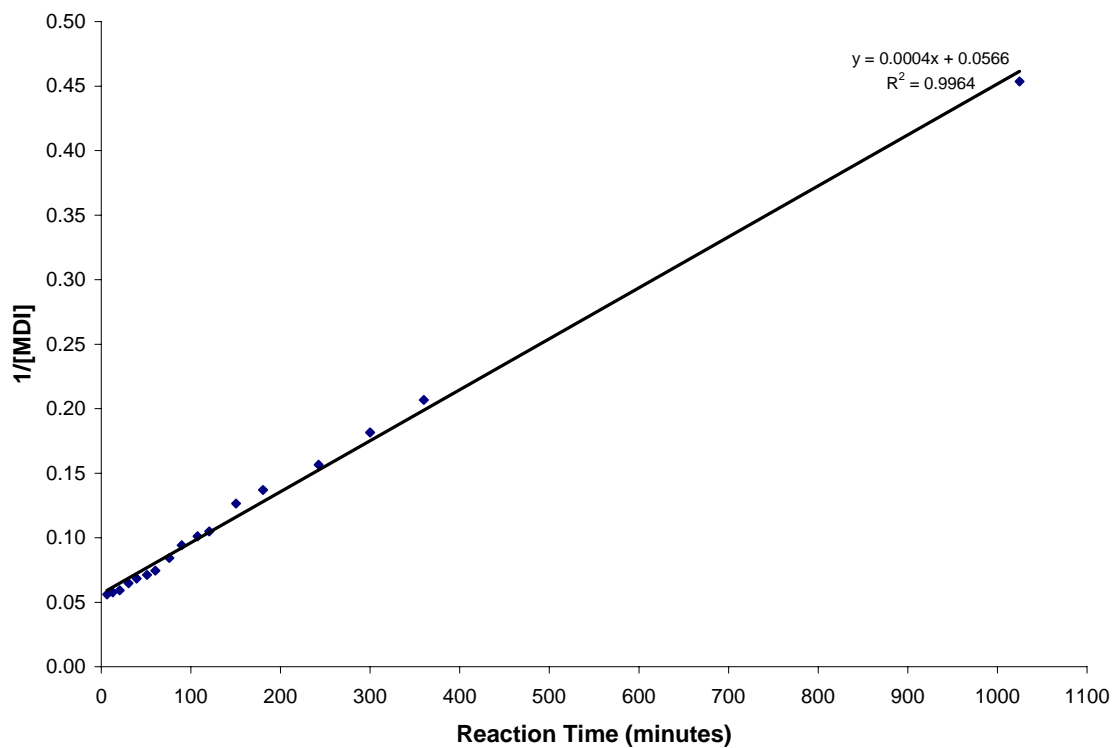


Figure 12. Plot of $1/[MDI]$ versus reaction time t for the reaction of 2000 polypropanyl polyether diol and MDI at 77°F.

The results of this study are shown in Table 1.

Polyol	Rate Constant	Relative Rate
Honey Bee 230	0.0109	27.25
Honey Bee 150	0.0073	18.25
1000 PPO diol	0.0007	1.75
2000 PPO diol	0.0004	1.00

The reactivity of Honey Bee 230 is about 49.3% higher than that of Honey Bee 150 and the reactivity of PPO 1000 diol is about 75.0% higher than that of PPO 2000 diol. Perhaps more importantly, however, the reactivity order of the four polyols examined is consistent with their functionality, rather than whether fossil fuel or natural oil based. The primary hydroxyl polyols (the Honey Bees) are an order of magnitude more reactive than the secondary hydroxyl polyols. That is, the reactivity order is soy primary OH >> fossil fuel secondary OH.

CONCLUSIONS

Standard Honey Bee polyols are high reactivity NOPS. The reaction rate of Honey Bee 150 was found to be 18 times the reaction rate of PPO 2000 diol, and about 10 times reaction rate of PPO 1000 diol. The reaction rate of Honey Bee 230 was found to be 27 times the reaction rate of PPO 2000 diol, and 16 times reaction rate of PPO 1000 diol. These results are “typical” for primary hydroxyl versus secondary hydroxyls, unlike other NOPS where “typical” reactivity has not been the norm. The hypothesis that Honey Bee reactivity follows that of fossil fuel polyols is confirmed by this work.

FUTURE WORK

Future studies will demonstrate the “tunability” of the Honey Bees by application. Optimal Honey Bee selection for flexible and rigid polyurethane, visco, HR and isocyanurate foams, as well as rigid and flexible CASE applications will be made available in the form of standard starting point formulations. Guest molecules have been optimized for solubility in blending with aromatic and aliphatic polyether and polyester polyols. Patents are pending for these technologies.

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- * Author to whom correspondence should be addressed.
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BIOGRAPHIES

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Tom Garrett is President and Research Director at MCPU Polymer Engineering, A Division of MCP Industries, Inc. Also known as MCP Urethanes, MCPU was founded in 1937 as the research arm of the WS Dickey Clay Company with the hiring of chemistry professor Elmer R. Ligon. MCPU has been manufacturing polyurethanes since the late 1950's and has received over 25 patents. Dr. Garrett holds a B.S. with honors from Stanford University and a Ph.D. from the University of California at Berkeley, both in chemistry. Prior to joining MCPU, Dr. Garrett was a postdoctoral fellow at the Université Louis Pasteur in Strasbourg. The author of over 30 papers and patents, Dr. Garrett is a graduate of Harvard Business School in Boston.

Xian Xian Du



Frank Du is Principal Scientist at MCPU Polymer Engineering. Dr. Du holds a B.S. from Sichuan University, a M.S. from Concordia University, and a Ph.D. from the University of Montreal, all in chemistry. Prior to joining MCPU, Dr. Du was a research scientist at Los Alamos National Laboratory.