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Spectroscopic Characterization of Model Urea, Urethane Compound, and Diamine Extender for Polyurethane−Urea

Shi-Kwun Wang and Chong Sook Paik Sung*

Polymer Program, Department of Chemistry, Institute of Materials Science, University of Connecticut, 97 North Eagleville Road, Storrs, Connecticut 06269-3136

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ABSTRACT: During the reaction injecting molding process of polyurethane−urea (PUU) based on 4,4′-methylenebisphenyl diisocyanate (MDI), urethane as well as urea linkages are produced when a highly fluorescent aromatic diamine is used as a chain extender. To explore intrinsic fluorescence as a cure characterization technique, model urethane and urea compounds with similar chemical structures to MDI-based PUU were synthesized. Their fluorescence behavior were compared with that of diethyltoluenediamine (DETDA), which is often employed as a chain extender. The emission maxima for DETDA in polypropylene oxide (PPO) polyol occurred at 336 nm, while the urea (diphenylurea) and the urethane (ethyl *N*-phenylcarbamate) model compounds showed emission maxima at 301 and 303 nm, respectively. The relative quantum yield for DETDA was determined to be 57 times greater than the urea compound, while the urethane compound possessed a relative quantum yield 11 times greater than the urea compound. The viscosity effect increased DETDA fluorescence intensity greater than the observed fluorescence intensity decrease associated with a temperature increase of 55 °C. DETDA was found to be an effective collisional quencher for the urea and the urethane model compounds. The urea compound does not appear to quench the urethane compound's fluorescence significantly. Study of FT-IR spectra of model urea, urethane compounds, and DETDA provided characteristic peaks for each compound: 1727 cm^{-1} for urethane, 1647 cm^{-1} for urea, and 1623.7 cm^{-1} for DETDA, which were also proportional to their concentration in PPO. NIR spectra of model compounds and DETDA indicate characteristic peaks for the urea, the urethane compounds, and DETDA. However, the urea peak absorbance was difficult to use for quantitative analysis, while the urethane and DETDA peaks could be readily applied for such analysis.

Introduction

Recently, our laboratory has been involved in developing intrinsic fluorescence, phosphorescence, and UV−vis spectroscopic techniques for the characterization of cure in several polymers and composites such as epoxy,[1] polyimide,[2] bis(maleimide),[3] polyurethane,[4] vinyl polymers,[5] and polycyanurate.[6]

In polyurethanes based on nonfluorescent 4,4′-*p*-methylenebisphenyl diisocyanante (MDI), fluorescence intensity at the emission maxima of 314 nm was found to increase about 87 times when MDI was converted to diurethane, following reaction with 1-butanol or hydroxy-terminated poly(propylene oxide).[4b] The rate constants and the activation energies for the model reaction (MDI with 1-butanol) and polyurethane formation (MDI with hydroxy terminated polyol) were obtained from the fluorescence results, which were correlated to the extent of reaction determined by IR.

In polyurethane−ureas (PUU) which are often the polymers made by reaction injection molding (RIM), the chain extender is usually a highly fluorescent aromatic diamine such as diethyltoluenediamine (DETDA), with MDI and polyol as the other components.[7] Thus, during cure to form PUU, urethane linkage is formed from the MDI−polyol reaction, while urea linkage is formed from the MDI−DEDTA reaction. To explore intrinsic fluorescence for cure characterization in PUU, we first needed to characterize the fluorescence behavior of the three fluorophores present in PUU: the urethane derivative of MDI, the urea derivative of MDI, and DETDA, individually. Furthermore, the fluorescence intensities of these fluorophores may be influenced by the interaction with each other (e.g., quenching) as well as by the changes in viscosity and temperature during cure.

Hoyle and Kim[8] investigated the emission spectra of model urethane or amine compounds to follow the photolysis mechanism of MDI-based polyurethanes in solution. They assigned the fluorescence peak at 301± 2 and 335± 2 nm to urethane and aromatic amine, respectively, in dimethylformamide. Nevertheless, there is little information published on the effects of their interactions on the fluorescence emission spectra.

In this study, we report on the fluorescence behavior of three model compounds representing the urea and the urethane compounds as well as DETDA. Possible interactions between the three model compounds and their effects on the fluorescence characteristics were investigated in addition to the effect of changes in viscosity or temperature during cure. FT-IR and N IR studies are also reported in an attempt to identify the characteristic peaks for these three model compounds and to evaluate whether such peaks can be used for quantitative analyses.

Experimental Section

Model Compounds. Diethyltoluenediamine (DETDA) with a 80/20 isomer ratio as shown in Scheme 1 was received from Ethyl Corp. and was purged with argon before storage in a refrigerator. For the model compound representing monourethane, ethyl *N*-phenylcarbamate was synthesized from the reaction of excess ethanol with phenyl isocyanate from Aldrich Chemical Co. by refluxing in ethanol at 70 °C in an oil bath for 16 h under an argon gas purge. After removing unreacted ethanol and phenyl isocyanate via vacuum distillation at 10 mmHg, the products were dissolved in cyclohexane at 50 °C, followed by recrystallization upon slow cooling. The urea model

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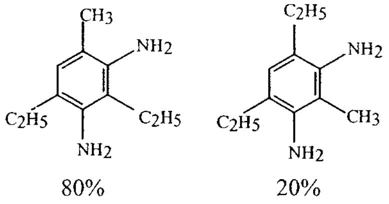
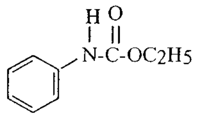
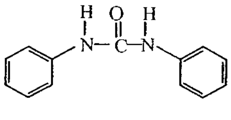
Scheme 1. Chemical Structures of Model Compounds



Diethyl toluene diamine (DETDA)



Ethyl N-phenyl carbamate



Diphenyl urea

compound, diphenylurea, also shown in Scheme 1, was synthesized from the reaction of phenyl iscocyanate with aniline, using a procedure similar to that described for the preparation of ethyl *N*-phenylcarbamate. Diphenylurea was recrystallized by cooling in dry ice from hot ethyl acetate solution, to yield long needle-shaped fine crystals. Purity of ethyl *N*-phenylcarbamate and diphenylurea model compounds were confirmed by FT-IR, DSC, and NMR.

Spectroscopic Characterization of Model Compounds. For UV–vis and fluorescence measurements, all model compounds were dissolved in hydroxyl terminated poly(propylene oxide), PPO (MW 2000 g/mol or MW 2800 g/mol, used as received from Aldrich Chemical Co.). The UV–vis, NIR, and fluorescence emission measurements were obtained using a 3 mm path length, fused silica cuvette. A Perkin-Elmer Lambda 6 UV–vis spectrometer, a Perkin-Elmer Lambda 900UV–vis NIR spectrometer, and a Perkin-Elmer LS50B luminescence spectrometer were used to obtain the UV–vis, NIR, and fluorescence emission spectra of the model compounds, respectively. FT-IR studies were performed using a Nicolet 680DSP Spectral workstation. NMR spectra were collected in deuterated DMSO or $CDCl_3$ using a Bruker AC-270 or DMX-500 NMR spectrometer.

Results and Discussion

Fluorescence Characteristics of Model Compounds. For simulating the urethane portion in PUU, ethyl *N*-phenylcarbamate was used, while diphenylurea synthesized from phenyl isocyanate and aniline was used as the model compound for urea portion in PUU. Poly(propylene oxide) (PPO) was used as a solvent to obtain the UV and fluorescence spectra, since it is often the soft segment used in PUU. Figure 1 shows the fluorescence emission spectra of ethyl *N*-phenylcarbamate, diphenylurea, and DETDA as well as the low background emission from PPO, when excited at 275 nm where all three models have UV absorption. Table 1 lists the emission maxima when excited at 275 nm and the relative quantum yields according to eq 1,

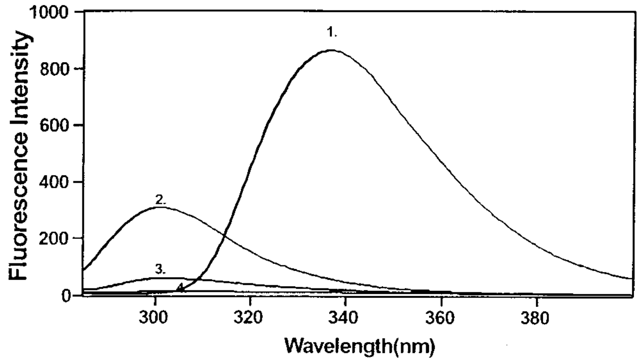


Figure 1. Emission fluorescence spectra of DETDA (1), ethyl *N*-phenylcarbamate (2), and diphenyl urea (3) in ethylene oxide terminated PPO (MW 2800) (4). Concentration at mole ratios of 2/8, 8/8, and 2/8, respectively, when excited at 275 nm.

Table 1. Fluorescence Emission Maxima and Relative Fluorescence Quantum Yields (ϕ_f) of Model Compounds in PPO

	λ_{max}, nm	relative ϕ_f
DETDA	336	57
ethyl *N*-phenylcarbamate	303	11
diphenylurea	301	1

$$(\phi_f)_{rel} = \frac{\left(\frac{I_f}{A}\right)_{rel}}{\left(\frac{I_f}{A}\right)_{ref}} \qquad (1)$$

where $(\phi_f)_{rel}$ is the relative quantum yield, I_f the fluorescence intensity, and A the absorbance at 275 nm. The subscript “ref” represents the diphenylurea compound, since it had the lowest fluorescence intensity. The emission maximum of ethyl *N*-phenylcarbamate (at 303 nm) was similar to that previously reported by Hoyle and Kim,[8] while the emission maximum of DEDTA (at 336 nm) was close to that reported for aniline in dimethylformamide. The results in Table 1 indicate that DEDTA is most fluorescent (about 57 times) followed by ethyl *N*-phenylcarbamate (about 11 times) than the urea model compound, which has emission maximum at 301 nm. Thus, the emission maxima for ethyl *N*-phenylcarbamate and diphenylurea are quite close.

Simulation of Physical Changes during RIM Polymerization of PUU. During the RIM process to make PUU, both temperature and viscosity can rise sharply. In general, an increase in temperature will lower the fluorescence intensity, while an increase in viscosity will raise the fluorescence intensity. To evaluate these effects, we measured the fluorescence behavior of DETDA in various temperature/viscosity environments, since it possessed the strongest fluorescence. Fluorescence emission spectra of DETDA in 2000 MW PPO at a concentration of 0.05 mol of DETDA in 1 mol of PPO was studied as a function of temperature. The fluorescence emission intensity decreased about 25% without a change in the peak position when the temperature increased from 25 to 80 °C in a fairly linear fashion, as shown in Figure 2a. To mimic the viscosity

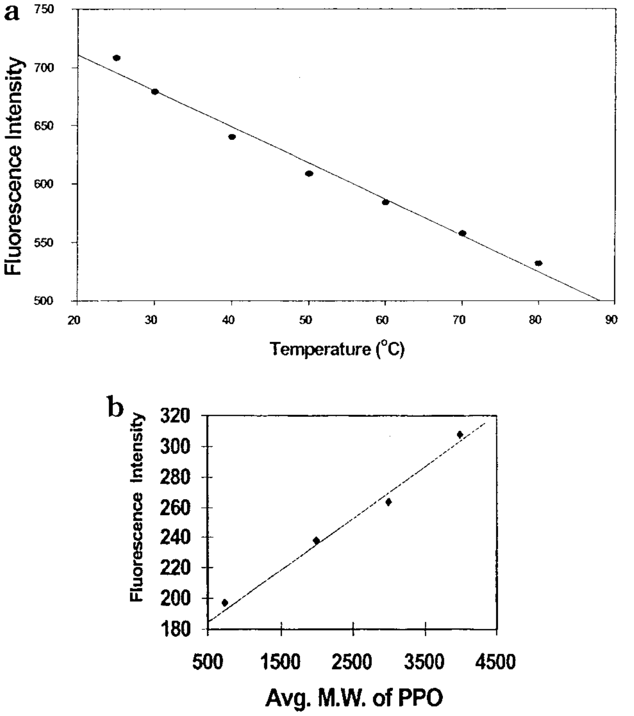


Figure 2. (a) Fluorescence intensity of DETDA at 336 nm in PPO 2000 at 0.05/1 mole ratio as a function of temperature, when excited at 275 nm. (b) Fluorescence intensity of DETDA at 336 nm in PPO at 0.05/1 mol ratio as a function of molecular weight of PPO, when excited at 275 nm.

changes, at least during the early stages of cure, varying molecular weights of PPO were used to observe the fluorescence of DETDA. As the molecular weight of PPO increases from 750 to 4000 g/mol, the fluorescence intensity increased approximately 60% without a change in the emission peak maxima, as shown in Figure 2b. The increase in fluorescence intensity with PPO molecular weight appears to approximate a linear relationship. Since the viscosity is approximately proportional to the molecular weight, we may assume fluorescence intensity increases with viscosity. However, the viscosity range investigated is relatively small compared to the viscosity changes which occur throughout the cure reaction. Therefore, the viscosity effect during cure is expected to be greater than the temperature effect on the fluorescence intensity.

Interactions among Model Compounds. During PUU cure, all three fluorophores (DETDA, urea, and urethane model compounds) can contribute to the fluorescence. Furthermore, in the early stages of cure, DETDA may be able to diffuse so as to quench the fluorescence of the urea or the urethane fluorophores, since aromatic amines are generally known to be good quenchers.[9b] Before we can relate fluorescence characteristics to the specific reactions (urea formation vs urethane formation), we need to investigate the interactions of these fluorophores.

(a) Quenching of Ethyl *N*-Phenylcarbamate Fluorescence by DETDA. Ethyl *N*-phenylcarbamate, the urethane model compound, shows a strong emission at 301 nm when excited at 275 nm in PPO. When successively greater amounts of DETDA were added, the fluorescence intensity at 301 nm due to ethyl *N*-phenylcarbamates decreased sharply, as illustrated in Figure 3a. This behavior suggests quenching by DETDA, which can be caused by energy transfer, complex formation, and collisional encounters.

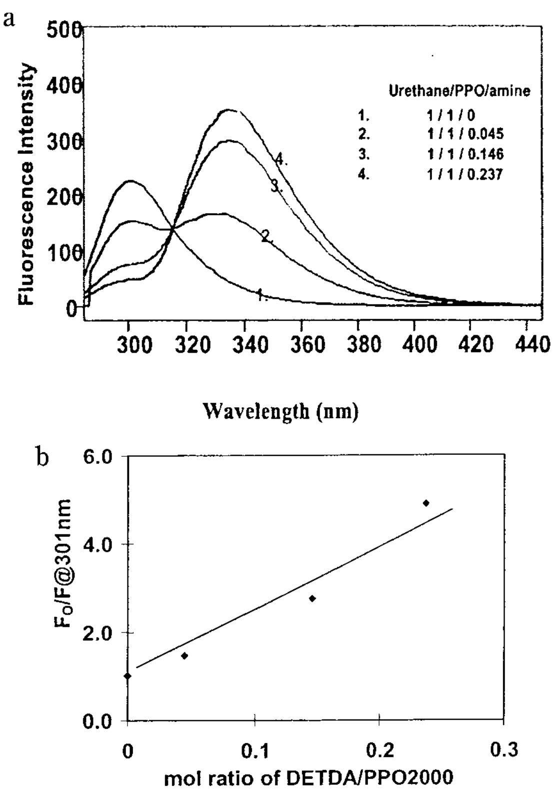


Figure 3. (a) Changes in fluorescence spectra of ethyl *N*-phenylcarbamate in PPO 2000 as a function of added DETDA, when excited at 275 nm. (b) Stern−Volmer plot for the quenching of ethyl *N*-phenylcarbamate by DETDA.

Collisional quenching can be described by the Stern−Volmer eq 9 as shown in eq 2.

$$F_0/F = 1 + k_q\tau_0[Q] = 1 + K_D[Q] \tag{2}$$

where F_0 is the fluorescence intensity in the absence of quencher and F is the fluorescence intensity in the presence of quencher. The terms k_q, τ_0, and K_D represent the biomoleuclar quenching constant, the fluorophore lifetime in the absence of quencher, and the Stern−Volmer quenching constant, respectively. Figure 3b shows a Stern−Volmer plot, which is fairly linear with an intercept of 1 as predicted by the Stern−Volmer equation. Therefore, it is likely that the quenching may be collisional. Since the fluorescence from urethane compound can be reabsorbed by DETDA due to its UV absorption characteristics, the observed quenching may in part be caused by such an energy transfer.

(b) Quenching of Diphenylurea by DETDA. Figure 4 shows the quenching effect of DETDA on diphenylurea fluorescence. When DETDA is added to diphenylurea in PPO2000, urea fluorescence at 303 nm disappears. Therefore, we can conclude that DETDA is an effective quencher of urea fluorescence.

(c) Interaction of Ethyl *N*-Phenylcarbamate with Diphenylurea. During PUU formation, urea linkages may be formed earlier than urethane linkage, since DETDA may react faster than the OH group of PPO. Therefore, we tried to study the interaction between the urethane and the urea model compound by fixing the urea concentration, followed by adding increasing amounts of the urethane model compound, ethyl *N*-phenylcarbamate. Since the emission maxima for the urea and the urethane model compounds are very close, we cannot distinguish one compound from the other.

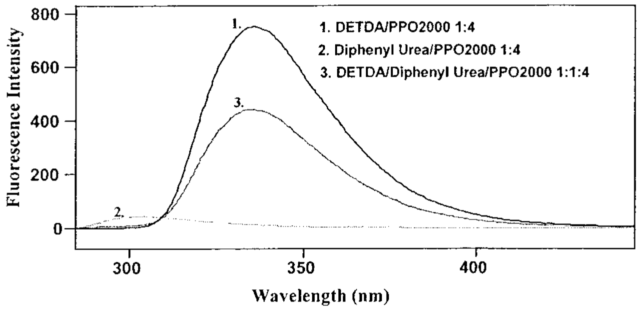


Figure 4. Changes in emission fluorescence spectra of diphenylurea in PPO 2000 as a function of added DETDA, when excited at 275 nm.

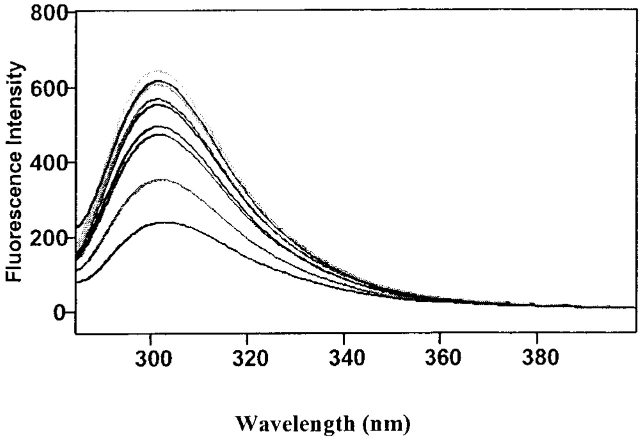


Figure 5. Changes in emission fluorescence spectra of diphenylurea in PPO (mole ratio: 0.2/0.8) as a function of added ethyl *N*-phenylcarbamate (mole ratios of ethyl *N*-phenylcarbamate/diphenyl urea, 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 from bottom to top spectra).

Figure 5 shows the fluorescence emission spectra of diphenylurea in PPO as a function of added ethyl *N*-phenylcarbamate. At lower molar ratios, the increase in intensity was proportional to the molar concentration of ethyl *N*-phenylcarbamate, which is about 11 times more fluorescent than diphenylurea. Therefore, it appears that the urea compound does not seem to quench the fluorescence of the urethane compound (ethyl *N*-phenylcarbamate) significantly.

FT-IR Spectra of Model Compounds. Even though the IR spectra of other urethane, urea compounds, and aromatic amines have been extensively reported in the literature,[10] it was desirable to obtain IR spectra of these three model compounds in a PPO environment as a function of increasing concentration in order to properly identify these functional groups during the formation of PUU and to assess whether their characteristic IR absorbances were proportional to their concentration.

Ethyl *N*-Phenylcarbamate in PPO. Figure 6 shows the FTIR spectral changes observed with varying concentration of ethyl *N*-phenylcarbamate in PPO. Characteristic peaks are the C=O stretching band at 1727 cm^{-1}, the amide II combination band at 1542 cm^{-1}, and the amide III combination band at 1223 cm^{-1}, while the band at 1601 cm^{-1} is due to C−H bending in the aromatic ring.[11]

According to the assignment made by Priester,[11] the C=O stretching of the free urethane appeared at 1730 cm^{-1}, while the H-bonded urethane appeared at 1715 cm^{-1}. It seems that most of the ethyl carbamate C=O stretching band was free from hydrogen bonding in PPO solutions at lower molar ratios, since it appears at 1727 cm^{-1}. A shoulder at 1715 cm^{-1} appearing at high ethyl carbamate concentrations suggests that some hydrogen bonding may be occurring. The absorbance at 1727 cm^{-1} due to urethane was fairly linear with concentration, when ratioed with the absorbance at 1373 cm^{-1} due to CH_2 wagging mode, which is only present in PPO.[10] On the basis of these results, we selected the band at 1727 cm^{-1} to represent the urethane group to correlate its absorbance with fluorescence emission in the following paper.[12]

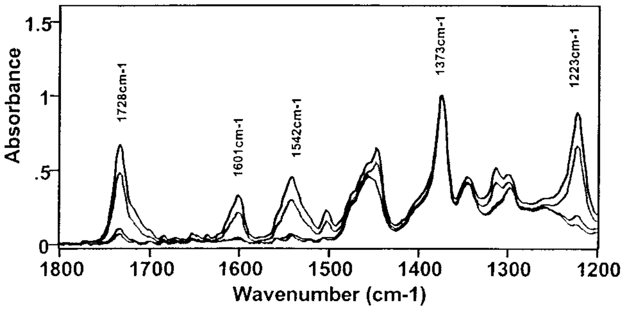


Figure 6. FTIR spectra of ethyl *N*-phenylcarbamate in PPO 2000 at varying mole ratios (0.1, 0.2, 0.5, and 1 from bottom to top curves).

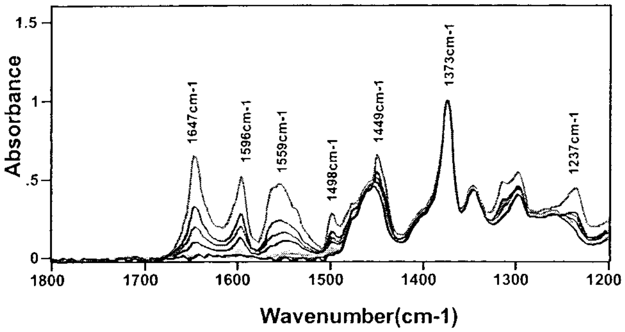


Figure 7. FTIR spectra of diphenylurea in PPO 2000 at varying mole ratios (0.005, 0.008, 0.01, 0.02, 0.04, 0.08, 0.1, 0.25 from bottom to top spectra).

Diphenylurea in PPO. Figure 7 shows the FTIR spectral changes associated with varying concentrations of diphenylurea in PPO. Characteristic peaks in diphenylurea are the C=O stretching band at 1647 cm^{-1}, the amide II combination band (at 1559 cm^{-1}), and the amide III combination band at 1237 cm^{-1}, while the band at 1596 cm^{-1} is due to C−H bending in the aromatic ring.[11]

According to the assignment made by Priester,[11] free urea appeared at 1715 cm^{-1} and loosely H-bonded urea appeared at 1700−1650 cm^{-1}, while hydrogen-bonded urea appeared at 1640 cm^{-1}. From Figure 7, there appears to be little free urea observed at any concentration. Urea appears hydrogen bonded as indicated by a strong peak at 1647 cm^{-1}. This trend may indicate aggregation of urea in PPO. The absorbance at 1647 cm^{-1} is proportional to its concentration, when referenced to the 1373 cm^{-1} band due to PPO. Therefore, we selected to use this urea band for subsequent correlation with fluorescence emission.[12]

DETDA in PPO. Figure 8 shows the concentration dependence of aromatic amine chain extender, DETDA in PPO. The only characteristic peak in the 2000−1200 cm^{-1} range is the band at 1623.7 cm^{-1}, which can be assigned to C−N stretching. Its absorbance is propor-

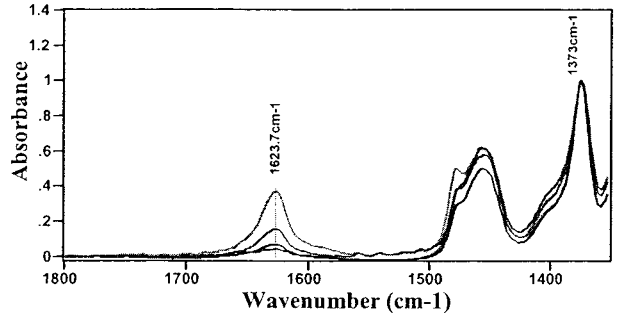


Figure 8. FTIR spectra of DETDA in PPO 2000 at varying mole ratios (0.05, 0.1, 0.15, 0.25 from bottom to top spectra).

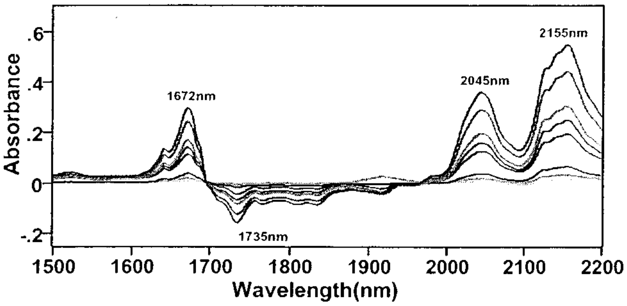


Figure 9. NIR difference spectra of ethyl *N*-phenylcarbamate in PPO 2000 at varying mole ratios (0.05, 0.1, 0.2, 0.5, 0.8, 1, 1.6, and 2 from bottom to top spectra), after subtracting PPO 2000 spectra.

Table 2. IR Band Positions (in cm^{-1}) for Ethyl *N*-Phenylcarbamate and Diphenylurea in PPO

vibration modes	ethyl *N*-phenylcarbamate	diphenylurea
C=O stretching	1727	1647
amide II	1542	1559
amide III	1223	1237
aromatic C−H bending	1601	1596

tional to its concentration when referenced to 1373 cm^{-1} band due to PPO.

Table 2 compares the band positions for the urethane and the urea model compounds for several characteristic vibration modes. We can see from Table 2 that the C=O stretching bands are well-separated ($\Delta\nu = 81$ cm^{-1}), thus making them good choices to be used for distinguishing the urethane group from the urea group.

NIR Spectra of Model Compounds. The absorption spectral range of the model compounds was extended to the NIR region to explore its applicability in cure monitoring. Previous research demonstrated the potential of NIR spectroscopy on polyurethane ureas[13] and polyurethanes.[14] Dittman and Siesler also reported on NIR monitoring of the syntheses of diphenylurethane.[15] Miller has studied aliphatic urea model compound for NIR band assignments.[13] It appears that careful NIR studies using model compounds whose structures are similar to PUU based on MDI and DETDA are not available in the literature, especially with regards to whether NIR bands can be used for quantitative analyses. Therefore, we varied the concentrations of model urea, urethane compounds, or DEDTA in PPO and investigated their NIR spectra.

Ethyl *N*-Phenylcarbamate in PPO. Figure 9 shows the NIR difference spectra for the PPO solutions of ethyl *N*-phenylcarbamate at varying molar ratios, after subtracting the NIR spectra of PPO. Three positive absorbance changes and one negative absorbance change were observed. From the band assignment by Miller,[13b] the 1672 and 2155 nm bands might originate from the overtone of aromatic CH, 1735 nm from the overtone of CH group in the PPO soft segment, and 2045 nm from the urethane N−H stretching combination band. From the results of the model compounds study, the NIR spectra seemed very sensitive to changes in the urethane concentration. The absorbance values of all three bands at 1672, 2045, and 2155 nm showed linear correlations with concentration up to a very high molar ratio, greater than the usual urethane concentration in PUU. This result indicates that the urethane chromophore can be quantified by NIR by tracking the band at 2045 nm due to N−H group, if the sample thickness is thick enough to obtain an accurate absorbance.

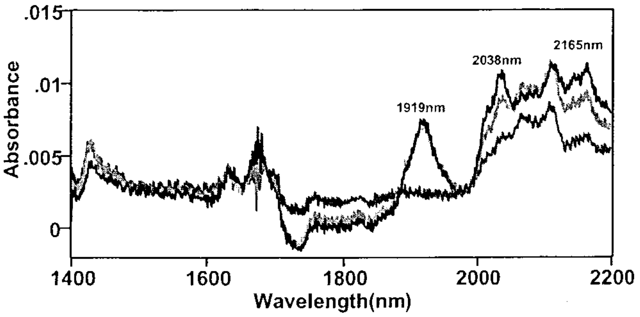


Figure 10. NIR difference spectra of diphenylurea in PPO 2000 at varying mole ratios (0.001, 0.004, and 0.008 from bottom to top) after subtracting PPO 2000 spectra.

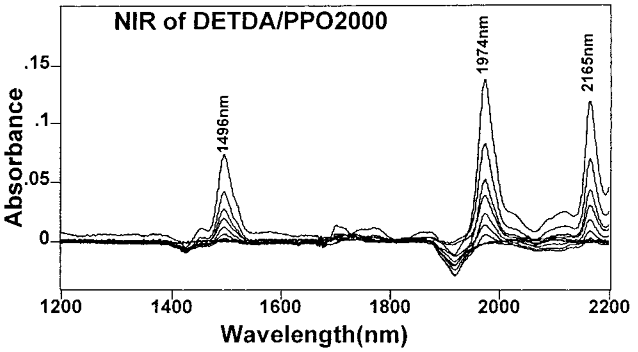


Figure 11. NIR difference spectra of DETDA in PPO 2000 at varying mole ratios (0.0005, 0.0008, 0.002, 0.02, 0.03, 0.07, 0.1, 0.15, and 0.25 from bottom to top) after subtracting PPO 2000 spectra.

Diphenylurea in PPO. For the NIR spectra of diphenylurea in PPO, as illustrated in Figure 10, only the band at 2038 nm showed linear changes with concentration at very low ratios. This band position coincides with the urea overtone band for free C=O stretching reported by Miller.[13b] At molar ratios above the range of 0.001−0.008 mol of diphenyl urea per 1 mol of PPO, the mixture becomes turbid, probably due to urea aggregation, making NIR absorbance meaningless. This phenomenon makes it difficult, if not impossible, to use the 2038 nm peak to quantify the urea group in PUU where the urea concentration is typically in the range of 0.2 mol of urea per 1 mol of PPO.

DETDA in PPO. Three positive NIR difference bands were observed for the NIR spectra of DETDA in PPO solutions as shown in Figure 11. The peak at 1496 nm was not assigned by Miller,[13b] but it possibly originates from the overtone of free aromatic amine N−H stretching while the 1974 nm band might be from the H-bonded aromatic amine N−H stretching overtone band. The

Table 3. Characteristic Bands in NIR Spectra of Model Compounds in PPO

model compounds	characteristic NIR absorption bands (nm)
ethyl *N*-phenylcarbamate	1672, 2045, 2155
diphenylurea	1919, 2038, 2165
DETDA	1496, 1974, 2165

2165 nm band was similar in all three model compounds and originates from the aromatic CH stretching overtone. The absorbance values of these three bands appeared to be linear with DETDA concentration up to high molar ratios.

Table 3 summarizes the characteristic bands found in the NIR study of the urethane, the urea model compounds, and aromatic amine chromophores. These bands were well isolated from each other. With the exception of diphenylurea, the bands for ethyl *N*-phenylcarbamate and DETDA may be used for quantitative analysis.

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