Cure Characterization in Polyurethane and Model Urethane Reactions by an Intrinsic Fluorescence Technique

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Received October 13, 1995; Revised Manuscript Received February 7, 1996⊗

ABSTRACT: Intrinsic fluorescence during the reactions between methylene 4,4′-diphenyl diisocyanate (MDI) and 1-butanol or hydroxy-terminated poly(propylene oxide) was investigated to characterize a model urethane reaction and polyurethane formation both in dilute solution and in bulk. Fluorescence intensity was found to increase about 87 times when MDI was converted to diurethane, with the emission maximum around 315 nm. The rate constants and the activation energies for the model reaction and polyurethane formation were obtained from the fluorescence results and compared with the IR results. The correlation between the fluorescence intensity and the extent of the reaction determined by IR has been established.

Introduction

Our laboratory has been involved in developing fluorescence and UV−visible spectroscopic techniques for the characterization of cure and water uptake in polymers and composites, such as epoxy,[1] polyimide,[2] polyamide,[3] polyurethane,[4] bismaleimide,[5] polycyanate,[6] and vinyl polymers.[7]

Our first approach was the route of the extrinsic fluorophoric sensor, which was added in a small amount, either to mimic the curing agent or to act as a water-sensitive sensor. For example, for epoxy cured with 4,4′-diaminodiphenyl sulfone (DDS), which is the dominant matrix resin for composites, 4,4′-diaminoazobenzene (DAA) has been found to show sensitive fluorescence intensity enhancement due to the much greater quantum yield of the tertiary amine form of DAA as a result of reaction with epoxide.[1] Another example of the extrinsic reactive sensor was in polyurethane cure monitoring where 1,5-naphthyl diisocyanate (NDI) was used to mimic methylene-4,4′-diphenyl diisocyanate (MDI), which is the most often used diisocyanate.[4] NDI exhibits red spectral shifts and large fluorescence intensity enhancement as it reacts with alcohol to form urethane.[4] These spectral changes were correlated to the extent of reaction of MDI.

However, using an extrinsic sensor is often inconvenient since its signals may be blocked by fillers, fibers, or impurities in the resin or composite. Therefore, the intrinsic spectral behavior of the monomer or curing agent has been investigated carefully during the last few years. In epoxy cured with DDS aromatic diamine, the excitation spectral red shifts of about 25 nm due to the conversion of the primary amine groups of DDS to the tertiary amines were found to correlate well with the extent of cure.[1] This DDS excitation behavior was successfully implemented for in-situ cure monitoring in the epoxy-based graphite composite by fiber-optic fluorescence.[8]

In this study, the UV and fluorescence behaviors of MDI as the intrinsic sensor are investigated in order to characterize a model urethane reaction and polyurethane, supported by the results obtained by IR technique.

While many kinetic studies of MDI-based urethane formation have been reported in the literature by other technique,[9−13] this study is the first exploring UV and fluorescence techniques to the best of our knowledge.

Experimental Section

1. Model Reaction Studies of MDI with 1-Butanol. Methylene-4,4′-diphenyl isocyanate (MDI) from Eastman Kodak (99% purity) was used without further purification, and 1-butanol (HPLC grade) from Aldrich was distilled before use. To 100 mL of saturated MDI solution in cyclohexane, a large excess of 1-butanol (0.02 mol) was added and allowed to react in an oil bath either at 50 or 70 °C, with a condenser connected to a $CaCl_2$ drying tube.

2. Polymerization of MDI with PPO in Solution. Hydroxy-terminated poly(propylene oxide) (PPO) from Aldrich Chemical Co. (MW 2000, functionality 2.0) was dried in high vacuum at 50 °C for 24 h before use. Anhydrous solvent, *N*,*N*-dimethylacetamide (DMAc); (HPLC grade) from Aldrich was used without further treatment. Stoichiometric amounts of MDI (0.50 g) and PPO (4.0 g) were dissolved in DMAc separately and preheated to the reaction temperature of 50 °C before mixing. The reaction was carried out in a sealed glass vial purged with dry nitrogen before the reaction started.

3. Bulk Polymerization of MDI with PPO. A 0.25 g (0.001 mol) sample of MDI was crushed quickly into fine powder and then mixed with 2.0 g (0.001 mol) of PPO. The mixture was heated at reaction temperatures (60, 80 °C) for 5 and 2 min, respectively. The estimated extent of reaction during mixing was less than 2% by IR. One drop of the solution was placed between two quartz plates with a Teflon spacer (1 mil in thickness). The quartz cell was placed in a heating device for in-situ fluorescence measurement.

4. UV and Fluorescence Measurements. A Perkin-Elmer diode array UV−visible spectrophotometer and a Perkin-Elmer MPF-66 fluorescence spectrophotometer were used for UV absorption and fluorescence measurement, respectively. In the model reaction study of MDI with 1-butanol, a 125 μL aliquot from the reaction solution was diluted into 3 mL of dry cyclohexane for UV measurement, while 25 μL of the solution was diluted into 3 mL of cyclohexane for fluorescence spectra. The background scattering and emission from the solvent at this wavelength was subtracted. The UV absorption at the excitation wavelength was kept below 0.1. Therefore, the emission intensity can be assumed to be proportional to the concentration of the sample. The spectra were taken at room temperature, unless otherwise noted. The extinction coefficient of MDI was estimated to be 3.23×10^3 M^{-1} cm^{-1} at 283 nm. The initial concentrations of MDI was calculated to be 5.7×10^{-3} M.

In the polymerization study of MDI with PPO in solution, a polar solvent (DMAc) was used. Due to the high absorptivity

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⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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Scheme 1. Chemical Structures for the Consecutive Reaction MDI with Excess Alcohol

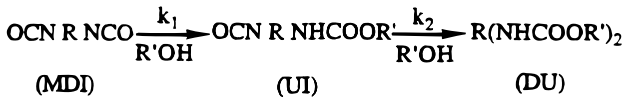

Table 1. Physical Characteristics of Model Compounds

	UI	DU
mp (°C)	56.8	107.0
IR (cm^{-1})	3325 N−H	3332 cm^{-1} N−H
	1709 C=O	1701 C=O
	1317 C−N	1313 C−N
	1067 C−O	1078 C−O
^{1}H NMR (ppm)	9.65 N−H	9.43 N−H
	7.2−7.5 Ar−H	7.0−7.4 Ar−H
	4.03−4.07 O−CH	4.01−4.05 O−CH
UV−Vis[a] (nm)	276	278
	286	288
fluor[b] (nm)	303	307

[a] Spectra were taken in cyclohexane. [b] Spectra were taken in cyclohexane and excitation was set at 280 nm.

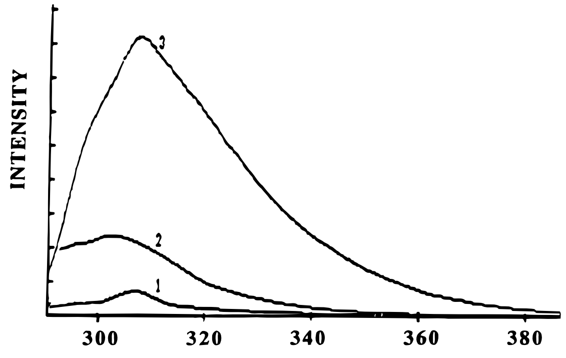

Figure 1. Fluorescence emission spectra of model reaction compounds: 1, MDI; 2, UI; 3, DU.

of DMAc for water, a 0.5 μL aliquot from the reaction solution was diluted into 3 mL of dry cyclohexane for fluorescence study, in order to avoid the reaction of MDI with water during UV and fluorescence measurement, following the dilution of the product.

For bulk polymerization studies, the front surface fluorescence measurements were employed. IR was used to calibrate the extent of reaction in all the polymerization studies.

5. Synthesis and Characterization of Model Urethanes. The diurethane (DU) and monourethane (UI) model compounds were synthesized by reacting an excess of 1-butanol with MDI and phenyl isocyanate (PI), respectively, in dry toluene.

Results and Discussion

1. Characterization of Model Reaction Products. The reaction of MDI with an alcohol is a consecutive reaction where the diisocyanate is first converted to UI, followed by formation of DU, as illustrated in Scheme 1. The synthesized model reaction products were purified using column chromatography. The melting points, infrared, NMR, UV, and fluorescence data of UI and DU are shown in Table 1. Red shifts in the UV spectra were observed as MDI was converted into urethane. The UV absorption peaks of MDI appeared at 274 and 283 nm while those of DU were present at 278 and 288 nm. The UV absorption in the region longer than 240 nm is mainly due to the π−π* transition. When a hydroxyl group reacted with the NCO group, the resonance structure of the isocyanate group was destroyed. The unpaired electrons on the nitrogen atom in urethane can be stabilized by the neighboring phenyl group, where the unpaired electrons delocalize over the benzene ring and a longer conjugating system is formed. This process lowers the energy level of the excited π* state. Therefore, the UV spectra of the urethane product appeared at longer wavelength as compared with MDI.

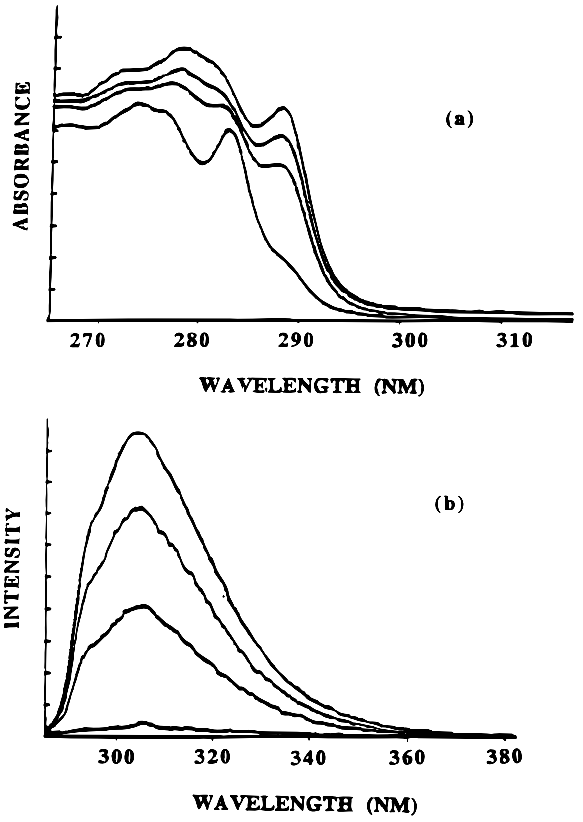

Figure 2. (a) Changes in UV spectra for the reaction of MDI with excess 1-butanol in cyclohexane at 50 °C as a function of reaction time. From left to right, the reaction time corresponds to 0, 10, 20, and 240 min. (b) Changes in fluorescence emission spectra for the reaction of MDI with excess 1-butanol in cyclohexane at 50 °C as a function of reaction time. From bottom to top, the reaction time corresponds to 0, 10, 20, and 120 min.

There was only a small red shift observed when MDI was converted to UI and DU in the fluorescence emission spectra (Figure 1). However, a drastic increase in the intensity for DU was observed. It has been reported that the aromatic isocyanates[4] and amides[3] showed little fluorescence. The reason for this may arise from the different bonding of the C=O group with an adjacent atom. The C=O unit is known to have an excited triplet state which is usually close to the energy level of the excited singlet state. The excited singlet state could be deactivated through the excited triplet state by intersystem crossing. The excited triplet state has a longer lifetime and therefore is more easily quenched before emission. In the case of MDI, the energy of the excited singlet state could be transferred to the triplet state of C=O unit through the N=C double bond. Therefore, little fluorescence was observed. In the case of the urethane, the energy gap between the excited singlet state and the excited triplet state could be significant, making intersystem crossing difficult. As a result, the urethane products showed stronger fluorescence. The relative quantum yield (Q) of each species at 305 nm was to be as follows:

$$Q_{\mathrm{MDI}}:Q_{\mathrm{UI}}:Q_{\mathrm{DU}} = 1:22:87.$$

2. MDI Reaction with 1-Butanol in Cyclohexane. The reaction of MDI with a large excess of 1-butanol was carried out at 50 and 70 °C. As MDI reacted with 1-butanol in cyclohexane solution, the UV spectra of the reaction mixture showed a red shift indicating the formation of urethane (Figure 2a), while the extinction coefficient at the absorption maximum increased as well, from 3.2×10^3 to 4.3×10^3 M^{-1} cm^{-1}. The fluorescence intensity at 305 nm increased dramatically with reaction time (Figure 2b). Due to the closeness of UV spectra during reaction, UV deconvolution was not used to obtain the composition of UI and DU.

When there is no intermolecular quenching and self-quenching in the reaction mixture, the fluorescence intensity at a certain wavelength can be obtained by the linear addition of the emission intensity from all the species at this wavelength, from

$$I_f = Q_{MDI}A_{MDI} + Q_{UI}A_{UI} + Q_{DU}A_{DU} \tag{1}$$

where Q is a relative fluorescence quantum yield of each species and A_{MDI}, A_{UI}, or A_{DU} is the fraction of each species with their sum equal to unity, i.e., $A_{MDI} = (MDI)/(MDI)_o$, $A_{UI} = (UI)/(MDI)_o$, and $A_{DU} = (DU)/(MDI)_o$. It is found that the Q_{MDI} is negligible compared with Q_{UI} and Q_{DU}. Thus eq 1 can be written as

$$I_f \simeq Q_{UI}A_{UI} + Q_{DU}A_{DU} \tag{2}$$

The solutions for the kinetics in Scheme 1 are given as follows:[4]

$$A_{MDI} = e^{-2k_1t} \tag{3}$$

$$A_{UI} = \frac{2R}{1-2R}[e^{-2k_1t} - e^{-2k_1(t/R)}] \tag{4}$$

$$A_{DU} = \frac{2R}{1-2R}[(1/2R)(1 - e^{-2k_1t}) + (e^{-2k_1(t/R)} - 1)] \tag{5}$$

where $k'_1 = k_1(R'OH)_o$, $k'_2 = k_2(R'OH)_o$, and $R = k_1/k_2 = k'_1/k'_2$.

Substituting eqs 4 and 5 into eq 2, we have

$$I_f \cong Q_{ui}\left\{\frac{2R}{1-R}[e^{-2k_1t} - e^{-2k_1t}/R]\right\} + Q_{DU}\left\{\frac{R}{1-R}\left[\frac{1}{R}(1 - e^{-2k_1t}) + (e^{-2k_1t/R} - 1)\right]\right\} \tag{6}$$

The simulated curves (dashed and solid lines) and the experimental data (open and solid circles) at 50 and 70 °C are shown in Figure 3, where the R value corresponding to the best-fitting results is found to be 1.0. The k'_1 and k_1 values for these best-fitted curves are listed in Table 2. The activation energy based on the regression results from the fluorescence study was 3.0 kcal/mol.

The studies on the model compound reactions demonstrated that two isocyanate groups possess similar reactivities. Thus, the reaction of one isocyanate group does not affect the reactivity of the other. This conclusion seems reasonable because the two phenyl isocyanate groups in MDI are not in conjugation with each other.

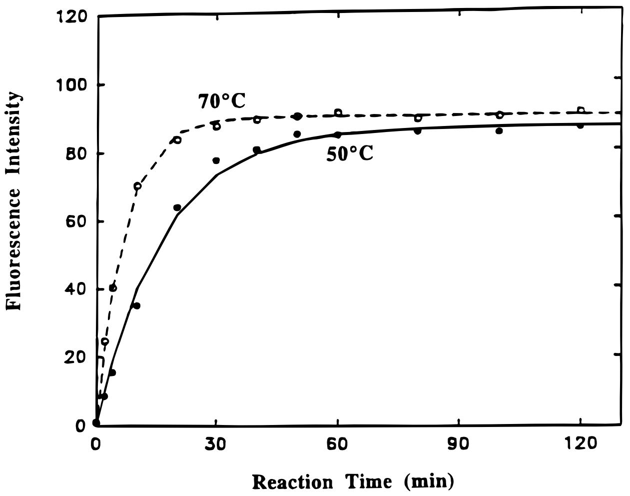

Figure 3. Changes in fluorescence intensity at 50 and 70 °C for the reaction of MDI with 1-butanol in cyclohexane. The curves represent the simulated results when R (k_1/k_2) is equal to 1.

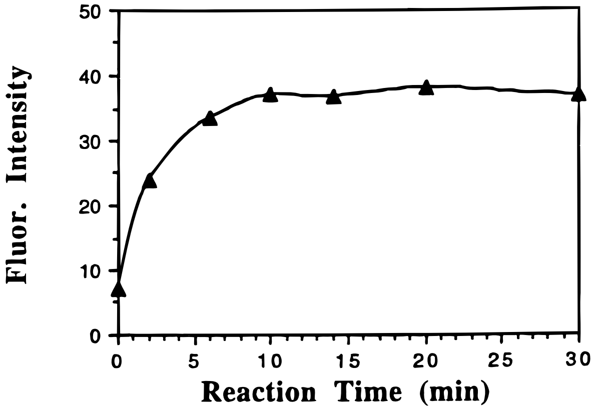

Figure 4. Changes in fluorescence intensity at 315 nm as a function of reaction time for a stoichiometric reaction of MDI and PPO in DMAc at 50 °C.

Table 2. Summary of Kinetic Parameters for Model Reaction between MDI and 1-Butanol in Cyclohexane by Fluorescence Studies

reaction temp (°C)	k'_1 (min^{-1})	k_1 (M^{-1} min^{-1})
50	0.099	0.50
70	0.15	0.76
ΔE (kcal/mol)	3.0	

3. Solution Polymerization of MDI with PPO in DMAc. The solution polymerization of the stoichiometric amount of MDI with PPO was carried out in anhydrous DMAc at 50 °C. The characteristic UV absorption peaks of each reaction species were obscured due to the intermolecular interactions among the reaction species and the solvent, making UV deconvolution difficult to perform. The emission of polyurethane appeared at 315 nm, without a significant spectral shift during the course of reaction. This trend is similar to the model reaction of MDI with 1-butanol as illustrated in Figure 2b. However, the reaction of MDI with PPO in DMAc seems faster than the reaction of MDI with 1-butanol in cyclohexane at the same temperature of 50 °C. As shown in Figure 4, the fluorescence intensity levels off after about 10 min, while it took about 40 min (Figure 3) for the model reaction in cyclohexane. This difference may be due to the increased polarity[8] of DMAc. If the reaction is assumed to be second order, the kinetic equation is then expressed, when the stoichiometric ratio is used, by

$$dC_{NCO}/dt = -kC_{NCO}C_{OH} = -kC_{NCO}^2 \tag{7}$$

where k is the rate constant for the second-order reaction and C_{NCO} or C_{OH} is the concentration of overall

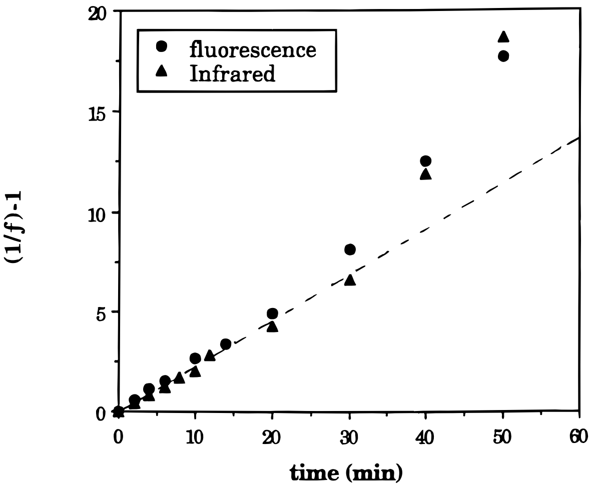

Figure 5. Second-order kinetic plot for a stoichiometric reaction of MDI and PPO in DMAc at 50 °C.

Table 3. Kinetic Parameters for Solution Polymerization of MDI and PPO in DMAc Fluorescence Studies

	IR		Fluor	
	$k' = kC_o$ (min^{-1})	k (M^{-1} min^{-1})	$k' = kC_o$ (min^{-1})	k (M^{-1} min^{-1})
50 °C	0.20	1.7	0.24	2.0
70 °C	0.46	3.9	0.52	4.4
ΔE_a (kcal/mol)	10.8		8.7	

NCO or OH groups, respectively. The solution for eq 7 is

$$(1/f) - 1 = kC_o t = k't \tag{8}$$

where f is the fraction of the unreacted reactant, C/C_o, and k' is equal to kC_o. Therefore, $(1/f) - 1$ was plotted against the reaction time to extract the rate constant, as shown in Figure 5. The plots followed a linear relation with an upward deviation occurring at a late stage (beyond 90% conversion). This phenomenon was attributed to the catalytic effect of urethane at high concentration.[14] The kinetic constants from the fluorescence results were given in Table 3. In order to validate the results from fluorescence, FT-IR studies were carried out for comparison. By monitoring NCO absorption at 2270 cm^{-1} while using the 1335 cm^{-1} band as the internal standard, and analyzing the data using eq 8, IR results in terms of $(1/f) - 1$ versus time were plotted in Figure 5. There is quite good agreement between the IR and fluorescence results. The kinetic parameters from IR results, which are also summarized in Table 3, compare well with those from fluorescence. The rate constants for these reactions in DMAc are greater than these reactions in cyclohexanes. Also noted is the higher activation energy for the MDI−PPO reaction in DMAc.

4. Bulk Polymerization of MDI with PPO. The bulk polymerization for the polyurethane was monitored by the in-situ measurement of the changes in both fluorescence and infrared spectra of the reaction system. In the system of MDI with PPO at the stoichiometric ratio, the fluorescence emission from the urethane groups increased at 314 nm. The reaction was carried out at 60 and 80 °C. Since the fluorescence intensity can be affected by the temperature and the viscosity of the medium, such intensities at different temperatures need to be normalized in order to compare with one another. The fluorescence intensity was thus normalized based on the fluorescence intensity ratio of the polyurethane samples at the same extent of urethane formation (at 90%). The normalization was carried out through

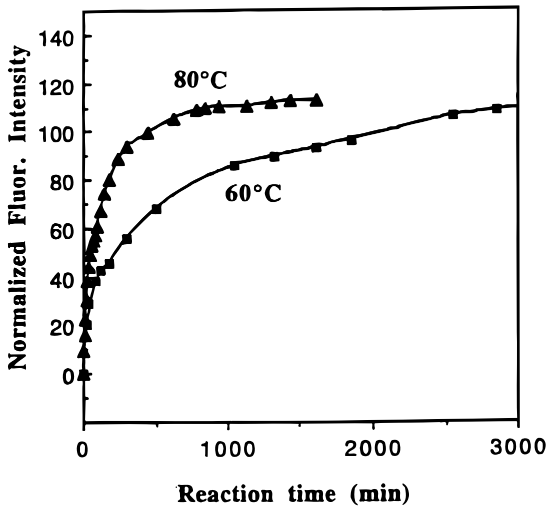

Figure 6. Changes in the normalized fluorescence intensity at 315 nm as a function of reaction time for the bulk reaction of MDI and PPO.

$$F_t^{80} = F_t^{60}F^{60}(\zeta=90)/F^{80}(\zeta=90) \tag{9}$$

where F_t^{80} and F_t^{60} are the fluorescence intensities at time t at 80 and 60 °C, respectively; $F^{60}(\zeta=90)$ and $F^{80}(\zeta=90)$ are the fluorescence intensities at 90% of urethane formation at 60 and 80°C, respectively. Figure 6 shows the plots of such normalized fluorescence intensity changes with reaction time at these two temperatures.

In order to separate the contribution of viscosity rise during cure to the observed increase in fluorescence intensity, a small amount of diurethane model compound (0.5%) made from MDI was added to a stoichiometric mixture of an aliphatic diisocyanate, cyclohexane-1,4-diisocyanate (CDI), and PPO at 50 °C. This matrix resin exhibits no fluorescence. Since the diurethane may not react further at 50 °C with CDI since CDI has much lower reactivity in comparison to MDI,[10] its fluorescence increase will be mainly due to the viscosity rise during cure. No significant enhancement in fluorescence intensity was observed during the reaction. As a result, the observed intensity increase in the MDI−PPO bulk reaction was interpreted as basically due to the chemical reaction between MDI and PPO.

While the reaction between MDI and PPO proceeds fast during the first half of the reaction at both temperatures, the second half of the reaction proceeds slower, as shown in Figure 6. This trend, in contrast to the same reaction in dilute DMAc solution as described in the preceding section, may be due to the lower dielectric constant of the bulk medium.

Second-order kinetic analysis was also used to interpret the IR data. When $(1/f) - 1$ was plotted against reaction time, two linear ranges were obtained as illustrated by two straight lines in Figure 7. The small window in Figure 7 shows the enlarged part of the first linear range covering 50% conversion. The kinetic parameters were listed in Table 4. At 60 °C, the rate constant for the first-stage reaction is about 3 times greater than that for the second stage. However, at 80 °C, this gap is much smaller where the first-stage reaction is only about 1.5 times faster. This trend was previously observed by Wang et al., who used an IR technique to study polyurethane curing kinetics to high

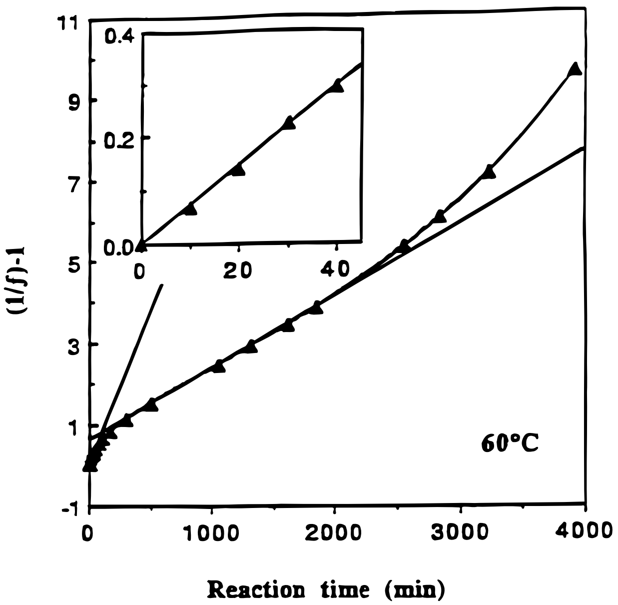

Figure 7. Second-order kinetic plot by IR results for the bulk reaction of MDI and PPO.

Table 4. Kinetic Parameters for Bulk Polymerization of MDI with PPO by Infrared

	first stage		second stage	
	$k'_1 = k_1C_0$ (min^{-1}) × 10^2	k_1 (M^{-1} min^{-1}) × 10^2	$k'_2 = k_2C_0$ (min^{-1}) × 10^2	k_2 (M^{-1} min^{-1}) × 10^2
60 °C	0.74	1.6	0.18	0.37
80 °C	1.5	3.2	0.60	1.3
ΔE_a (kcal/mol)	8.1		14	

conversion in bulk.[15] The activation energy for the first-stage reaction is comparable with that in solution, while the activation energy is much larger for the second-stage reaction.

Since the normalized fluorescence intensity is only due to the chemical reaction, we can correlate it to the extent of reaction determined by IR. Such a plot is shown in Figure 8. This correlation curve can be used to estimate the extent of reaction from the fluorescence intensity values after normalization.

Summary

In this research, fluorescence spectroscopy is utilized as a main tool for the characterization of the model reaction of MDI with 1-butanol and polymerization processes of MDI with hydroxy-terminated PPO, both in dilute solution and in bulk. The urethane products were used as intrinsic spectroscopic sensors to monitor the reaction processes. This monitoring technique avoids the inconvenient introduction of the extrinsic sensoring chemicals.

The intrinsic fluorescence resulting from the reactions of MDI with 1-butanol showed a high sensitivity to the formation of urethane. MDI showed virtually no fluorescence, but on its conversion to urethane, a strong fluorescence emission around 315 nm was observed. Model reactions were utilized to understand the photophysical behavior of the urethane reaction. Analysis of the experimental data suggests that the two isocyanate groups on MDI have almost the same reactivity. The rate constant for the solution polymerization of MDI with PPO was larger than that for the small molecule model reaction, which is probably due to the catalytic effect of DMAc. Second-order reaction kinetics were followed until high conversion was reached where autocatalysis of the urethane group became significant. For bulk reaction of MDI and PPO, the viscosity effect on the fluorescence intensity of the urethane group was found to be negligible. Therefore, the increase in the fluorescence intensity in the bulk polymerization was mainly due to the chemical reaction between MDI and PPO. The bulk reaction between MDI and PPO was found to be a two-stage second-order reaction, with the second stage slower than the first one. The transition from the first to the second stage was found around 50% conversion. IR results were used to correlate the extent of reaction with the fluorescence intensity.

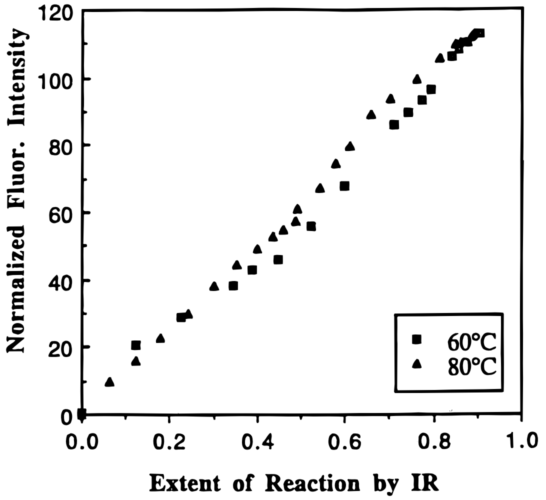

Figure 8. Correlation plot between normalized fluorescence intensity and the extent of reaction determined by IR for the bulk reaction of MDI and PPO.

Acknowledgment. We acknowledge the financial support in part by the National Science Foundation, Polymer Program (Grants DMR 91-08060, DMR 94-15385), the Army Research Office (Contract DAAL 03-92-G-0267), and the Office of Naval Research.

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MA9515339