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Model Acylation Reactions for Polyamides Studied by UV Absorption and Fluorescence Spectroscopy

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ABSTRACT: UV absorption spectroscopy and fluorescence spectroscopy were used in this study as the main tools to characterize the acylation reactions of 1,5-naphthylenediamine (NDA) with either *n*-propionic acid or benzoyl chloride to simulate polymerization for polyamides. IR spectroscopy was used to provide independent qualitative support for the acylation reactions. During acylation reactions, UV absorption spectra show blue shifts, while fluorescence emission spectra exhibit an initial red shift with a progressive reduction in intensity. With the use of the spectral parameters of NDA and two acylation products (monoamide and diamide), the kinetics of the acylation, which proceed in two stages, were analyzed. The rate constant of the conversion of NDA to monoamide is found to be faster (3–7 times) than that corresponding to the conversion of monoamide to diamide. This trend is confirmed by both UV absorption spectra and fluorescence spectra. The activation energies for the first- and second-stage reactions are about 20 kcal/mol, respectively. The reaction of NDA with benzoyl chloride is found to produce the same spectral results as the reaction with *n*-propionic acid. A calibration curve was established to correlate the extent of the acylation with the fluorescence intensity.

Introduction

Recently, we explored UV–visible and fluorescence spectroscopic methods as characterization tools to study polymerization, cure, and the imidization process in several polymers.[1-3] As a consequence of such chemical reactions, functional groups change in the para and para primed positions of aromatic precursors. For example, the diamine curing agent changes from primary amines to secondary and tertiary amines as it is reacted with epoxide.[1] For polyimides, the diamine is changed first to diamic acid, followed by the conversion to imide groups.[3] For polyurethanes, the diisocyanate becomes urethane groups.[2] In addition, there are several intermediate species having different functional groups in the "para and para primed" positions of the aromatic precursors, such as amic acid–imide or urethane–isocyanate. These functional groups have different extents of electron-withdrawing and electron-donating capabilities, which are manifested in the spectral shifts and/or the extinction coefficients in UV–visible spectra. Also, they often influence fluorescence intensity and/or emission maxima because of their effect on the competing processes of fluorescence such as intersystem crossing and internal conversion. Consequently, we can often distinguish between several cure species in some polymers when conjugated aromatic precursors are used, while other spectroscopic techniques such as IR or NMR cannot. This advantage allows us 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 some applications, a reactive aromatic compound that mimics the reactivity of one of the polymerizing precursors was used as a molecular sensor to characterize cure and polymerization.[1,2] These reactive sensors were chosen to exhibit spectral changes in the region of UV–visible and fluorescence spectra where the polymerizing matrix has little absorption or emission. By using a fiber optic fluorescence instrument, we have recently demonstrated that these molecular sensors can be implemented as an *in-process* cure monitoring technique during the actual cure process in the oven.[4]

In this paper, we apply UV absorption and fluorescence spectroscopy first to study model acylation reactions between an aromatic diamine, 1,5-naphthylenediamine (NDA), and an aliphatic acid, *n*-propionic acid (PA). As demonstrated in the preliminary study,[5] NDA can react with PA in a two-step process as illustrated in Scheme I. The first species to form is an amine–amide or monoamide (MA) with rate constant K_1 before diamide (DA) is formed with rate constant K_2. We attempt to obtain the rate constants for each step and the activation energies for the reaction. Some preliminary studies to follow the reaction between NDA and benzoyl chloride via UV absorption and fluorescence are also described.

Experimental Section

Model Acylation Reactions. 1,5-Naphthylenediamine (NDA) from Aldrich Chemical Co. was purified either by twice recrystallizing in water or by sublimation. *n*-Propionic acid (PA) from Fisher Scientific was purified by double distillation. 1-Methyl-2-pyrrolidone (NMP) of HPLC grade from Aldrich Chemical Co. was further purified by drying with 4-Å molecular sieves and phosphorus pentoxide prior to double vacuum distillation.

For acylation studies, NDA (31.6 mg, 2×10^{-4} mol) was added to a flask containing 20 mL of *n*-propionic acid (2.68×10^{-1} mol) and the reaction carried out at three temperatures, 95, 110, and 125 °C.

Syntheses of Model Acylation Compounds. Acetyl chloride from Aldrich Chemical Co. was purified by double distillation, and a middle fraction was used for reaction with NDA to synthesize diamide. To 10 mL of tetrahydrofuran (THF) solution containing 158 mg of NDA (10^{-3} mol) was added 5 mL of THF solution with 314 mg of pyridine as acid acceptor. At 10 °C, 5 mL of THF solution with 471 mg of acetyl chloride (6×10^{-3} mol) was mixed with 15 mL of THF solution containing NDA and pyridine. The solid precipitate was formed immediately upon addition of acetyl chloride. It was filtered and washed with cold THF, followed by additional washing with cold water to remove acetyl chloride and pyridinium salt from the diamide.

Careful observation of the acylation reaction between NDA and *n*-propionic acid indicated that the reactions proceeded in two stages, i.e., a faster initial stage and a slower second stage, as described in detail in the Results and Discussion. The monoamide (MA) was separated by stopping the reaction after the first stage, followed by precipitation and purification.

IR spectra of the monoamide (MA) and diamide (DA) in comparison to that of NDA confirm their chemical structures.

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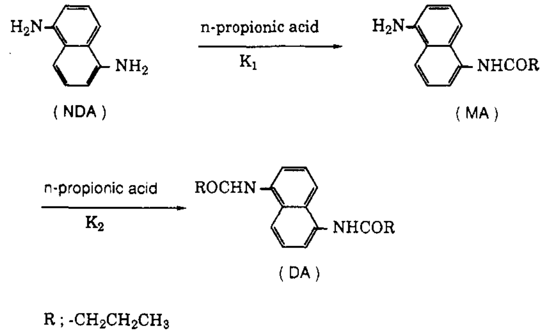
Scheme I
Chemical Structures of 1,5-Naphthylenediamine (NDA) and Its Monoamide (MA) and Diamide (DA) Products after Reaction with n-Propionic Acid



The IR spectrum of MA shows IR bands due to both amine (at 3416 and 3320 cm^{-1}) and amide (at 3271 and 1660 cm^{-1}), while DA shows IR bands due to only amide groups at 3270 and 1660 cm^{-1}, which were absent in the IR spectra of NDA.

Studies of Acylation of NDA with Benzoyl Chloride. Benzoyl chloride as received from Aldrich Chemical Co. was added in a stoichiometric ratio to an NMP solution containing NDA either at room temperature or at 0 °C.

UV Absorption and Fluorescence Measurements. A Perkin-Elmer Lambda diode array UV-vis spectrophotometer (Model 3840) and a Perkin-Elmer MPF-66 fluorescence spectrophotometer with a separate data station (Model 7500) were used for UV absorption and fluorescence, respectively. In model acylation studies of NDA with *n*-propionic acid or with benzoyl chloride, 3 μL of the reacted solution taken out at specific time intervals was diluted with 3 mL of NMP in a cuvette with a path length of 1 cm. The maximum UV absorption was about 0.15. The same solution in a cuvette was also used for fluorescence measurement, with the excitation wavelength at 345 nm, which is near the absorption maximum of NDA. The excitation and emission slit conditions were 1 and 2 nm, respectively. The deconvolution of UV absorption spectra was carried out with a deconvolution program (Quant Software) from Perkin-Elmer and with the spectra of the diamine (NDA), monoamide (MA), and diamide (DA).

Results and Discussion

1. Characterization of Acylation Products. We need to characterize the UV and fluorescence spectra of the pure acylation products, monoamide and diamide, as defined in Scheme I, in order to analyze the UV and fluorescence spectra obtained at certain reaction intervals to determine the composition. Monoamide and diamide were synthesized and purified according to the procedures described in the Experimental Section. Their chemical structures were confirmed by IR spectra in comparison with the starting diamine, NDA.

Figure 1 shows the UV-visible absorption and fluorescence spectra for NDA, monoamide (MA), and diamide (DA) in *N*-methylpyrrolidone (NMP) solvent. In the UV-visible spectra, successive blue shifts of 15 and 32 nm are observed for MA and DA, respectively, from the spectral maximum of 350 nm for NDA. The extinction coefficients change only to a small extent as summarized in Table I. The blue shifts are expected since the amide groups are less electron donating to the naphthalene ring than the amine groups. In contrast, the fluorescence emission maximum of MA is red shifted by 24 nm to 413 nm from the emission maximum of NDA at 389 nm, and its fluorescence intensity at 389 nm is reduced by about 50% as summarized in Table I. The diamide shows negligible fluorescence intensity (about 2%) in comparison to NDA when excited at 345 nm.

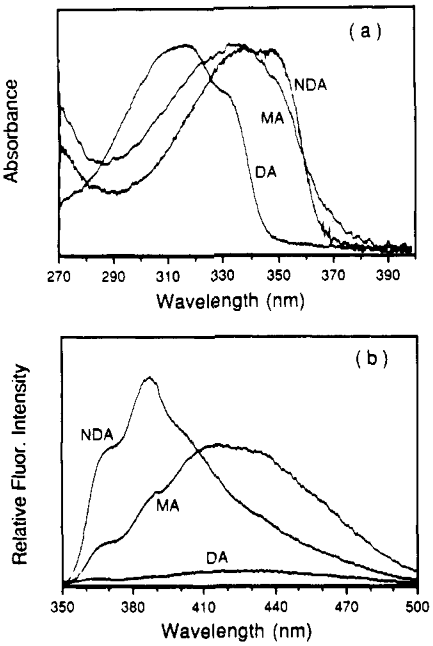


Figure 1. UV absorption spectra (a) and fluorescence spectra (b) of 1,5-naphthalenediamine (NDA), monoamide (MA), and diamide (DA) in *N*-methylpyrrolidone (NMP). The excitation wavelength was set at 345 nm for fluorescence spectra.

Table I
UV Absorption and Fluorescence Characteristics of Acylation Products of 1,5-Naphthylenediamine (NDA) in *N*-Methylpyrrolidone

compd	λ_{abs}, nm	$\Delta\lambda$, nm	ϵ, L mol^{-1} cm^{-1}	λ_{emis}, nm	Rel I_f[a] (at 389 nm)
NDA	350	0	13 000	389	54
monoamide (MA)	335	−15	10 000	413	22
diamide (DA)	318	−32	16 000		1

[a] $\lambda_{excitation}$ at 345 nm.

While MA showed a blue shift in the UV-visible absorption spectra, its fluorescence is red shifted in comparison to NDA. The blue shifts in absorption spectra are reasonable on the basis of the lesser electron-donating nature of the amide group. On the other hand, the red shift in the emission spectra may be due to the polar nature and/or hydrogen-bond formation with the solvent (NMP) used for spectral characterization. While UV-visible absorption spectra are somewhat sensitive to the polarity of the solvent, the fluorescence spectra of some compounds having large dipole moments in their excited state are known to be extremely sensitive to solvent polarity.[6] For example, several naphthalene derivatives such as 1-anilinonaphthalene-8-sulfonate or 2-anilinonaphthalene are known to exhibit strong red shifts in polar solvents. This trend is due to the lowering of the energy level of the first singlet excited state following solvent relaxation, which is in response for the solvent to reorganize surrounding the fluorophore with a high dipole moment in the excited state.

2. Kinetics of Acylation between NDA and *n*-Propionic Acid. The reaction between NDA and *n*-propionic acid was carried out at 95, 110, and 125 °C. Neat *n*-propionic acid was used without any solvent in order to accelerate the reaction rates and to simplify the reaction kinetics as first-order reactions. The UV absorption spectra in general show blue shifts as reaction time progresses. Close observation of the spectra indicates that the reaction proceeds by two clear steps. For example, as shown in Figure 2a, the absorption maximum is shifted from 350 to 335 nm after a reaction time of 290 min at 110 °C with two isosbestic points at 320 and 363 nm. This

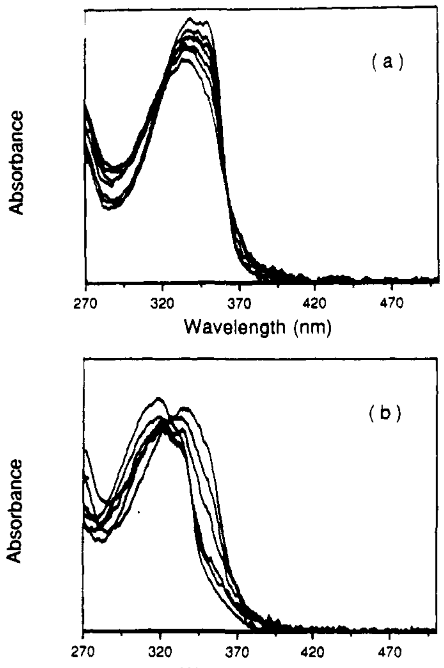
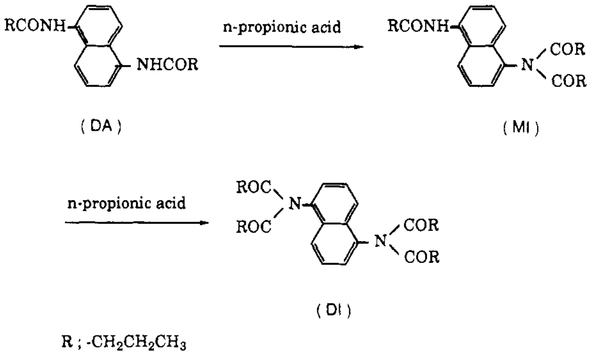


Figure 2. UV absorption spectra as a function of reaction time at 110 °C for NDA in n-propionic acid for reaction times of (from the top of the curves) (a) 0, 70, 140, 180, 230, and 290 min and (b) 290, 420, 595, 895, 1280, and 1640 min, showing the blue shift.

Scheme II
Chemical Structures of Diamide (DA) and Its Monoimide (MI) and Diimide (DI) Products after Reaction with n-Propionic Acid



first step indicates that there are only two species involved, most likely due to the acylation of NDA to MA. On the other hand, the second step is slower, as shown in Figure 2b, when the reaction time changes from 290 to 1640 min at 110 °C. In this second step, an additional blue shift is observed on the absorption maximum from 335 nm due to MA to 318 nm, which is attributed to DA. An isosbestic point is seen around 325 nm for most of the reaction times, but after a very long time of reaction, the spectrum is further blue shifted with subsequent deviation from the isosbestic point. This trend indicates that there are only two species involved, most likely MA and DA, as long as the isosbestic point is maintained. In fact, the IR spectrum of the reaction mixture after reaction for 2880 min at 110 °C is very similar to that of DA when n-propionic acid is removed from the reaction mixture. After very long times of reaction, more than two species are involved, probably involving monoimide and/or diimide species as shown in Scheme II as a result of additional reaction of the amide NH group with n-propionic acid. The absorption spectrum of diimide shows an additional blue shift with its maximum at 290 nm,[3b] due to the greater electron-withdrawing effect of imide groups in comparison to the amide groups. At reaction temperatures of 95 and 125 °C, the same trends of two-step reactions with progressive blue shifts are observed.

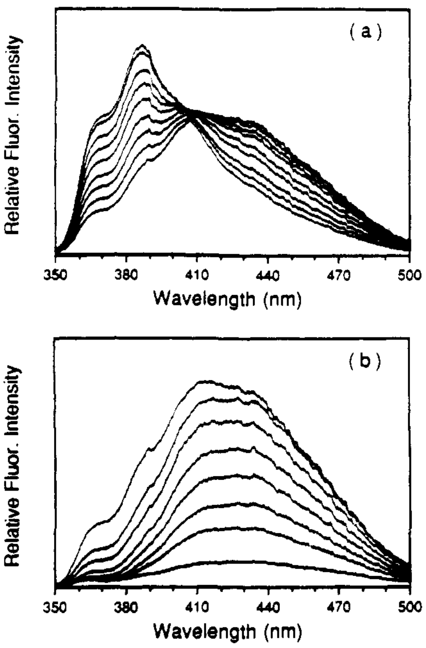


Figure 3. Fluorescence spectra as a function of reaction time at 110 °C for NDA in n-propionic acid for reaction times of (from the top of the curves) (a) 0, 20, 40, 70, 100, 140, 180, 230, and 290 min and (b) 290, 420, 505, 715, 895, 1280, 2180, and 4470 min.

In the fluorescence spectra, these two-step reactions are also manifested as illustrated in Figure 3. During the first stage of reaction (up to 290 min at 110 °C), the fluorescence spectra show red shifts from 389 to 413 nm with an isosbestic point around 406 nm. This first step is thus attributed to the conversion of NDA to MA. The second step is manifested in Figure 3b for fluorescence, where a continuing decrease in fluorescence intensity is illustrated without any isosbestic point. This trend is due to the fact that DA (diamide) has negligible fluorescence, as demonstrated in Figure 1b. At long reaction times, diimide species can be formed and can be detected in UV spectra because of additional blue shifts. However, diimide or monoimide species have negligible fluorescence.[3b,d] Therefore, it is not possible to decide whether more species than MA and DA are formed in the reaction from the fluorescence spectra alone. Again, the same spectral trends in fluorescence are observed at reaction temperatures of 95 and 125 °C.

The fractional composition of NDA, MA, and DA (A_{NDA}, A_{MA}, and A_{DA}) and the kinetic parameters, namely, the rate constants K_1 and K_2 as defined for the first reaction (NDA → MA) and the second reaction (MA → DA), respectively, have been estimated from both UV absorption spectra and fluorescence spectra. From the UV spectra, the spectral deconvolution was carried out by assuming only the presence of NDA and MA for the first step and of MA and DA for the second step in order to obtain the fraction of each species. The analysis of the second stage was limited to the time range when the isosbestic point was present. Figure 4 shows how the composition changes as a function of reaction time at 110 °C. Specifically, NDA disappeared completely, while MA was formed to 100% after 290 min of reaction, corresponding to the end of the first step. The slow emergence of DA with concomitant disappearance of MA is also noted in the second stage. From these composition data, the rate constants K_1 and K_2 are estimated from the first-order kinetic plots of ln

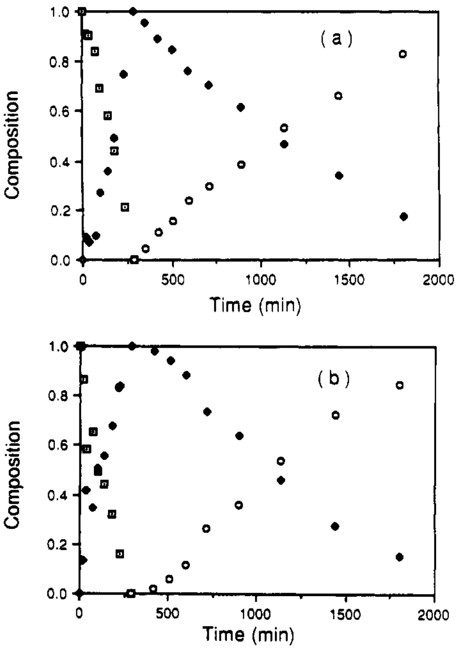


Figure 4. Fractional composition of three reaction species (a) from the deconvolution of the UV spectra and (b) from the fluorescence analysis for reaction of NDA with *n*-propionic acid at 110 °C ((□) A_{NDA}; (◇) A_{MA}; (○) A_{DA}).

Table II
Summary of Kinetic Parameters for the Reaction of 1,5-Naphthylenediamine with *n*-Propionic Acid by UV and Fluorescence Techniques

reacn temp, °C	UV		fluorescence	
	$K_1 \times 10^4$, min^{-1}	$K_2 \times 10^4$, min^{-1}	$K_1 \times 10^4$, min^{-1}	$K_2 \times 10^4$, min^{-1}
95	14	6	22	4
110	65	9	72	10
125	125	34	156	38
ΔE^*, kcal/mol	22	28	19	22

A_{NDA} versus time or ln A_{MA} versus time, since we can treat each reaction step as a separate first-order reaction. Table II summarizes the rate constants estimated from UV spectral deconvolution at three reaction temperatures. The rate constants for the first step are always greater than the second rate constants (K_2) by about 3–7 times. The activation energy is approximately 22 and 28 kcal/mol for each step, respectively.

The fractional compositions of NDA, MA, and DA were also estimated from fluorescence spectra by using the fluorescence intensities rather than spectral deconvolution. During the first stage, the fraction of NDA (A_{NDA}) can be expressed in terms of fluorescence intensity at 389 nm as in eq 1. The fraction of MA during the first stage

$$A_{\mathrm{NDA}} = \frac{I_{\mathrm{f}}(t) - I_{\mathrm{f}}(\mathrm{MA})}{I_{\mathrm{f}}(\mathrm{NDA}) - I_{\mathrm{f}}(\mathrm{MA})} \qquad (1)$$

is obviously equal to $(1 - A_{\mathrm{NDA}})$, since only two species (NDA and MA) are involved.

During the second stage, the fraction of MA (A_{MA}) is equal to $I_{\mathrm{f}}/I_{\mathrm{f}}(\mathrm{MA})$ at 413 nm, since DA has negligible fluorescence. The composition of NDA, MA and DA obtained from fluorescence analysis is illustrated in Figure 4b for the reaction carried out at 110 °C. The general trend and the compositional values compare well with the results obtained by UV spectral deconvolution. The rate constants, K_1 and K_2, were also estimated on the basis of two separate first-order reactions from the composition results of fluorescence analyses. The right-hand column in Table II summarizes such rate constants. The first rate constant, K_1, is again greater than the second one by a factor of 4–7 times. The activation energy for the first process is about 19 kcal/mol while the second process is about 22 kcal/mol. The rate constants and the activation energies between UV and fluorescence results are comparable.

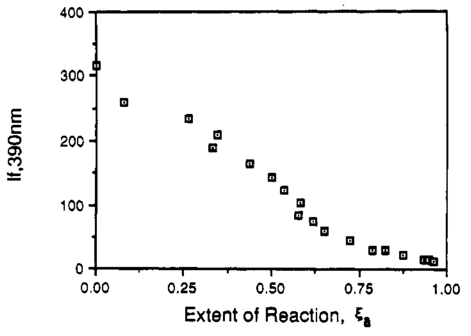


Figure 5. Correlation of relative fluorescence emission intensity at 390 nm with the overall extent of reaction, ξ_a.

The reason for the smaller rate constant K_2 in comparison to K_1 is due to the reduced basicity of the amine group in MA compared to that in NDA. In fact, Borkent et al. reported the K_1/K_2 ratio in the acylation of *p*-phenylenediamine and terephthaloyl chloride to be about 12.[7] We find in this study the K_1/K_2 ratio to be in the range 3–7.

As for the activation energies, we find the value in the range 19–28 kcal/mol. Morawetz and Otaki found the activation energies for the acylation of aliphatic amines with aliphatic acid to be in the range 15–20 kcal/mol.[8]

We can now establish a correlation curve of fluorescence intensity, I_{f}, with the overall extent of reaction, ξ_a, which is defined by eq 2. As seen in eq 2, ξ_a is calculated from

$$\xi_a = 0.5(A_{\mathrm{MA}} + 2A_{\mathrm{DA}}) \qquad (2)$$

either UV results or fluorescence results for a corresponding I_{f} at 390 nm at the same reaction time and temperature. As illustrated in Figure 5, all of the data points at three temperatures fall into a smooth calibration curve, which shows a continuously decreasing trend of fluorescence intensity as a function of reaction extent.

3. Reaction of NDA with Benzoyl Chloride. In the syntheses of aromatic polyamides, aromatic diamines are often reacted with aromatic acid chlorides such as terephthaloyl chloride. In order to model such reactions, we carried out the reaction of NDA with benzoyl chloride in NMP. Immediately after the two reactants are mixed at room temperature, UV spectra are shifted to 315 nm and the fluorescence is almost negligible. It was apparent that the reaction is too fast to follow at room temperature. At lower temperatures such as 0 °C, the reaction is slowed down, as demonstrated in Figure 6. The UV spectra (Figure 6a) show blue shifts to 315 nm, while the fluorescence spectra (Figure 6b) show a sharp decrease in intensity as the reaction proceeds from 12 to 326 min. These trends, which are the same as observed with the reaction of NDA with an aliphatic acid (*n*-propionic acid), can be used in the future to monitor polymerization between aromatic amines and aromatic acids or acid chlorides for the syntheses of aromatic polyamides.

Summary

In this study, we used UV absorption and fluorescence spectroscopy to characterize the kinetic parameters of

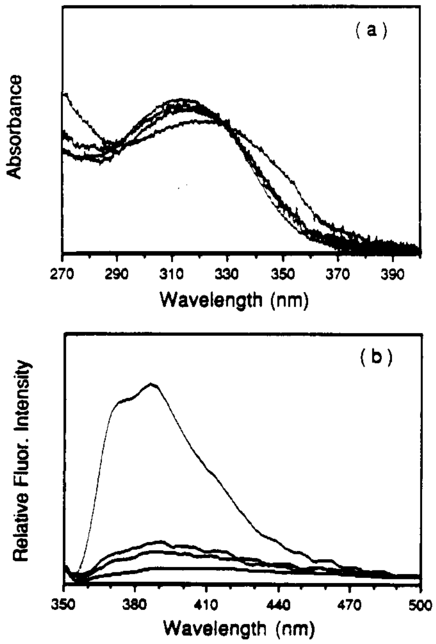


Figure 6. UV absorption spectra (a) and fluorescence spectra (b) as a function of reaction time at 0 °C between NDA and benzoyl chloride. (Reaction times are 0, 12, 26, and 326 min from left to right for (a) and from top to bottom for (b).)

model acylation reactions between 1,5-naphthylenediamine (NDA) and *n*-propionic acid. The reaction between NDA and neat *n*-propionic acid was carried out at 95, 110, and 125 °C. First, two acylation products, monoamide (amide–amine) and diamide, were synthesized, and their chemical structures were verified by IR spectroscopy. As NDA is converted to monoamide and diamide, the UV absorption spectra show blue shifts from 350 to 335 and 318 nm at their absorption maxima. The extinction coefficients change from 13 000 to 10 000 and 16 000 as NDA changes to monoamide and diamide. The fluorescence intensity is reduced about 50% from NDA to monoamide, while the intensity of diamide is negligible. The emission maxima are red shifted from 389 nm for NDA to 413 nm for monoamide when NMP is used as the solvent.

During the acylation reaction, the UV absorption spectra show blue shifts, while the fluorescence emission spectra exhibit an initial red shift with a progressive reduction in intensity. The IR spectra support the conversion of NDA to monoamide and diamide during reaction. The reactions as manifested in the UV and fluorescence spectra appear to proceed in two stages, the first stage from NDA to monoamide followed by a slower second stage for the reaction from monoamide to diamide. With the use of the UV absorption and fluorescence spectral characteristics of NDA, monoamide, and diamide, the UV absorption spectra and fluorescence spectra were analyzed to obtain the fractional composition of the three species. On the basis of two separate first-order kinetics, the rate constants representing each stage were estimated from the fractional composition. The results from both UV spectra and fluorescence spectra support the trend that the first-stage reaction from NDA to monoamide is faster than the second-stage reaction from monoamide to diamide. This is due to the reduced basicity of the amine group in monoamide in comparison to that in NDA. The activation energies for the first- and second-stage reactions are about 20 kcal/mol.

In order to simulate the polymerization between terephthaloyl chloride and diamine to make polyamides, benzoyl chloride was reacted with NDA. When the reaction was carried out at 0 °C, the UV absorption spectra exhibited a measurable blue shift, while the fluorescence spectra showed a pronounced decrease in intensity. These spectral changes were similar to those observed in the reaction between NDA and *n*-propionic acid. Thus, a calibration curve obtained for the case of NDA reaction with *n*-propionic acid can be used in the future to relate the fluorescence intensity with the extent of polymerization.

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Registry No. NDA, 2243-62-1; PA, 79-09-4; MA, 130614-03-8; DA, 130614-04-9; benzoyl chloride, 98-88-4.