$$I_e = c[A_{pp} + 9p(A_{pp}{}^{q} - A_{pp}) + 45p^2(-2A_{pp}{}^{q} + A_{pp} + A_{pp}{}^{r/2}) + 100p^2[(r+2)A_{pp}{}^{q} - rA_{pp} - (2-r)A_{pp}{}^{1/2} - 2A_{pp}{}^{r/2} + (2-r)A_{pp}{}^{r/4}] + 230p^2[-rA_{pp}{}^{q} + (r^2/4)A_{pp} + (r/p)A_{pp}{}^{1/2} + A_{pp}{}^{r/2} - (2-r)A_{pp}{}^{r/4} + (r/2-1)^2]] \quad (9)$$

relates I_e in terms of A_{pp}. The constant c in eq 9 has been adjusted based on the excitation spectra of the model cure species. From eq 9, we can estimate the fraction of unreacted diamine label (A_{pp}) as a function of cure time from the corresponding excitation intensity after calibration. Once A_{pp} is estimated, the rest of the cure compositions can be calculated on the basis of the solutions of the kinetic equations (eq 3–7). Figure 6 illustrates the results by the analysis of the excitation spectra in comparison to the deconvolution results of UV–vis absorption spectra.[1] The results by excitation spectra show the trends of the formation and the disappearance of the cure species. In comparison to the results by the deconvolution of the UV–visible absorption spectra, the results by the excitation spectra show somewhat slower appearance/disappearance of the cure species. This may be due to the error in the deconvolution of overlapping peaks in absorption spectra. Therefore, the compositional analysis may be more reliable by fluorescence excitation spectra, especially for tertiary amine species.

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Registry No. DAA, 538-41-0; PGE, 122-60-1; (DAA)(DGEBA)(DDS) (copolymer), 123933-43-7.

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Studies of Model Urethane Reactions and Cure in Polyurethanes by UV Absorption and Fluorescence Spectroscopy

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ABSTRACT: UV absorption and fluorescence spectroscopy are used as main tools to characterize the kinetics of the reaction between 1,5-naphthyl diisocyanate (NDI) and 1-butanol and the cure in polyurethanes using NDI as a chemical sensor. When advantage is taken of the red shifts in UV absorption and of a large enhancement in fluorescence intensity as the reaction progresses, the kinetics of the reaction are analyzed. The reactivity of the first isocyanate group in NDI is found to be similar to that of the second isocyanate group, both in model reactions in dilute solution and in polyurethane matrix. The kinetic plots for the reaction of NDI with dihydroxy-terminated poly(tetramethylene oxide) (PTMO) were linear up to 70–80% conversion but displayed an upward curvature beyond such conversion, probably due to the weak catalytic effect of the urethane groups. Similar trends were observed from IR monitoring of methylenediphenylene diisocyanate (MDI) used for the polyurethane matrix with PTMO. The rate constants for MDI are found to be slightly greater than those for NDI, with similar activation energies for both diisocyanates. From these results, a calibration curve was established to correlate the extent of the reaction for MDI with that for NDI.

Introduction

During the last few years, we have developed a method to track cure products throughout the cure process, based on labeling with reactive compounds as molecular sensors to mimic one of the polymerizing reactants. These reactive labels were chosen to exhibit spectral changes in the region of UV–visible and fluorescence spectra where the polymerizing matrix has little absorption or emission. In this method, we take advantage of the magnified effects of the substituent changes in the para and para′ positions of conjugated aromatic reactive labels on the UV–visible and fluorescence spectra. We have applied this method to characterize the kinetics and mechanisms of the cure in epoxy networks,[1] the imidization process in polyimides,[2] and the acylation in polyamides.[3]

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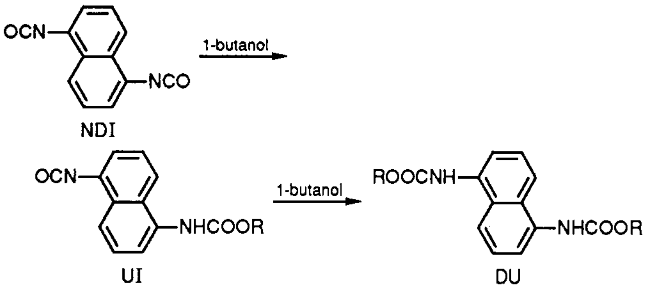
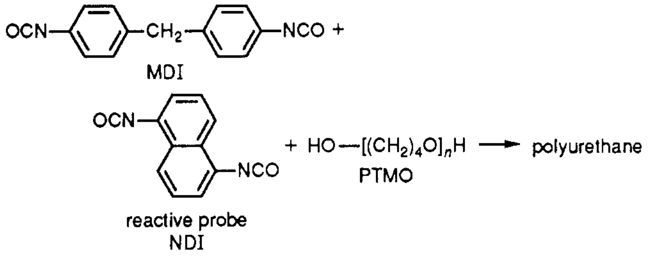
Scheme I
Chemical Structures of 1,5-Naphthyl Diisocyanate (NDI) and Its Monourethane (UI) and Diurethane (DU) Products after Reaction with 1-Butanol[a]



[a] R = 1-butyl.

Scheme II
Chemical Structures of the Polyurethane Matrix Containing a Small Amount of 1,5-Naphthyl Diisocyanate (NDI) Label



As pointed out in our previous work, one particular advantage of this method is that we can often distinguish between several cure species in some polymers[2a,4] while other spectroscopic techniques such as IR or NMR cannot. This advantage makes it possible to follow cure composition throughout the cure process and to analyze the kinetics and the mechanisms of several consecutive polymerization steps in some polymers.

In this paper, we extend this approach to the studies of model urethane reactions and cure in polyurethanes by using 1,5-naphthyl diisocyanate (NDI) as the molecular sensor. We chose NDI for the following reasons: first, NDI is reported to have similar reactivity to methylenediphenylene diisocyanate (MDI),[5] which is often used in polyurethanes; second, NDI shows UV–vis absorption and fluorescence emission at longer wavelengths than MDI; and last, NDI exhibits a drastic change in fluorescence intensity as it is transformed to its urethane species.[6]

Before we can quantitatively analyze the polymerization reactions between NDI and diol, it is necessary to characterize the spectroscopic parameters of the model reaction products. Therefore, we first studied the reaction of NDI with 1-butanol by separating reaction products such as monourethane (UI) and diurethane (DU) from NDI by HPLC. Scheme I illustrates the chemical structures of UI and DU. The reaction kinetic parameters were obtained by estimating the product composition based on the deconvolution of UV spectra and nonlinear regression analysis of fluorescence intensity. A correlation curve of fluorescence intensity and the extent of reaction from UV spectra was established. The polyurethane consisting of MDI, dihydroxy-terminated poly(tetramethylene oxide) (PTMO), and a small amount of NDI sensor was then studied to follow the reaction of NDI with PTMO. Scheme II shows the chemical structures of the polyurethane matrix investigated. In order to correlate the extent of reaction of MDI with that of NDI, IR spectroscopy was used to monitor the cure of MDI, resulting in a correlation curve. The kinetics of polymerization were analyzed on the basis of the solutions of second-order reaction kinetics, first by assuming the same reactivity of both isocyanates in MDI and NDI. The fluorescence results from NDI in polyurethane matrix was later analyzed to obtain the reactivity ratio between the first isocyanate and the second one.

Experimental Section

Model Urethane Reaction Studies. 1,5-Naphthyl diisocyanate (NDI) from Columbia Chemicals (99.7% purity) was used without further purification. A saturated NDI solution was obtained by rapid filtering of a NDI (0.0005 mol) solution using a paper filter in 1000 mL of toluene, which was stirred at 50 °C for 24 h prior to filtering. The reaction of NDI in saturated toluene with 1-butanol was studied under N_2 atmosphere in a three-necked flask with a reflux condenser in the center neck, which was connected to a tube packed with $CaCl_2$ powder to prevent moisture coming into the reaction system. The reaction was carried out at 50, 60, and 70 °C.

Cure Studies in Polyurethanes. Stoichiometric amounts of methylenediphenylene diisocyanate, MDI from Aldrich (0.3125 g), and hydroxy-terminated poly(tetramethylene oxide), PTMO (1.25 g, of MW 1000), were preheated separately to the reaction temperatures (50 and 70 °C), before they were quickly mixed with 50 μL of filtered saturated NDI solution in toluene. The reactants were mixed with a magnetic stirrer at reaction temperatures for 3 min in a beaker. Two circular quartz plates were clamped together with two thin mylar films (0.025 mm thick) on the edges, leaving a center space for the sample. The clamped quartz plates with mylar spacers were dipped into sample, which was drawn into the center space by capillary action. Another drop of the reaction mixture was placed between two salt plates with a spacer that has a thickness of 0.015 mm. The quartz plates and the salt plates were placed in an oven for a specific time and cooled to room temperature before UV–vis and fluorescence spectra and FT-IR spectra were taken, respectively.

UV Absorption and Fluorescence Measurements. A Perkin-Elmer Lambda diode array UV–vis spectrophotometer and a Perkin-Elmer MPF-66 fluorescence spectrophotometer were used for UV absorption and fluorescence, respectively. In the model reaction study of NDI with 1-butanol, 50 μL of the reacted solution was diluted in 2.5 mL of toluene for UV measurement, while 10 μL of the reacted solution was diluted in 2.5 mL of toluene for fluorescence measurement. The maximum absorbance for fluorescence measurement was less than 0.1, so that we may assume that the fluorescence intensity is proportional to the concentration of the fluorophore. The excitation and emission slits were set at 1 and 3 nm, respectively. The excitation wavelength was set at 314 nm throughout the reaction. The maximum emission at 357 nm was used to correlate with the reaction kinetics.

For polyurethane cure studies, front surface fluorescence measurements and transmission UV absorption were used.

Synthesis of Model Cure Species. Model reaction products, monourethane and diurethane products of NDI with 1-butanol, were separated by the analytical HPLC system (Varian 5000 LC), using a normal phase column (Alltech/CN/10 μm) and a programmable solvent gradient with tetrahydrofuran (THF) and hexane. When 100 μL of the model compound mixture was injected into the hexane-fluxed HPLC column, the solvent gradient was immediately turned on so that THF would increase at the rate of 1%/min until all three components had been eluted out. The collected solutions of the model products were dried by using a water pump, before dissolving in toluene for UV absorption and fluorescence spectra. Diurethane species of NDI was also made by fully reacting NDI with 1-butanol.

Results and Discussion

1. Characterization of Model Reaction Products.

In order to quantify the compositions of the reaction mixtures from UV absorption and fluorescence spectra, we need to acquire the spectra of pure reaction products.

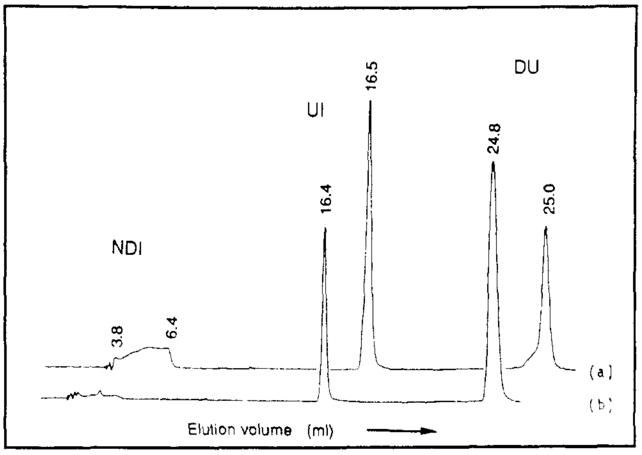


Figure 1. HPLC elution profiles of model compound mixtures (NDI, UI, and DU) using a solvent gradient of hexane and tetrahydrofuran (a) at early reaction times (e.g. 800 min at 70 °C) and (b) at later reaction times (e.g. 1500 min at 70 °C). The number on the diagram indicates the elution time in minutes.

As shown in Scheme I, the first reaction product between NDI and 1-butanol is an urethano isocyanate (UI) of NDI before the other isocyanate group is also reacted to form a diurethane product (DU) of NDI. By using HPLC as described in the Experimental Section for details, the three species (NDI, UI, and DU) were separated by applying a solvent gradient from hexane to tetrahydrofuran, as shown in Figure 1. The solvent with an increasing gradient from hexane to tetrahydrofuran elutes NDI, first, which is less polar than either UI or DU. UI is eluted next before the most polar DU is eluted out, with increasing concentration of THF. The same elution positions were observed when the reaction mixture after longer reaction time was injected, except that the peak height due to DU was higher than UI with negligible NDI peak. The chemical structures of these three compounds were confirmed by IR spectroscopy. The IR spectrum of the first and the third compound corresponds respectively to that of NDI and DU, which was synthesized by fully reacting NDI with 1-butanol. The IR spectrum of the second compound shows the absorption due to free NCO as well as the urethane groups. The melting points of NDI and DU are 126.6 and 167.5 °C, respectively, as determined by differential scanning calorimetry. The amount of the precipitated UI was too small for the melting point measurement.

Parts a and b of Figure 2 show the UV absorption spectra and the fluorescence spectra of all three species (NDI, UI, and DU), respectively. In UV spectra, red shifts are observed as NDI is reacted with UI and DU. This is due to the increasing electron-donating nature of the urethane substituent compared to that of the isocyanate substituent. The extinction coefficients are about the same for all three species. On the other hand, a drastic change in the fluorescence intensity is observed as the diisocyanate group is changed to the urethane groups. NDI is hardly fluorescent probably because of the efficient intersystem crossing to the triplet state through the conjugated isocyanate bond. When the isocyanate group is converted to the urethane group, the intersystem crossing must become less efficient, leading to increased fluorescence intensity. Thus, the ratio of the fluorescence intensity at 357 nm (F) was as follows:

$$F_{NDI}:F_{UI}:F_{DU} = 1:60:630$$

We also tested if the presence of the NDI or 1-butanol affects the fluorescence intensity of UI or DU. It was found that such a presence had no effect on the inherent fluorescence intensity of UI or DU. Therefore, we can use the fluorescence intensity of the UI or DU in the kinetic analysis of the reaction between NDI and 1-butanol.

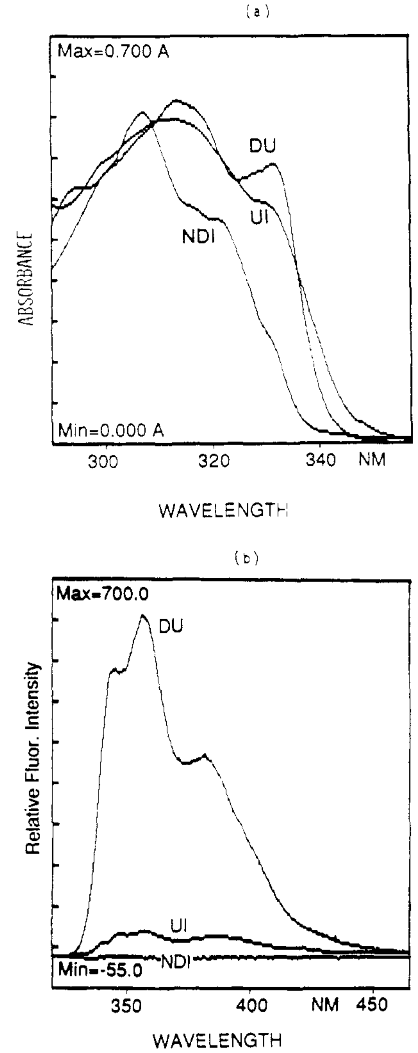


Figure 2. UV absorption spectra (a) and fluorescence emission spectra (b) of three model reaction species (NDI, UI, and DU) in toluene. The excitation wavelength was set at 314 nm.

2. Kinetics of the Reaction between NDI and 1-Butanol. The reaction between NDI and a large excess of 1-butanol was carried out at 50, 60, and 70 °C in toluene. The UV absorption spectra show the red shifts as the reaction time increases, indicating the formation of UI and DU products, as shown in Figure 3a. The fraction of each species (NDI, UI, or DU) has been obtained by the linear regression analysis using a linear combination of the spectra of the pure model species to fit the UV spectra. Because the UV spectra of all three species have two peaks, the error for deconvolution was less than the case for a single peak deconvolution. The maximum error was about 2% except when the fraction of one of the species is very small (<0.05) or large (>0.95). An example of the fraction of each species obtained by deconvolution is shown in Figure 4, which corresponds to the reaction at 70 °C. The trends in Figure 4 illustrate a continuing decrease in the NDI fraction, an initial increase followed by decrease in the UI fraction, and a gradual buildup of the DU fraction. The kinetics of the reaction between NDI and a large excess of 1-butanol can be treated as two consecutive pseudo-first-order reactions where k_1

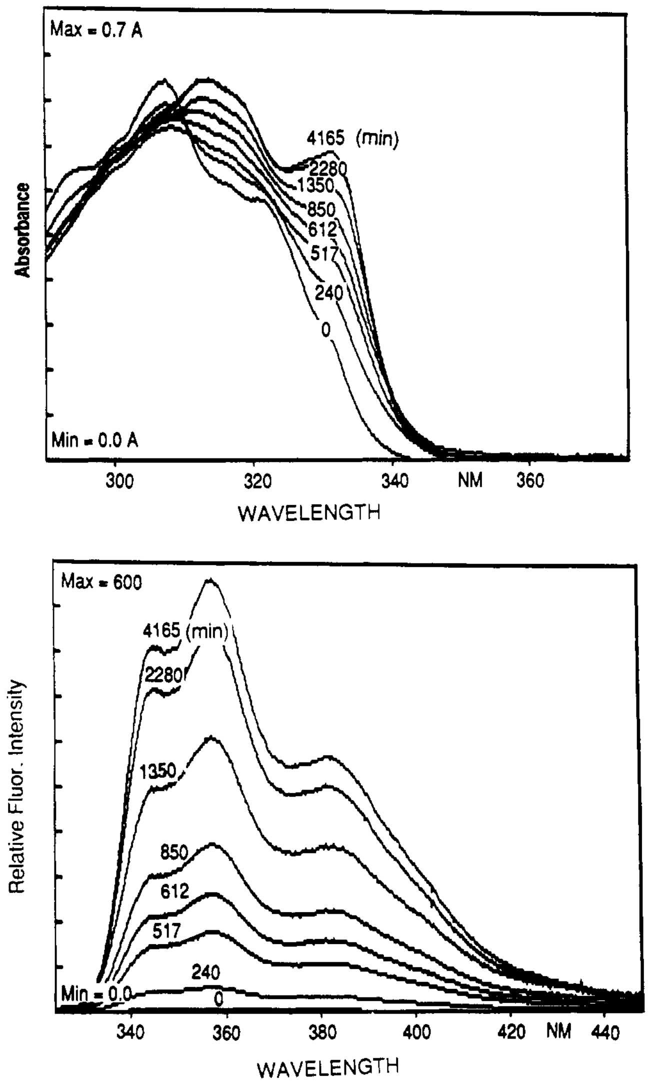


Figure 3. UV absorption spectra (a) and fluorescence emission spectra (b) for the reaction of NDI with excess 1-butanol in toluene at 70 °C, as a function of reaction time. The excitation wavelength was set at 314 nm.

and k_2 represent the rate constants for the first isocyanate reaction and the second isocyanate reacton, respectively, as described.

$$\underset{\text{NDI}}{\text{OCNRNCO}} \xrightarrow[\text{ROH}]{k_1} \underset{\text{UI}}{\text{OCNRNHCOOR}} \xrightarrow[\text{ROH}]{k_2} \underset{\text{DU}}{\text{R(NHCOOR)}_2}$$

The solutions for such reactions are known to be

$$A_{\mathrm{NDI}} = e^{-k'_1 t} \tag{1}$$

$$A_{\mathrm{UI}} = \frac{2R}{1-2R}[e^{-2k_1't} - e^{-k_1't/R}] \tag{2}$$

$$A_{\mathrm{DU}} = \frac{2R}{1-2R}\left[\frac{1}{2R}(1 - e^{-2k_1't}) + (e^{-k_1't/R} - 1)\right] \tag{3}$$

where $k_1' = k_1[\mathrm{OH}]_0$, $k_2' = k_2[\mathrm{OH}]_0$, $R = k_1'/k_2' = k_1/k_2$ and A_{NDI}, A_{UI}, and A_{DU} are the fraction of each species, respectively, with their sum equal to unity. Since the concentration of 1-butanol is in large excess to NDI, we assume $[\mathrm{OH}]_0$ is constant throughout the reaction.

We obtained k_1' from the slope of the plot of ln A_{NDI} versus time. The value of k_1' is then substituted into eq 2 and eq 3. With use of a series of R values, we can generate a series of curves of A_{UI} and A_{DU} as a function of reaction time. By comparing these curves with the experimental points as in Figure 4, we found the best fitted R values. The dotted lines in Figure 4 correspond to the best fit R value of 1.0 for the reaction of 70 °C, when k_1' was found to be 0.0023 min^{-1}. Even though the R value of unity seems to fit the data best, R values in the range of 1.0 ± 0.2 seem to fit the data reasonably well. Table I summarizes the results on k_1', k_1, and R values and the activation energies obtained at 50, 60, and 70 °C. At all three temperatures, the R values of 1.0 ± 0.2 were obtained. This means that the reactivity of both diisocyanates is similar. In other words, the reactivity of isocyanate at the 1-position of NDI is not influenced by having a urethane group at the 5-position of NDI. The activation energy of about 4 kcal/mol similar to that of the first isocyanate group in NDI by other technique[5] was obtained, supporting the validity of UV analysis.

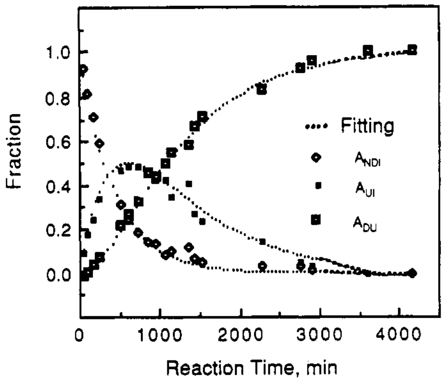


Figure 4. Fractional composition of three reaction species from the deconvolution of UV spectra for reaction of NDI with excess 1-butanol at 70 °C. Dotted lines represent best-fit curves based on eq 1–3 when the R value was 1.0.

We also attempted to extract kinetic parameters from the fluorescence intensity results. Figure 5 illustrates the fluorescence intensity at 357 nm (I_f) as a function of reaction time. Since the fluorescence of NDI is negligible even at high concentration, we can write eq 4 to account for the overall intensity. By substituting eq 2 and eq 3 for A_{UI} and A_{DU} in eq 4, we obtain eq 5. From the experimental points of I_f versus time as in Figure 5, we found the best-fit values of R and k_1' through nonlinear regression analysis by initially using the set of R and k_1' values from UV spectral deconvolution results. The curves correspond to a set of the best-fit values of R and k_1' which are also listed in Table I. The agreement between UV spectral analysis and fluorescence analysis is quite reasonable in R values and the activation energies.

$$I_f = 60A_{\mathrm{UI}} + 630A_{\mathrm{DU}} \tag{4}$$

$$I_f = \frac{120R}{1-2R}[e^{-2k_1't} - e^{-k_1't/R}] + \frac{1260R}{1-2R}\left[\frac{1}{2R}(1 - e^{-2k_1't}) + (e^{-k_1't/R} - 1)\right] \tag{5}$$

We can now establish a correlation curve of I_f with the overall extent of reaction, ξ_α. The overall extent of reaction, ξ_α, defined by eq 6 was calculated from the UV spectral analysis for a corresponding I_f at the same reaction time and temperature. All the data points at three temperatures fall into a smooth calibration curve as shown in Figure 6.

$$\xi_\alpha = \frac{1}{2}(A_{\mathrm{UI}} + 2A_{\mathrm{DU}}) \tag{6}$$

Table I
Summary of Kinetic Parameters for the Reaction of 1,5-Naphthyl Diisocyanate (NDI) with 1-Butanol by UV and Fluorescence Techniques

	UV technique			fluor technique		
reactn temp, °C	$10^2k'_1$, min^{-1}	10^2k_1, M^{-1} min^{-1}	$R = k_1/k_2$	$10^2k'_1$, min^{-1}	10^2k_1, M^{-1} min^{-1}	$R = k_1/k_2$
50	0.080	0.52	1.0 ± 0.2	0.065	0.44	1.0 ± 0.2
60	0.095	1.13	1.0 ± 0.2	0.080	0.96	1.0 ± 0.2
70	0.120	1.87	1.0 ± 0.2	0.100	1.60	1.0 ± 0.2
ΔE^*, kcal/mol	4			4		

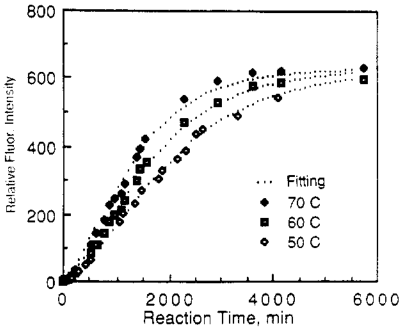


Figure 5. Relative fluorescence emission intensity (I_f) at 357 nm for the reaction of NDI with excess 1-butanol as a function of reaction time at 50, 60, and 70 °C. Dotted lines represent best-fit curves based on eq 5 when the R value was 1.0.

As demonstrated in both UV and fluorescence results, the main conclusion of the kinetic studies of model urethane reation between NDI and 1-butanol is that the reactivity of the first isocyanate reaction is about the same as the second isocyanate reaction. It is worthwhile to think about this conclusion in view of the reported studies on the reaction of isocyanates and diisocyanates and alcohols. The reaction of isocyanates and alcohols is believed to involve an attack by the nucleophilic center of the alcohol is believed to involve an attack by the nucleophilic center of the alcohol on the electrophilic carbon of the isocyanate. Therefore, an electron-donating group attached to the isocyanate will alleviate the positive charge on the carbon atom of the isocyanate and consequently reduce reactivity. In contrast, if an electron-withdrawing group is attached, it will enhance the rate of reaction. For example, Baker and Holdsworth found that the relative reactivity of the isocyanate with methanol decreases as the para substituent in phenyl isocyanate becomes more electron-donating in the following order:[7]

p-nitrophenyl:phenyl:*p*-methylphenyl:
p-methoxyphenyl isocyanate = 303:2.3:1.2:1

It is noted from the above ratios that the electron-donating group reduces the reactivity moderately (about twice) while the strongly electron-withdrawing group such as the nitro group enhances the reactivity by a large factor (about 130 times). This type of electronic effect seems to be also possible by the inductive effect since the substituents in the ortho and meta positions are found to have similar effects on the reactivity.[8,9]

Because of such an electronic effect, the reactivity of the first isocyanate group in the diisocyanate was believed to be greater than that of the second isocyanate group. This is reasonable since the isocyanate group is more electron withdrawing than the urethane group toward the other isocyanate group if the conjugation is an important factor. However, inductive effect is also found to be important for diisocyanates, as indicated by the similarity of rate constants for the *m*- and *p*-phenylene diisocyanates and by the decreased reactivity of an aryl diisocyanate containing an ortho substituent.[9] For the diisocyanates whose isocyanate groups are separated on different aromatic rings through nonconjugating chemical groups such as in MDI, the presence of one isocyanate is not expected to influence the reactivity of the other. However, conflicting kinetic results on MDI have been reported; i.e., while most studies reported similar reactivity for both isocyanates in MDI,[8] other studies show a slightly greater reactivity (about 1.5 times) of the first isocyanate group.[5,10] As for the reactivities of NDI, the same studies that reported different reactivity in MDI also reported a slightly greater reactivity (about 1.4–1.7 times) of the first isocyanate in NDI. Our studies based on UV and fluorescence results showed similar reactivities for both isocyanates in NDI.

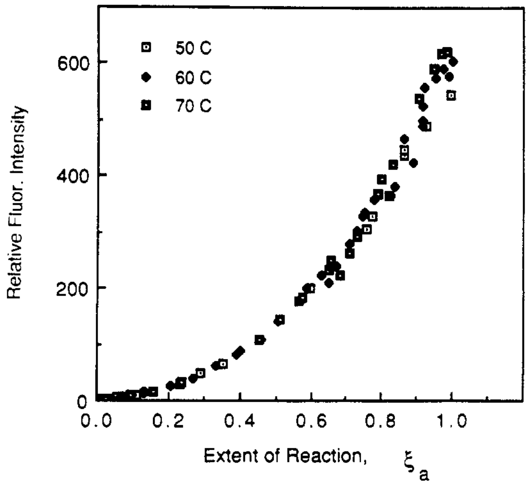


Figure 6. Correlation curve of relative fluorescence intensity (I_f) at 357 nm and the extent of reaction (ξ_α).

3. Studies of Polymer Cure. In order to demonstrate the feasibility of using NDI as a molecular sensor to monitor cure reactions in polyurethanes, we chose a MDI-based polyurethane matrix, based on two reasons. First, the overall reactivity of MDI and NDI are reported to be close.[5] Secondly, the majority of the previous results showed that the reactivities of two isocyanates in MDI are similar as found in NDI. For polyurethane matrix, a stoichiometric ratio of MDI and hydroxy-terminated PTMO (MW 1000) was reacted to form a rubbery linear polyurethane, containing a very small amount of NDI. Figure 7 shows the UV absorption spectra of the mixture of MDI and NDI in toluene. The strong peak at 284 nm is due to MDI, which has very little absorption above 300 nm. Absorption above 300 nm in Figure 7 is mostly due to NDI. In a polyurethane matrix containing a small amount of NDI, the absorption above 300 nm due to NDI is shadowed by the tail end of MDI. Therefore, it would require careful subtraction to obtain UV spectra of NDI in polyurethanes. For this reason, we decided to focus on the fluorescence spectra of NDI in polyurethanes. Because MDI has very little absorption at 314 nm where NDI shows maximum absorption, the fluorescence from the polyurethane matrix alone (with-

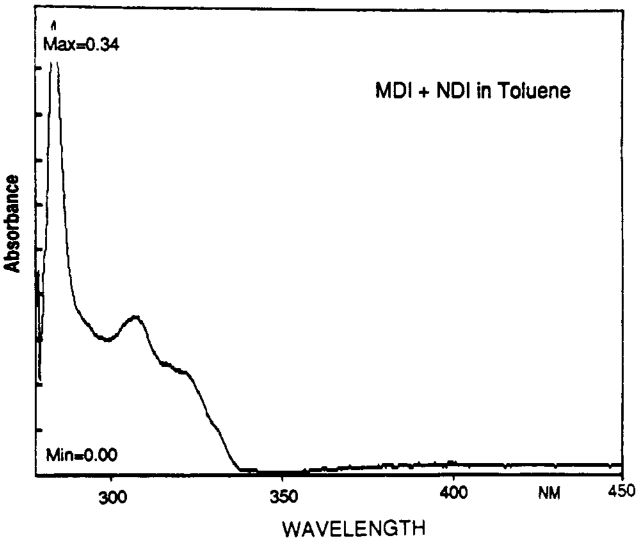


Figure 7. UV absorption spectrum of MDI and NDI mixture with a molar ratio of 20/1 in toluene.

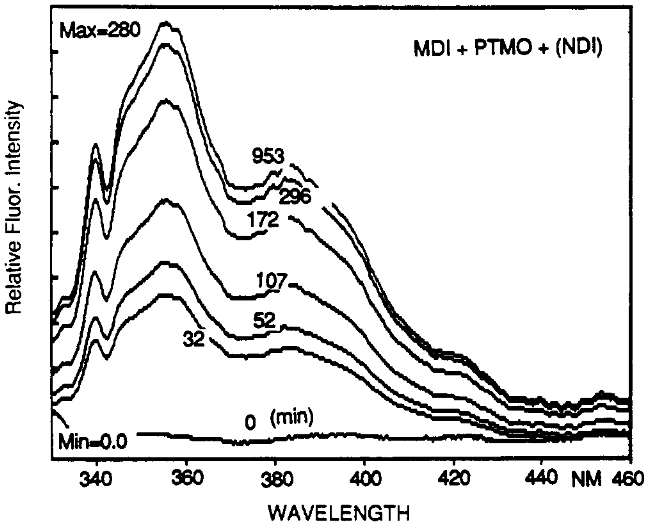


Figure 8. Fluorescence emission spectra of reactive label (NDI) in polyurethane matrix composed of MDI and PTMO during cure at 70 °C. The excitation wavelength was set at 314 nm.

out NDI sensor) was found to be negligible throughout the cure process. In NDI-containing polyurethane matrix, a strong fluorescence intensity is observed as a function of cure time at 70 °C, as shown in Figure 8. The trends in the fluorescence spectra in Figure 8 are very similar to those of NDI as reacted with 1-butanol (Figure 3b). In order to ensure that the fluorescence intensity is only due to the reaction of NDI with PTMO and not due to the viscosity changes during cure, we checked the fluorescence intensity of DU, a source for most of fluorescence in the same polyurethane matrix. Throughout the cure, fluorescence intensity turned out to be constant. Therefore, the extent of reaction, ξ_α, at each reaction time can be obtained from the fluorescence intensity in Figure 8 by using the constructed correlation curve shown in Figure 6. From the extent of reaction ξ_α, we can convert to the fraction of unreacted NCO by eq 7. The fraction of NCO is plotted as a function of reaction time in Figure 9 for reactions at 50 and 70 °C.

$$\text{fraction of NCO} = 1 - \xi_\alpha \tag{7}$$

Since the stoichiometric ratio of MDI and PTMO were used and we further assume that NDI reacts at approximately the same rate as MDI, we can write the reaction kinetics of NDI as second order as expressed in eq 8, where K is the second-order reaction rate constant and

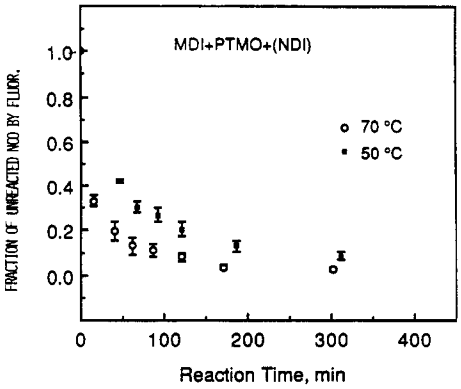


Figure 9. The fraction of unreacted NCO group in NDI as a function of cure time at 50 and 70 °C in polyurethane matrix composed of MDI and PTMO. The NCO fraction was obtained, using a correlation curve (Figure 6) and eq 8.

$$\frac{\mathrm{d}(C_{\mathrm{NCO}})}{\mathrm{d}t} = -KC_{\mathrm{NCO}}C_{\mathrm{OH}} = -KC_{\mathrm{NCO}}^2 \tag{8}$$

C_{NCO} and CO_{H} are the concentrations of the overall NCO and OH groups, respectively. The solution for eq 8 is given in eq 9, where f is the fraction of unreacted NCO

$$\frac{1}{f} - 1 = KC_0t = k't \tag{9}$$

($= c/c_0$). Therefore, we plotted $[(1/f - 1)]$ versus reaction time to extract the rate constant, as shown in Figure 10. The kinetic plots in Figure 10 are linear up to a certain time (corresponding to about 70–80% conversion) meaning that the kinetics follow the second-order kinetics. However, beyond such conversions, the kinetics showed an upward curvature in Figure 10. This behavior of increased rate may be due to the weak catalytic effect of the urethane linkage on the reaction. Baker and Holdsworth reported on the similar catalytic effect of added phenylurethane on the reaction of phenyl isocyanate with methanol.[7] Other researchers reported on a similar catalytic effect.[10]

Next we need to correlate the extent of reaction by NDI as exhibited by fluorescence to that of MDI in the polyurethane matrix. For the purpose of following the reaction of MDI, we used IR spectroscopy by monitoring the NCO concentration at 2270 cm^{-1}. Typical IR spectra during the reaction at 70 °C are shown in Figure 11. The absorption due to NCO decreases quickly at this temperature, and the reaction is almost complete after 585 min. The fraction of unreacted NCO was plotted as a function of reaction time at 50 and 70 °C as shown in Figure 12. The kinetic plot according to eq 9 is illustrated in Figure 13. A similar deviation from the linearity is observed, especially for 70 °C reaction at longer reaction times, as observed in the kinetic plot for NDI reaction (Figure 10). The kinetic parameters of NDI and MDI in the polymer matrix cure are summarized in Table II. The rate constants are similar between NDI and MDI with MDI reacting slightly faster than NDI. The activation energies are also quite similar, as was the case for the second isocyanate group in NDI and MDI by other technique.[5] In comparison to model studies between NDI and butanol in dilute solution, the activation energy is

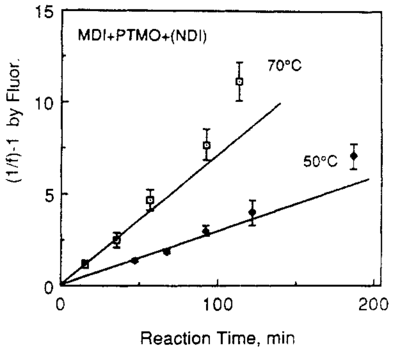


Figure 10. Second-order kinetic plot for NDI at 50 and 70 °C in polyurethane matrix composed of MDI and PTMO, according to eq 9.

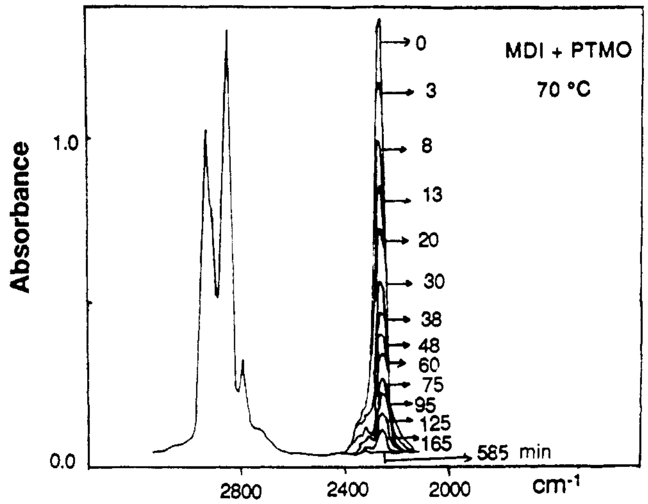


Figure 11. FT-IR spectra of polyurethane composed of MDI and PTMO as a function of cure time at 70 °C.

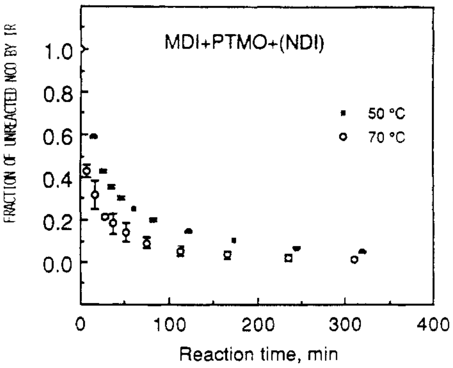


Figure 12. The fraction of unreacted NCO group in MDI determined by IR spectroscopy in polyurethane matrix composed of MDI and PTMO, as a function of cure time at 50 and 70 °C.

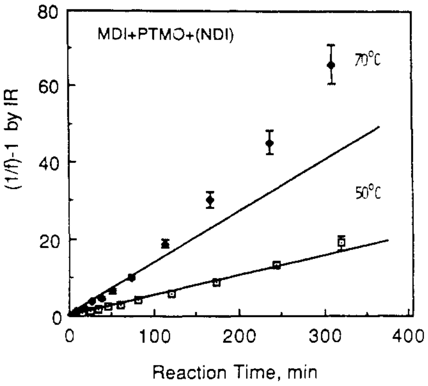


Figure 13. Second-order kinetic plot for MDI at 50 and 70 °C in polyurethane matrix composed of MDI and PTMO, according to eq 9.

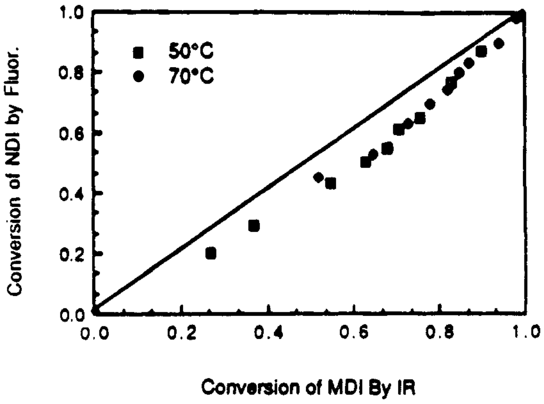


Figure 14. Calibration curve to correlate the conversion of NDI (ξ_α) obtained by fluorescence measurement with the conversion of MDI determined by IR in polyurethane matrix composed of MDI and PTMO.

Table II
Summary of Kinetic Parameters of 1,5-Naphthyl Diisocyanate (NDI) and Methylenediphenylene Diisocyanate (MDI) in Polyurethane Matrix by Fluorescence and IR Techniques, Respectively

	MDI (by IR)		NDI (fluor)	
reactn temp, °C	$k' = kC_0$, min^{-1}	k, M^{-1} min^{-1}	$k' = kC_0$, min^{-1}	k, M^{-1} min^{-1}
50	0.062	0.050	0.044	0.035
70	0.17	0.13	0.11	0.085
ΔE_a*, kcal/mol	11		10	

slightly greater, perhaps due to the high viscosity in bulk polyurethane.

Finally, we can compare the extent of reaction for NDI with MDI by establishing a calibration curve as in Figure 14. In this correlation, the extent of conversion (ξ_α) of NDI by the fluorescence method is plotted against the extent of coversion of MDI by the IR method. If they reacted with exactly the same rate, a straight line at 45° angle would have been observed. Instead, MDI reacts slightly faster than NDI, making the correlation curve to be situated below the straight line. This type of correlation curve can be used in actual cure monitoring of MDI-containing polyurethanes using NDI as a sensor.

4. Kinetics of the Reaction in Polyurethanes. In the preceding section, we analyzed the overall cure kinetic reactions in the polyurethane matrix assuming that both isocyanates in MDI or NDI have equal reactivity. In this section, we attempt to obtain the kinetic parameters, namely, the ratio of the first isocyanate rate constant (K_1) to the second isocyanate rate constant (K_2) from the fluorescence results from polyurethane cure studies.

In the polyurethane matrix, a stoichiometric amount of MDI and PTMO had been used. Since we assume that the reactivities of NDI and MDI are similar, we can write the following kinetic differential equations to describe the reaction between NDI and PTMO

$$\frac{\mathrm{d}(A_{\mathrm{NDI}})}{\mathrm{d}t} = -2K_1(A_{\mathrm{NDI}})(A_{\mathrm{OH}}) \tag{10}$$

$$\frac{\mathrm{d}(A_{\mathrm{UI}})}{\mathrm{d}t} = 2K_1(A_{\mathrm{NDI}})(A_{\mathrm{OH}}) - K_2(A_{\mathrm{UI}})(A_{\mathrm{OH}}) \tag{11}$$

$$\frac{\mathrm{d}(A_{\mathrm{DU}})}{\mathrm{d}t} = K_2(A_{\mathrm{UI}})(A_{\mathrm{OH}}) \tag{12}$$

where A_{NDI}, A_{UI}, and A_{DU} are the fraction of each spe-

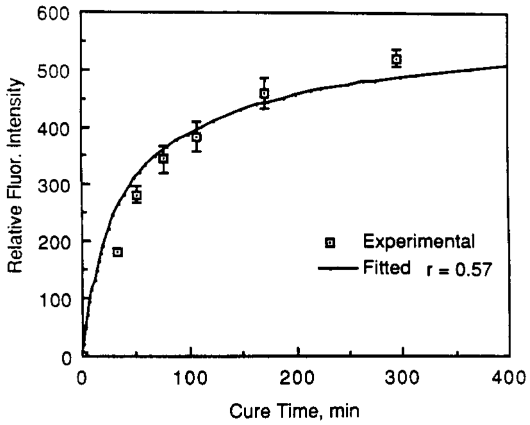


Figure 15. Relative fluorescence intensity (I_f) at 357 nm for the reaction of NDI in polyurethane matrix as a function time at 50 °C. Dotted line represents best-fit curve based on eq 18, when the r value was 0.57.

cies as defined in section 2 and A_{OH} is the fraction of PTMO.

The solutions of similar type of kinetics were reported as eq 13 and 14 when r is equal to $K_2/2K_1$ by Dusek et al.[12]

$$A_{UI} = \left[\frac{1}{1-r}\right][A_{NDI}{}^r - A_{NDI}] \quad (13)$$

$$A_{DU} = \left[\frac{r}{1-r}\right]\left[A_{NDI} - \frac{A_{NDI}{}^r}{r}\right] + 1 \quad (14)$$

Since $A_{NDI} = A_{OH}$, integration of eq 10 gives the following solution for A_{NDI}.

$$A_{NDI} = \frac{1}{2K_1t + 1} \quad (15)$$

Substituting eq 15 into eq 13 and eq 14 makes it possible to express A_{UI} and A_{DU} in terms of r and K_1 only.

$$A_{UI} = \left[\frac{1}{1-r}\right]\left[\left(\frac{1}{2K_1t+1}\right)^r - \left(\frac{1}{2K_1t+1}\right)\right] \quad (16)$$

$$A_{DU} = \left[\frac{r}{1-r}\right]\left[\left(\frac{1}{2K_1t+1}\right) - \left(\frac{1}{2K_1t+1}\right)^r\Big/r\right] + 1 \quad (17)$$

Therefore, the overall fluorescence intensity (I_f) observed from the polyurethane matrix can be expressed now as follows

$$\begin{aligned} I_f &= 60A_{UI} + 630A_{DU} \\ &= 60\left[\frac{1}{1-r}\right]\left[\left(\frac{1}{2K_1t+1}\right)^r - \left(\frac{1}{2K_1t+1}\right)\right] \\ &\quad + 630\left[\frac{r}{1-r}\right]\left[\left(\frac{1}{2K_1t+1}\right) - \left(\frac{1}{2K_1t+1}\right)^r\Big/r\right] + 630 \end{aligned} \quad (18)$$

Figure 15 shows the plot of experimentally obtained I_f as a function of cure time at 50 °C. If we can estimate K_1 from the early stage of cure, then we can find the best-fit r values by curve fitting the experimental curve as in Figure 15 by eq 18. From the model reactions, we can relate I_f with A_{NDI} obtained by deconvolution of UV spectra, as illustrated in Figure 16. In this figure, the data obtained at all three temperatures are superimposed resulting in a universal curve. Using such a curve, we estimated A_{NDI} from I_f measurements at early stages of cure (up to 60 min at 50 °C and 40 min at 70 °C) and obtained K_1 values by plotting $(1/2[1/A_{NDI}) - 1]$ according to eq 15. The values of K_1 were 0.0675 and 0.1132 at 50 and 70 °C, respectively. With these K_1 values, the best-fit value for r was found to be about 0.5–0.6 for both temperatures, as illustrated as a dotted curve in Figure 15. The fluorescence data points beyond 200 min of cure time at 50 °C are not expected to be fit with these types of kinetic equations because of the catalytic effects due to the urethane groups, as mentioned in the previous section. With these r values, the ratio (R) of K_1/K_2 is found to be close to unity. This result means that there is little difference between the reactivity of the first isocyanate and the second one, even in the polymer matrix.

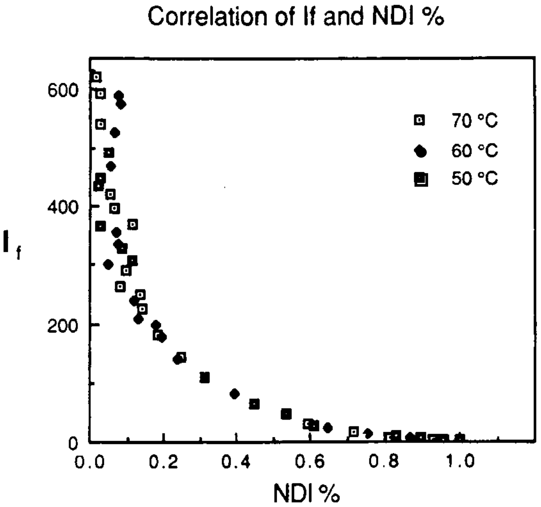


Figure 16. Correlation curve of relative fluorescence intensity (I_f) at 357 nm and the fraction of unreacted NDI (A_{NDI}).

Summary

In this study, UV absorption and fluorescence spectroscopy are used as main tools to characterize, first, the kinetics of the reaction between 1,5-naphthyl diisocyanate (NDI) and 1-butanol and, secondly, the cure in polyurethanes using NDI as a chemical sensor. The reaction between NDI and excess 1-butanol has been studied in toluene solution at 50, 60, and 70 °C. UV absorption spectra show red shifts while fluorescence emission spectra exhibit a large enhancement in intensity as the reaction progresses. With use of analytical HPLC, reaction products such as urethano isocyanate and diurethane products of NDI were separated. With use of their UV absorption and fluorescence spectral characteristics, the kinetics of urethane formation was analyzed on the basis of pseudo-first-order kinetic equations. The reactivity of the first isocyanate group in NDI is found to be similar to that of the second isocyanate group, by both methods. The activation energy of about 4 kcal/mol is found by both methods. A calibration curve to correlate fluorescence intensity to the extent of reaction by UV spectra was established from the model reaction studies. The cure in polyurethane composed of stoichiometric mixtures of methylenediphenylene diisocyanate (MDI), dihydroxy-terminated poly(tetramethylene oxide) (PTMO), and a small amount of NDI as a cure sensor was then studied to follow the reaction of NDI with PTMO at 50 and 70 °C. The kinetics of reaction between NDI and PTMO were analyzed by second-order kinetic equations. Such kinetic plots were linear up to 70–80% conversion. Beyond such conversion, the kinetic plots displayed an upward curvature, probably due to the weak catalytic effect of the urethane groups on the reaction.

The cure reactions in the polyurethane matrix were studied by IR spectroscopy and also analyzed by second-order kinetic equations. Similar trends in the kinetic plot were also observed from IR monitoring of MDI, as were found from fluorescence monitoring of NDI. The second-order rate constants for MDI were found to be slightly greater than those for NDI at 50 and 70 °C. The activation energy of about 10 kcal/mol were estimated for both NDI and MDI. From these results, a calibration curve was established to correlate the extent of reaction for MDI with that for NDI. When the fluorescence results from polyurethane matrix were analyzed on the basis of two consecutive second-order reactions, the reactivity of the first isocyanate turned out to be similar to that of the second one in NDI.

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Registry No. NDI, 3173-72-6; UI, 124244-57-1; DU, 124244-58-2; (MDI)(NDI)(PTMO) (copolymer), 124244-61-7; 1-butanol, 71-36-3.

Site-Selective Fluorescence Spectroscopy of Poly(vinylcarbazole)

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ABSTRACT: Site-selectively excited low-temperature fluorescence spectra are reported for matrix-isolated poly(styrene-*co*-vinylcarbazole) and poly(vinylcarbazole) in MTHF glass and for films of cationically and radically polymerized PVCA. The spectra of the copolymer indicate that isolated carbazole chromophores emit resonantly, the electron–phonon coupling constant being $S \leq 1$. Both in PVCA/MTHF and PVCA film excitations execute a random walk, as expected for an energetically disordered system, if initially generated above a localization energy ν_{loc} within the low-energy tail of the inhomogeneously broadened distribution of intrinsic CA states (ν_{loc} = 28.380 cm^{-1} for PVCA/MTHF and 27.700 cm^{-1} for PVCA film). In the glass emission comes from states at ν_{loc} while in PVCA films structural traps (excimer-forming sites and trap II sites) capture the excitations involving a combination of random walk and long-range Förster transfer. Upon exciting at $\nu_{\text{ex}} < \nu_{\text{loc}}$, defect states, showing up as a shoulder in the absorption and fluorescence excitation spectra of both PVCA/MTHF glasses and PVCA films, are populated directly, giving rise to fluorescence that shifts linearly with ν_{ex} and displays a Stokes shift of 800 and 1100 cm^{-1}, equivalent to an electron–phonon coupling constant $S = 3$. They are identified as the ground-state configurations of trap II.

1. Introduction

Poly(vinylcarbazole) (PVCA) can be considered as a prototype pendant group polymer whose electronic properties, for instance, the capability to transport charge carriers or optical excitations, are all controlled by the substituent rather than the main chain. In view of its principal importance for the photophysics and photochemistry of polymers, transfer of excitation (ET) has long been the subject of extensive work. It has meanwhile been established that PVCA does transport electronic excitation energy, albeit not quite as efficiently as molecular crystals do. Transport is envisaged as the random walk of excitations among the carbazole (CA) chromophores until trapping occurs at chemical or physical defects, although long-range Förster transfer may be involved in the ultimate capture process. (For a review see ref 1–3.)

Identification of ET is usually based on either steady-state luminescence experiments monitoring the fractional emission intensity of deliberately added guest molecules acting as energy sinks[4] or time-resolved studies of the decay of the host emission and buildup of a trap emission.[5–9] The traps can be of structural origin such as the strongly or weakly overlapping CA pairs in PVCA, giving rise to genuine excimer emission near 24 000 cm^{-1} and trap II emission near 26 600 cm^{-1}.[1,10–12] Although principally straightforward and well-tested on molecular crystals, these methods are often inconclusive if applied

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