J. Phys. Chem. A **2000,** *104,* 3952−3957

In-Situ Monitoring of Urethane Formation by FTIR and Raman Spectroscopy

Lifeng Xu,[†,§] Chi Li,[‡] and K. Y. Simon Ng*,[†]

Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan 48202, and Ford Research Laboratories, Ford Motor Company, Dearborn, Michigan 48121

Received: July 27, 1999; In Final Form: October 29, 1999

Reactions of 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and 2-octanol with phenylisocyanate were monitored by FTIR and Raman spectroscopy. The results show that Raman spectroscopy is as effective as FTIR spectroscopy in following urethane reaction kinetics. The activation energies calculated are 10.0, 10.5, 11.9, 12.8, and 14.8 (kcal/mole) for 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and 2-octanol reacting with phenylisocyanate without catalyst, respectively. The steric hindrance effects of primary, secondary, and tertiary butanol with phenylisocyanate reaction kinetics were observed. The initial reaction rates of these alcohol systems have a typical ratio of 1:0.3:0.1, respectively. The reaction kinetics simulation, based on a simple kinetics model, fits reasonably well with experimental data obtained by Raman spectroscopy. This agreement further demonstrates the effectiveness of Raman spectroscopy in monitoring urethane reaction kinetics and suggests an effective method for verifying the reaction kinetics and mechanism under nonisothermal conditions. The results of this work will form the basis for our future in-situ study of thermoset polymerization kinetics under exposure to radio frequency electromagnetic (RF) fields.

Introduction

Vibrational spectroscopy techniques are among the most popularly used techniques in studying thermoset polymerization kinetics. Although spectroscopic techniques often require extensive data processing and detailed calibration, they have the advantage of providing a detailed fundamental understanding of the polymerization by following the changes of specific bands during the reaction process. A series of spectra acquired as a function of time can provide in-situ reaction kinetics data and possibly information about reaction intermediates.[1] Vibrational spectroscopic techniques are also more sensitive at high conversion than such conventional techniques as differential scanning calorimetry (DSC), densitometry, and dilatometry.[2]

FTIR spectroscopy is one of the most popularly used spectroscopic techniques for polymer characterization and for monitoring the in-situ reaction kinetics of polymerization. Both urethane monomers and polymers have major and distinctive absorption peaks in the FTIR spectrum. The accuracy of FTIR in monitoring urethane polymerization was demonstrated by comparing the reaction kinetics results obtained by FTIR spectroscopy with those obtained by the thermal analysis technique.[2] FTIR spectroscopy has already been widely used in monitoring urethane polymerization.[2−4] Raman spectroscopy, with selection rules different from those of FTIR spectroscopy, can provide complementary information about molecular bands. Raman spectroscopy has also been widely used for monitoring in-situ polymerization kinetics for the polymerization of styrene,[5,6] MMA,[7] and styrene in microemulsions.[8] In some cases, reaction intermediates can also be detected by Raman spectroscopy.[1]

To our knowledge, no study of monitoring in-situ urethane reaction kinetics by Raman spectroscopy has been reported. This may be due to the fact that the main isocyanate double band ($N{=}C{=}O$ at about 1450 cm^{-1}) overlaps with carbon−hydrogen bands (1460 cm^{-1}) of urethane in the Raman spectrum, and thus peak area integration is not as straightforward and accurate as that in the FTIR spectrum (2284 cm^{-1}).

The overall objective of our program is to monitor in-situ urethane polymerization kinetics under the exposure of an intense radio frequency electromagnetic (RF) field. Since thermoset polymerization under an electric field has high reaction rates,[9−11] spectroscopic techniques which can collect data instantly and provide detailed in-situ reaction kinetics information should be good candidates. FTIR spectroscopy has been used extensively in studying thermoset polymerization kinetics, and thus was our first choice. However, there are two major difficulties of using FTIR under an RF field: first, only a very thin layer of sample (about 0.05 mm) can be used in the absorption mode because of high absorption of IR radiation by the sample. This configuration does not allow easy control of the RF field or accurate measurement of the sample temperature under the RF field. Second, the distance between the sample and FTIR electronics is relatively short. This makes shielding the RF field interference, which is essential to minimize electromagnetic interference, a very difficult task. On the other hand, Raman spectroscopy is a scattering technique based on a laser beam as the irradiation source. The sample configuration in a Raman spectrometer is much more flexible, to accommodate RF field control and temperature measurement. Moreover, shielding the detector from the interference of the RF field can be much more effectively accomplished since the distance between detector and sample is long (about three feet).

This paper reports our study of the applicability of Raman spectroscopy to monitoring urethane reaction kinetics. We will demonstrate that Raman spectroscopy is a reliable technique for measuring urethane reaction kinetics and can be applied to

---

[*] To whom correspondence should be addressed. Current address: Department of Chemical Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260 (from July 1999 − July 2000).

[†] Wayne State University.

[‡] Ford Motor Company.

[§] Current address: Chemical Engineering Department, Ford Research Laboratories, Ford Motor Company, Dearborn, MI 48121.

10.1021/jp992622g CCC: $19.00

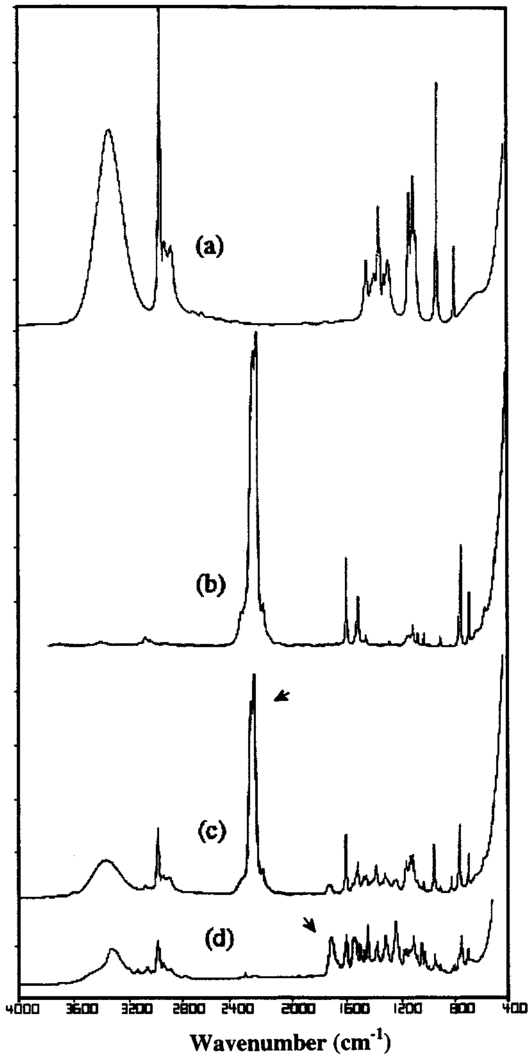

Figure 1. FTIR spectra of (a) 2-propanol, (b) phenylisocyanate, and (c) their reaction (9:1 molar) at 23 °C for $t = 2$ min and (d) $t = 60$ min. These spectra were plotted on the same *y*-axis scale. The isocyanate band at 2286 cm^{-1} was decreasing and the urethane band was increasing at 1700 cm^{-1} during the reaction.

monitoring urethane reaction under an RF field. The goals of this paper are (1) to show that urethane reaction kinetics results obtained by Raman spectroscopy and by FTIR spectroscopy are essentially identical; (2) to demonstrate the sensitivity of the Raman spectroscopic technique by studying the steric hindrance effect of the urethane reaction; and (3) to simulate urethane reaction kinetics based on a simplified kinetics model and to compare this with experimental results.

Experimental Section

All the chemicals used in this study were acquired from Aldrich Chemical Co. and used as received. The purity of these chemicals is typically >98%. A semipermanent circular aperture liquid cell (Wilmad Glass Co.) with sodium chloride windows was used in the FTIR studies. The cell was wrapped uniformly with a heating wire, which was connected to an OMEGA microprocessor-based temperature controller (CN2011J) via a regulator. The temperature of the samples was controlled to an accuracy of ±2 °C. FTIR spectra were obtained on a Nicolet 20 SXC Fourier Transform Infrared (FTIR) spectrometer at a resolution of 4 cm^{-1}. Each spectrum was signal-averaged with about thirty scans, and for each spectrum the total acquisition time was from one to three minutes. Raman spectra were obtained by a Spex 1877 0.6m Triplemate with a Spex CD 2A compudrive at a resolution of 4 cm^{-1}. A Tracor-Northern large surface area rapid-scan diode array detector was used. The laser wavelength used was 514.5 nm (green) from a Coherent Innova-70 argon laser with three-stage light control mode. The sample cell was an NMR tube (0.197" OD). Typically, thirty to sixty scans were averaged for each spectrum. The isothermal reaction temperatures were obtained with a special temperature-controlled sample holder connected to a circulating water bath. This device has a reported accuracy of ±1 °C.[7] The schematics of the FTIR and Raman setup are shown in the Appendix.

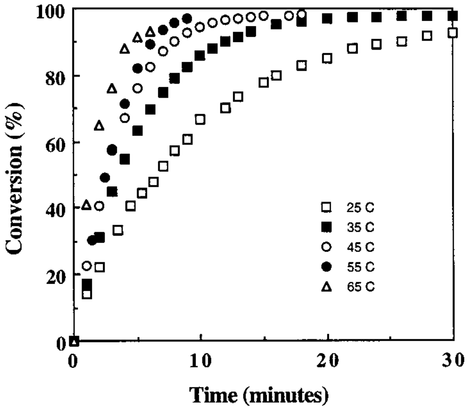

Figure 2. Conversion vs time profiles of 2-propanol and phenylisocyanate (9:1 molar) isothermal reactions at different temperatures monitored by FTIR spectroscopy. The initial reaction rate increased by a factor of about six when the reaction temperature increased from 25 to 65 °C.

TABLE 1: Activation Energy of Urethane Reactions Calculated Based on FTIR Spectra[a]

reaction system	activation energy (kcal/mole)
2-propanol + phenylisocyanate	9.3 ± 0.39
2-butanol + phenylisocyanate	9.9 ± 0.35
2-pentanol + phenylisocyanate	11.3 ± 0.51
2-hexanol + phenylisocyanate	12.2 ± 0.43
2-octanol + phenylisocyanate	14.5 ± 0.52
n-propanol + hexanediisocyanate + DMSO (2:1:1 molar)	14.0 ± 0.45
n-butanol + hexanediisocyanate + DMSO (2:1:1 molar)	14.8 ± 0.34
n-pentanol + hexanediisocyanate + DMSO (2:1:1 molar)	15.3 ± 0.53
n-hexanol + hexanediisocyanate + DMSO (2:1:1 molar)	16.0 ± 0.38
n-octanol + hexanediisocyanate + DMSO (2:1:1 molar)	18.0 ± 0.49

[a] The activation energy increases from 9.3 to 14.5 (kcal/mole) in secondary alcohol and phenylisocyanate reactions when the alcohol chain length increases from three to eight carbon atoms.

Results and Discussion

Urethane Reaction Kinetics by FTIR Spectroscopy. The urethane systems studied were alcohols and isocyanates. For simplicity, we concentrated on reactions of isocyanate with primary and secondary alcohol, which have the simplest reaction mechanism.[12] The primary alcohols used were *n*-propanol, *n*-butanol, *n*-hexanol, and *n*-octanol, and the secondary alcohol used were 2-propanol, 2-butanol, 2-hexanol, and 2-octanol. The isocyanates used were phenylisocyanate and hexanediisocyanate. Figure 1 shows the FTIR spectra of pure 2-propanol, pure

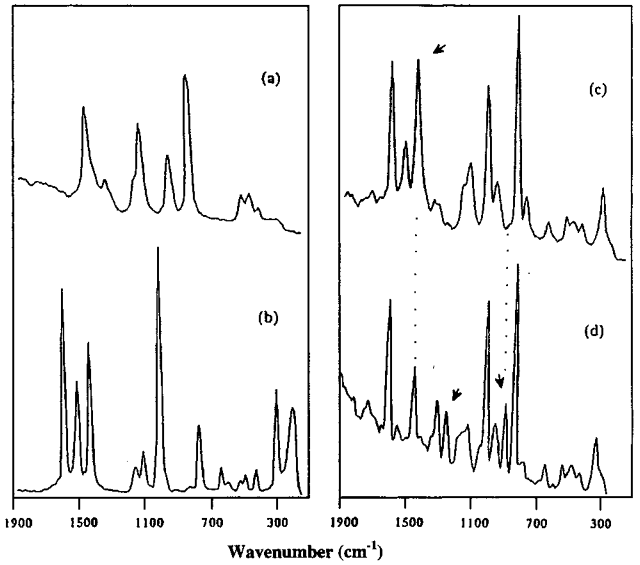

Figure 3. Raman spectra of (a) 2-propanol, (b) phenylisocyanate, and (c) their reaction (9:1 molar) at 23 °C for $t = 1$ min and (d) $t = 30$ min. These spectra were plotted on the same *y*-axis scale (count). The isocyanate band at 1448 cm^{-1} was decreasing and the urethane band was increasing at 1250 and 850 cm^{-1} during the reaction.

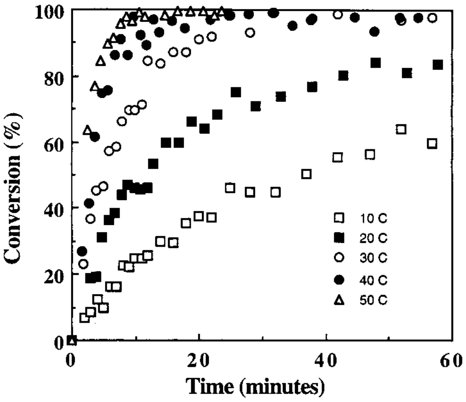

Figure 4. Conversion vs time profiles of 2-propanol and phenylisocyanate (9:1 molar) isothermal reactions at different temperatures monitored by Raman spectroscopy. The initial reaction rate increased by a factor of 9 when the reaction temperature increased from 10 to 50 °C.

phenylisocyanate, and a mixture of 2-propanol and phenylisocyanate (10% molar) at 2 and 60 min at 23 °C. These spectra are plotted with the same *y*-axis scale. The isocyanate double band (N=C=O) peak is at 2284 cm^{-1},[13] which was consumed during the reaction. The peak intensity decreased as a function of reaction time and totally disappeared at sixty minutes, when the reaction was completed. During the reaction, a new peak appeared at about 1700 cm^{-1}. The intensity of this peak increased as a function of time until the reaction was completed at about sixty minutes. This peak can be attributed to the carbonyl band (C=O) in the reaction product, urethane.[14] The conversion of isocyanate can be calculated based on either the disappearance of the isocyanate double band or the appearance of the carbonyl band. The peak area was integrated and normalized by using a reference peak at 820 cm^{-1} (carbon oxygen symmetric stretch), which does not participate in the reaction. The reaction kinetics calculated based on the disappearance of isocyanate bands and the appearance of carbonyl bands agree well. All the results of urethane reactions monitored by FTIR spectroscopy in this work were obtained based on the disappearance of isocyanate bands.

TABLE 2: Activation Energy of Urethane Reactions Calculated Based on Raman Spectra[a]

reaction system	activation energy (kcal/mole)
2-propanol + phenylisocyanate	10.0 ± 0.38
2-butanol + phenylisocyanate	10.5 ± 0.29
2-pentanol + phenylisocyanate	11.9 ± 0.28
2-hexanol + phenylisocyanate	12.8 ± 0.34
2-octanol + phenylisocyanate	14.8 ± 0.43

[a] The activation energy increases from 10.0 to 14.8 (kcal/mole) in secondary alcohol and phenylisocyanate reactions when the alcohol chain length increases from three to eight carbon atoms.

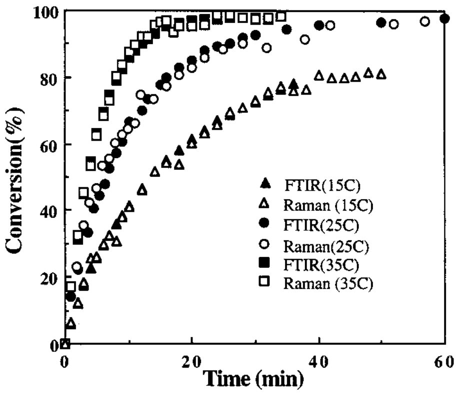

Figure 5. Conversion vs time profiles of 2-propanol and phenylisocyanate (9:1 molar) reactions at different temperatures monitored by Raman (open symbol) and FTIR (closed symbol) spectroscopy. The difference of the conversion calculated from the two methods is within 5%.

Figure 2 shows the conversion versus time profiles of 2-propanol and phenylisocyanate (10% molar) isothermal reactions at different temperatures. The results showed that the initial reaction rate increased by a factor of about six when the reaction temperature increased from 25 to 65 °C. The intrinsic rate constant and activation energy of this reaction system were calculated from these profiles. Table 1 shows the activation energies of our experimental results. As shown in the table, the activation energies obtained in this work increase with increasing alcohol chain length for isocyanate and alcohol reaction systems.

The reaction activation energies of the primary alcohol and hexanediisocyanate systems shown in Table 1 were calculated based on the assumption that the relative reactivity of both isocyanate radicals in an aliphatic diisocyanate molecule reacting with alcohol are the same.[12] In the alcohol and hexanediisocyanate reaction, the DMSO polar solvent was used to avoid gelation of the reaction mixture due to hydrogen bonding.

Urethane Reaction Kinetics by Raman Spectroscopy. The reaction systems studied by FTIR were also investigated by Raman spectroscopy. Figure 3 shows the Raman spectra of 2-propanol and the phenylisocyanate system. Spectra (a) and (b) were obtained from the pure 2-propanol and phenylisocyanate. Spectra (c) and (d) were taken at 23 °C for the reaction of 2-propanol and phenylisocyanate (10% molar) at 1 and 30 min. These spectra were plotted in same *y*-scale (count). The isocyanate double band (N=C=O) appears at 1448 cm^{-1} in the Raman spectrum.[15] In addition, two other peaks are also in the same spectral region. They can be attributed to the symmetric and antisymmetric stretch of C−H bands in 2-propanol at 1456 and 1476 cm^{-1}.[16] These two bands were assumed to be unchanged during the reaction and thus should not affect the accuracy of the integrated area of the isocyanate double band. The validity of this assumption will be discussed later. The

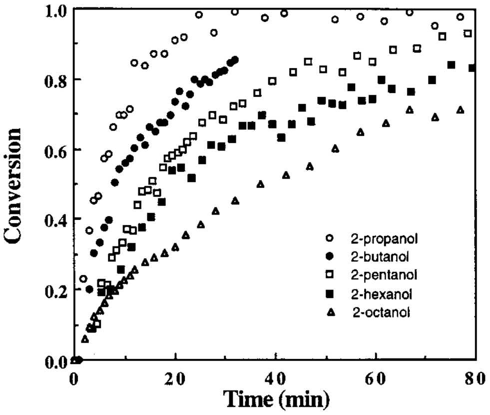

Figure 6. Conversion vs time profiles of different secondary alcohol and phenylisocyanate (9:1 molar) reactions at 30 °C monitored by Raman spectroscopy. The initial reaction rate increased more than 10 times when the alcohol chain length decreased from eight to three carbon atoms.

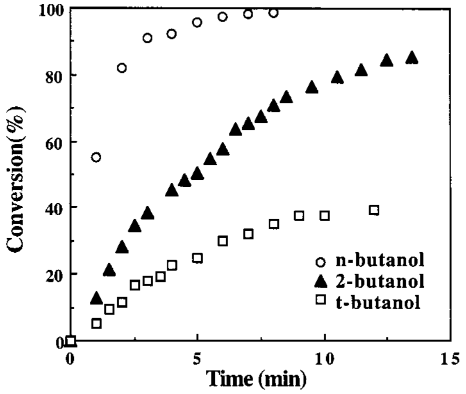

Figure 7. Conversion vs time profiles of primary, secondary, and tertiary butanol and phenylisocyanate (9:1 molar) reactions at 30 °C detected by Raman spectroscopy. The initial reaction rates of these three reactions are in the ratio of 1:0.3:0.1.

intensity of the isocyanate double-band peak decreased with increasing reaction time. There were two new peaks that appeared at 850 and 1250 cm^{-1} as reaction progressed, and the intensity of these two peaks increased significantly between 1 and 30 min (spectra c and d in Figure 3). These two peaks can be attributed to amide bands (C—N and N—H) of urethane in the reaction products.[16] The reaction conversion versus time were calculated from a series of spectra taken as a function of time, based on the disappearance of the isocyanate band or the appearance of amide bands. Essentially, these methods give identical results. However, since the intensity of the isocyanate peak is much stronger, it allows a more accurate conversion calculation. Thus, all conversion calculations of urethane reactions studied by Raman spectroscopy in this work were based on the disappearance of the isocyanate peak.

Figure 4 shows the conversion versus time profiles of 2-propanol and phenylisocyanate (10% molar) isothermal reactions monitored by Raman spectroscopy as a function of temperature. These profiles demonstrated the effect of temperature on the urethane reaction rate. The initial reaction rate increased by a factor of 9 when the reaction temperature increased from 10 to 50 °C. These conversion versus time profiles were curve-fitted to calculate the reaction orders. For all alcohol and isocyanate reaction systems, the reaction orders were equal to 2 within experimental error (±0.4). The reaction rate constants were calculated from the initial rate (from 0.0 to 5.0 min) at different temperatures. Table 2 summarizes the

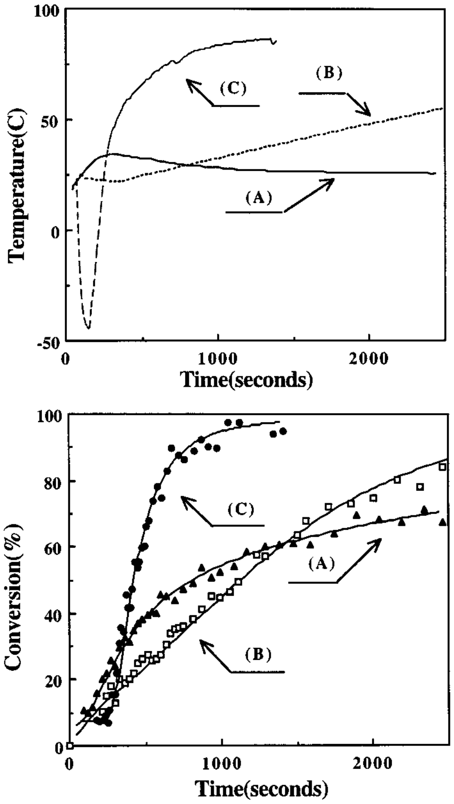

Figure 8. (a) Different temperature profiles (A, B, and C) of 2-octanol and phenylisocyanate (equal molar) reactions. These reaction temperature profiles were results of different cooling and heating rates using liquid nitrogen and an external heating source. (b) Conversion vs time profiles of 2-octanol and phenylisocyanate (equal molar) reactions (A, B, and C) under three different temperature profiles as in (a). The experimental results (symbols) and simulation results (lines) are quite comparable (<5%) for all three reactions.

activation energies of the secondary alcohol and phenylisocyanate from the experimental results obtained by Raman spectroscopy. The activation energies calculated from in-situ Raman spectra for all these reaction systems (Table 2) were slightly larger than those calculated from in-situ FTIR spectra (Table 1); these differences were within the experimental error range.

Figure 5 shows the conversion versus time of 2-propanol and phenylisocyanate (10% molar) at three different temperatures detected by Raman and FTIR spectroscopy. As shown in the figure, the data obtained by these two techniques agree quite well, and the conversion difference is within 5%. All five urethane reaction systems studied show similar agreement. Since activation energy is calculated from a series of reaction rate constants at different temperatures, the uncertainty in the activation energy calculation was propagated from the uncertainty of each reaction rate at different temperatures. These results indicate that the difference in reaction rate measurements for each reaction is small and that the urethane reaction kinetic parameters of a specific reaction system calculated based on Raman and FTIR spectroscopy are quite close to each other. The reaction activation energies of methanol, ethanol, and 2-propanol reacting with phenylisocyanate without catalyst are reported in the literature[12] as 10.0, 11.0, and 10.0 (kcal/mol), respectively, which are very comparable to the results we obtained.

Steric Hindrance Effect. Figure 6 shows the conversion versus time profiles of secondary alcohol: 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and 2-octanol with phenylisocyanate (10% molar) reactions at 30 °C obtained by Raman spectros-

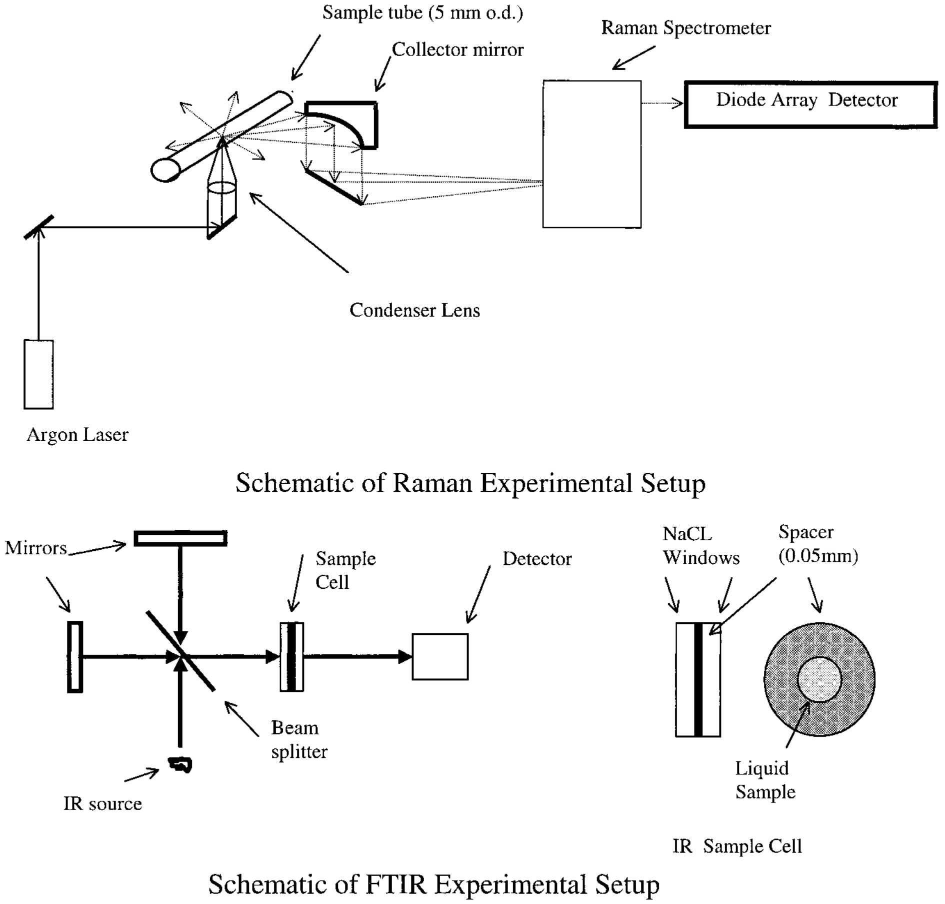

Figure 9.

copy. The results clearly show that the reaction rate decreased as the alcohol chain length increased. The initial reaction rate decreased by a factor of more than 10 when the alcohol chain length increased from three to eight carbon atoms. The reaction activation energy also showed an increase with alcohol chain length. As shown in Table 2, the corresponding activation energy increased from 10.0 to 14.8 (kcal/mol) when alcohol chain length increased from three to eight carbon atoms. Figure 7 shows the conversion versus time curves of primary, secondary and tertiary butanol with phenylisocyanate (10% molar) at 30 °C obtained by Raman spectroscopy. The initial reaction rates of these reactions are 63.0, 17.0, and 6.0 (%/minute) for primary, secondary, and tertiary butanol systems, respectively. These results show a typical ratio of a steric hindrance effect: the ratio of the initial reaction rates of primary, secondary, and tertiary alcohol with phenylisocyanate are about 1.0:0.3:0.1.[12] This apparent agreement indicates that our measurements are intrinsic rates not limited by mass transport effects.

Our results indicate that Raman spectroscopy could be used successfully to study aromatic isocyanate and alcohol reactions. However, we were not able to use this technique to monitor the aliphatic isocyanate and alcohol reactions. This is because aliphatic isocyanate (e.g., hexanediisocyanate) is not a rigid body as compared to the phenylisocyanate. Thus, the bending and scissoring modes of hydrogen−carbon vibrations (1456 and 1476 cm^{-1}) from aliphatic isocyanate will change during the reaction. Such changes interfere with the intensity of the isocyanate double band (1448 cm^{-1}) on which the conversion calculations are based. Moreover, the amide bands (CN and NH) also overlap with some carbon−carbonyl bands. It is not a trivial task to deconvolute these peaks accurately to calculate the reaction kinetics.

Simulation of Urethane Reaction Kinetics. To apply Raman spectroscopy to follow nonisothermal urethane reactions, especially under the influence of an RF field, it is desirable to have a simulation model to evaluate the experimental results. The reaction mechanisms and kinetics of isocyanate and monohydroxylic alcohols have been studied extensively.[12] For a reaction with equal molar isocyanate and alcohol, the reaction kinetics can be approximately presented as

$$\int_{x_0}^{x} \frac{\mathrm{d}x_{\mathrm{NCO}}}{(1 - x_{\mathrm{NCO}})^n} = \int_{t_0}^{t} k_0 \exp\left(-\frac{\Delta E}{RT(t)}\right) \mathrm{d}t$$

where n, k_0, ΔE, and $T(t)$ are the total reaction order, intrinsic rate constant, activation energy, and reaction temperature, respectively. A simulation program was developed to calculate the conversions versus time, according to this kinetics expression, with a second-order reaction. Intrinsic reaction rate constants and activation energies used were calculated from isothermal reactions, and the temperature−time relationships were measured from the experiments.

To verify this reaction kinetics model and the simulation method, several alcohol and isocyanate reactions were conducted with different reaction temperature profiles controlled by liquid nitrogen cooling and external fields heating. The reaction kinetics of these reactions were monitored by Raman spectroscopy and compared with the conversion versus time results calculated from the simulation model. Figure 8a shows the temperature profiles of 2-octanol and phenylisocyanate (equal molar) reactions under different external heating or cooling sources. Figure 8b shows the conversion versus time data of these three reactions. The lines in this figure are the simulation results, and the data points (symbols) are the results calculated from Raman spectra. It showed clearly that the experimental and simulation results agree quite well, and the error was less than 5%. Other alcohol−isocyanate systems also show similar agreement. This simulation method demonstrates an effective way of verifying the nonisothermal reaction kinetics measurement. On the other hand, the model can also be used in identifying any deviation from the experimental results, which would suggest a different reaction mechanism.

Conclusions

Raman spectroscopy has been successfully used to monitor the urethane reaction kinetics, and the conversion versus time data obtained by Raman spectroscopy agreed well with that measured by FTIR spectroscopy. The activation energies calculated in this study agree well with values reported in the literature. The reaction results monitored by Raman spectroscopy demonstrated clearly the steric hindrance effects of the alcohol structure and chain length on the alcohol and isocyanate reactions. The agreement between the reaction kinetics simulation and experimental results further demonstrated the applicability of Raman spectroscopy in monitoring the in-situ urethane reactions. The simulation paves the way to elucidating reaction mechanisms under nonisothermal conditions as a result of the exposure to external fields. The results in this study established a basis for our future work of studying the in-situ urethane reaction kinetics under an RF field, which will be reported in a subsequent paper.

Acknowledgment. Financial support from Ford Motor Company and the Institute for Manufacturing Research of Wayne State University for this project is gratefully acknowledged. The authors would like to thank Dr. Robin Hood, Director of the Central Instrumentation Facility at Wayne State University for his assistance.

Appendix

Schematic of Raman and FTIR experimental setup for in-situ monitoring of urethane formation (Figure 9).

References and Notes

(1) Yang, Y. S.; Lee, L. J.; *Journal of Appl. Polym. Sci.* **1988**, *36*, 1325−1342.

(2) Gulari, E.; McKeigue, K.; Ng, K. Y. S. *Macromolecules* **1984**, *17*, 1822−1825.

(3) Coleman, M. M.; Skrovanek, D. J.; Hu, J.; Painter, P. C. *Macromolecules* **1988**, *21*, 59−65.

(4) Xu, Z.; Huang, Z.; Xu, H. *J. of International Society for Optical Engineering* **1989**, *1145*, 346−347.

(5) Sears, W. M.; Hunt, J. L.; Stevens, J. R. *J. Chem. Phys.* **1981**, *75*(4), 1589−1602.

(6) Chu, B.; Fytas, G.; Zalczer, G. *Macromolecules* **1981**, *14*, 395−397.

(7) Feng, L.; Ng, K. Y. S. *Macromolecules* **1990**, *23*, 1048−1053.

(8) Feng, L.; Ng, K. Y. S. *Colloids Surf.* **1991**, *53*, 349−361.

(9) Li, C.; Dickie, R. A. *International J. Adhes. and Adhesives* **1991**, Oct, p 241.

(10) Hahn, O.; Ewerszumrode, A. Laboratory for Material and Joining Technology (LWF), University of Paderborn, Paderborn, D-33098, Germany. *Weld. World* **1998**, *41*(2), 149−155.

(11) Charles L. Lambda Technologies, Inc., Morrisville, NC, 27560, USA. *Mater. Res. Soc. Symp. Proc.* **1997**, *445* (Electronic Packaging Materials Science IX), 125−130.

(12) Saunders, J. H.; Frish, K. C. In *Polyurethanes Chemistry and Technology; Part I, Chemistry*; John Wiley & Sons: 1962; Chapters 3 and 4.

(13) Lin-Vien, D.; Colthup, N. B.; Fately, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequency of Organic Molecules*; Academic Press: New York, 1991; Chapters 9 and 13.

(14) Szymanski, H. A. *Interpreted Infrared Spectra*; Plenum Press Data Division: New York, 1966; Vol. 2.

(15) Stephenson, C. V.; Coburn, W. C., Jr.; Wilcox, W. S. *Spectrochim. Acta* **1961**, *17*, 933−946.

(16) Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; John Wiley & Sons: New York, 1973; Chapters 3 and 9.