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Excimer Formation of a Naphthalene Diisocyanate Based Polyurethane in Solution

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Received August 3, 1987

ABSTRACT: Naphthylcarbamates are shown to form excimers that are stabilized by hydrogen bonding inherent in the participating species. Substitution of a methyl group on the central nitrogen atom of the carbamate moiety severely limits excimer formation. A polyurethane based on 1,5-naphthalene diisocyanate forms intramolecular excimers in dilute solutions of both good and poor solvents; however, excimer formation is significantly enhanced in poor solvents, where intramolecular contact between naphthylcarbamate groups is favored. The photophysics of excimer formation in the polyurethane is interpreted on the basis of an "isolated monomer" scheme. By measurement of the excimer to monomer intensity ratio in pure and mixed solvent systems, the solubility parameter of the polymer is estimated to be between 21 and 22 $\times 10^3$ $(J/m^3)^{1/2}$.

Introduction

Excimers are defined as excited-state complexes between two equivalent species, one of which is in the excited state prior to formation of the complex. Excimers have lower excited-state energies than the monomeric chromophores of which they are comprised and consequently are characterized by a red-shifted emission. Their lifetimes may be longer or shorter than the monomer species from whence they are derived.

Since their discovery in polymeric systems, excimers have continued to be a topic of significant activity. Several excellent reviews of excimer formation in polymer solutions and films have been published in recent years.[1-3] In most of the reports of excimer formation in polymer systems to date, the excimers are comprised of fluorescent species attached as pendant chromophores to the polymer backbone. These polymers are capable of forming excimers between nearest and nonnearest neighbors. In contrast to the large number of reports of excimers formed from pendant fluorescent groups, there are only a few reports of excimers formed between interactive chromophores that are spaced periodically at large distances from each other in the same polymer backbone.[4-11] In addition, there are also some reports of excimer formation between interactive chromophores located at polymer chain ends.[12-14]

We recently reported that polyurethanes based on 1,5-naphthalene diisocyanate form intramolecular excimers between two naphthylcarbamate groups located in the same polymer chain.[10,11] By comparison of the fluorescence decay parameters with model naphthyl carbamates, it was suggested that an "isolated monomer" scheme could account for the complex photophysics of these naphthyl-containing polyurethanes. The extent of excimer formation was found to be related to the intrinsic viscosity of the dilute polymer solutions.[10] In this paper, our earlier work is expanded, and complete details of the effect of solvent on the photophysics of a 1,5-naphthalene diisocyanate based polyurethane is presented. In particular, the ratio of excimer to monomer emission is used to predict the polymer solubility parameter. Additionally, by utilization of model compound studies, it is found that the strong degree of excimer formation between naphthyl carbamate chromophores can be attributed, at least in part, to a hydrogen-bonding effect between participating chromophores.

Experimental Section

Materials. Dichloromethane, 1,2-dichloroethane, *N,N'*-dimethylformamide (DMF), cyclohexane, and benzene were purchased from Burdick and Jackson and used without further purification. Xylene (Baker), toluene (Baker), ethylbenzene (Gold Label, Aldrich), 1-butanol (Aldrich), 1,2-propanediol (Aldrich), 1,4-butanediol (Aldrich), and 2,3-butanediol (Aldrich), were used as received. Propylbenzene (Aldrich) was distilled prior to use. Deionized water was used.

Equipment. Steady-state emission spectra were recorded on a Perkin-Elmer 650-10S fluorescence spectrophotometer. UV spectra were obtained on a Perkin-Elmer 320 UV spectrophotometer. Fluorescence decay curves were obtained on a single-photon-counting apparatus from Photochemical Research Associates. All samples were thoroughly purged with nitrogen prior to fluorescence measurements. The data were analyzed by a

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Table I
Fluorescence Decay Parameters for PNC, 1,5-DNB, and NDI-650 in 1,2-Dichloroethane[a]

compd	concn	τ_1,[b] ns	A_1	τ_2,[c] ns	A_2	τ_3, ns	A_3
PNC	1.31×10^{-4} M	3.8					
PNC	0.84 M			0.49	0.949	16.1[d] (18.1)[e]	0.085
1,5-DNB	0.01 g/dL	1.81					
NDI-650	0.01 g/dL	2.04	3.04	1.18	6.91	15.5[d] (17.9)[e]	0.017

[a] N_2 atmosphere, λ_{ex} = 300 nm; monitoring wavelength = 330 nm except where noted. [b] Unquenched monomer lifetime. [c] Quenched monomer lifetime. [d] Excimer lifetime; monitoring wavelength = 330 nm. [e] Excimer lifetime; monitoring wavelength = 480 nm.

software package obtained from PRA based on the interative convolution method. ^{13}C NMR spectra were obtained on a JEOL FX90Q, and FT-IR spectra were recorded on a Nicolet 5DX. The elemental analyses were conducted by M-H-W Laboratories of Phoenix, AZ.

Solutions containing the NDI-650 polyurethane in mixed solvents were prepared by dissolving the NDI-650 polyurethane in the good solvent component (CH_2Cl_2 or DMF) followed by the addition of the nonsolvent (cyclohexane or H_2O). Each solution was vigorously stirred to ensure complete mixing of the two solvents before the fluorescence emission spectrum was obtained. In some instances, the initial fluorescence intensity ratio recorded immediately after the above mixing procedure changed upon solution aging. This phenomenon will be discussed in a separate paper dealing with fluorescence in mixed-solvent systems.

Synthesis of Model Compounds. 1,5-Naphthalene Diisocyanate (NDI). To a stirring solution of *p*-dioxane (50 mL) containing 1,5-diaminonaphthalene (Fluka, 5.1 g) was added trichloromethyl chloroformate (Fluka, 17 g) in *p*-dioxane (15 mL) through an addition funnel under a nitrogen stream. A white precipitate was immediately observed. After addition, the temperature was increased to reflux. The HCl subsequently formed was removed by passing through water. After 1 h, the solution turned clear and was allowed to react for another 3 h. The *p*-dioxane was evaporated under reduced pressure, and the resulting solid was vacuum sublimed twice to give the colorless crystals in 71% yield: mp 126–128 °C (lit.[15] mp 129.5–131 °C); IR 3022, 2300, 1600, 1500 cm^{-1}; ^{13}C NMR 130.9, 128.7, 127.7, 124.2, 122.2 ppm (benzene). Anal. Calcd for $C_{12}H_6N_2O_2$: C, 68.57; H, 2.88; N, 13.33. Found: C, 68.62; H, 2.91; N, 13.32.

Propyl *N*-(1-Naphthyl)carbamate (PNC). Into 50 mL of an ethyl acetate (distilled and dried) solution of 1-naphthyl isocyanate (Aldrich, distilled, 10 g) was added 1-propanol (Baker, distilled and dried, 7.1 g) through an addition funnel. The temperature was increased to the reflux temperature of ethyl acetate, and the mixture was allowed to react for 8 h under a nitrogen stream. The precipitates were removed by filtration, and ethyl acetate was evaporated under reduced pressure. The forming product was purified by recrystallization from CH_3CN: mp 72 °C; IR 3325, 2950, 1675, 1600, 1540, 1500 cm^{-1}; ^{13}C NMR 156.1, 135.3, 129.1, 126.8, 126.6, 125.5, 123.4, 120.9, 67.1, 23.2, 10.9 ppm (DMF). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 75.24; H, 6.59; N, 6.11. Found: C, 75.36; H, 6.51; N, 6.18.

Propyl *N*-Methyl-*N*-(1-naphthyl)carbamate (PNMNC). For the preparation of this compound, all reactions were carried out in an ice bath. NaH (Alfa, 50% in oil, 1.2 g) was dispersed in DMF (Burdick and Jackson, dried, 5 mL), and the solution was cooled in an ice bath. The propyl *N*-(1-naphthyl)carbamate (3.3 g) in DMF (15 mL) was added to a reactor through an addition funnel dropwise under a nitrogen stream. Immediately, hydrogen was generated and the reaction mixture turned green. The stirring was continued for 1.5 h. CH_3I (Aldrich, distilled, 4.0 g) in DMF (10 mL) was added dropwise, and the reaction mixture turned colorless. The solution was allowed to react for 2 h. When the reaction was complete, the precipitates were removed by filtration and DMF was evaporated under reduced pressure. The residue was redissolved in diethyl ether, and the insolubles were removed by filtration. After evaporation of solvent, the resulting liquid was vacuum distilled. A colorless liquid was obtained: bp 120–125 °C (0.5 mmHg); IR 3060, 2950, 1700, 1600, 1500 cm^{-1}; ^{13}C NMR 158.6, 142.9, 137.4, 133.3, 131.2, 130.4, 129.3, 128.9, 128.5, 127.7, 125.5, 69.5, 40.7, 25.0, 12.7 ppm (neat). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 74.05; H, 7.04; N, 5.75. Found: C, 74.16; H, 6.95; N, 5.69.

Dipropyl *N*,*N*'-Naphthalene-1,5-diylbiscarbamate (1,5-DNB). To a *p*-dioxane solution containing 1-propanol (1.71 g) and dibutyltin dilaurate (Polysciences, 0.2 g) was added 1,5-naphthalene diisocyanate (1.5 g) at once. The reaction mixture was heated to 80 °C and allowed to react for 4 h with stirring under a nitrogen stream. After evaporation of *p*-dioxane, the forming product was purified by recrystallization from CH_3CN/DMF (50/50): mp 203 °C; IR 3290, 3000, 1685, 1540, 1500 cm^{-1}. Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.38; H, 6.63; N, 8.59.

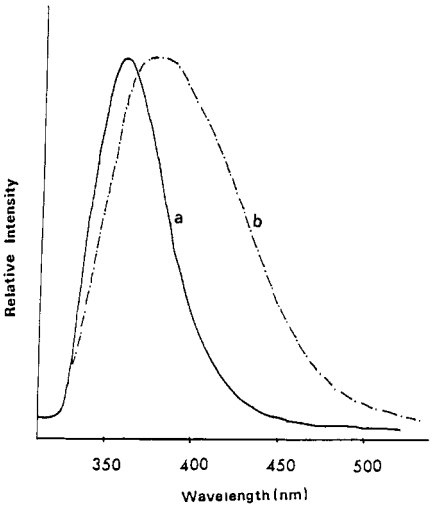
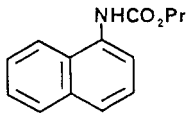


Figure 1. Steady-state fluorescence spectra (λ_{ex} = 300 nm) of PNC in 1,2-dichloroethane (curve a, 1.31×10^{-4} M; curve b, 1.9 M).

Synthesis of NDI Polyurethane (NDI-650). To 20 mL of 1,1,2,2-tetrachloroethane (Baker, distilled and dried) containing poly(tetramethylene ether glycol) (Polysciences, average MW 650, 2.17 g), dibutyltin dilaurate (Polysciences, 0.11 g), and 1,4-diazobicyclo[2.2.2]octane (Dabco), (Aldrich, 0.08 g) was added 1,5-naphthalene diisocyanate (0.7 g). The mixture was heated to 100 °C and allowed to polymerize for 2.5 h with stirring under a nitrogen stream. The 1,1,2,2-tetrachloroethane was evaporated under reduced pressure, and the products were dissolved in CH_2Cl_2. The CH_2Cl_2 solution was poured dropwise into 500 mL of cyclohexane. The precipitated polymer was collected and dried: IR 3310, 2930, 1740, 1695, 1540, 1500 cm^{-1}; ^{13}C NMR 157.2, 136.2, 130.4, 128.4, 122.3, 120.3, 73.1, 67.9, 29.1, 28.6 ppm (CH_2Cl_2). Anal. Calcd C, 65.71; H, 9.15; N, 3.26. Found: C, 65.99; H, 9.32; N, 3.29. The molecular weight of NDI-650 was 51 000 by GPC.

Results and Discussion

Excimer Fluorescence of Model Naphthylcarbamates. It is a well-known phenomenon that concentrated naphthalene solutions exhibit emission from both monomer and excimer (emission maximum at 400 nm) states.[16,17] If a propyl carbamate group is substituted on naphthalene in the 1-position, the monomer fluorescence of propyl *N*-(1-naphthyl)carbamate (PNC) is char-



PNC

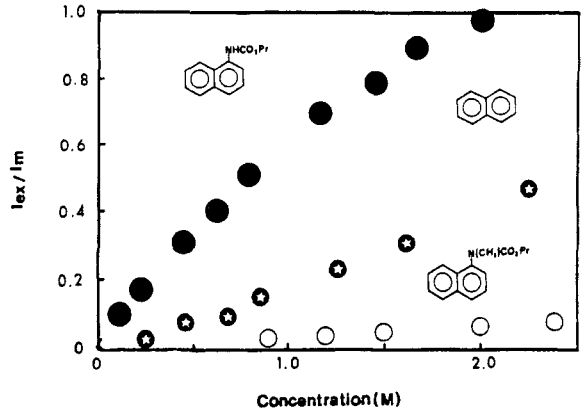
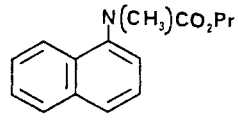


Figure 2. Ratios of excimer (I_{ex}) to monomer (I_m) intensity of model compounds as a function of concentration in 1,2-dichloroethane: I_{ex} = 430 (PNC), 415 (PNMNC), 385 nm (naphthalene); I_m = 355 (PNC), 340 (PNMNC), 325 nm naphthalene. I_{ex}/I_m is corrected by a fluorescence spectrum of each compound in a dilute solution (9.5×10^{-4} M for PNC, 7.8×10^{-3} M for PNMNC, and 3.9×10^{-4} M for naphthalene).

acterized in dilute 1,2-dichloroethane solution (Figure 1, curve a) by a modest red-shifted (in comparison to naphthalene) monomer emission and loss of vibrational structure due to asymmetric substitution by the carbamate chromophore on naphthalene. The decay curve of a dilute solution (1.31×10^{-4} M) of PNC is single exponential with a lifetime (τ_1) of 3.8 ns (Table I). As in the case of naphthalene, when the concentration of PNC is increased, the emission spectrum is red-shifted (Figure 1, curve b) as excimers are formed. Although it cannot be ruled out, UV absorption studies and fluorescence excitation spectra show no clear evidence for formation of a ground-state dimer. However, it should be noted that such dimer formation would be difficult to detect by front-face excitation spectra of concentrated solutions of PNC if the dimer had a low extinction coefficient and/or was present in small concentrations. Decay curves for both a dilute and a concentrated solution of PNC at wavelengths of monomer (330 nm) and excimer (480 nm) emission were recorded. For the concentrated solution (0.84 M), the decay curve obtained at 330 nm was readily fit to a double-exponential decay function with parameters of 0.49 (τ_2) and 16.1 ns (τ_3). The lifetimes for PNC in 1,2-dichloroethane are similar to those reported previously in dichloromethane and can be attributed to quenched monomer (0.49 ns) and excimer (16.1 ns) states.[10] In addition to these results, by a fit of the long-lived portion of the excimer emission decay curve obtained at 480 nm, a decay parameter of 18.1 ns (τ_3) was obtained. From these studies, which are summarized in Table I, it can be concluded that PNC forms excimers in concentrated 1,2-dichloroethane solutions.

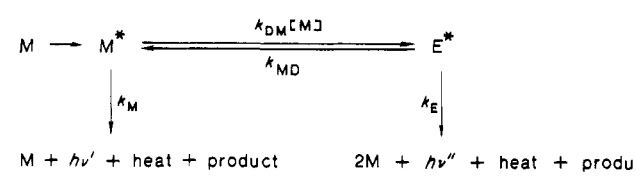
In contrast to the results for PNC, the emission spectrum of propyl *N*-methyl-*N*-(1-naphthyl)carbamate (PNMNC) shows little red-shifted excimer emission (see



PNMNC

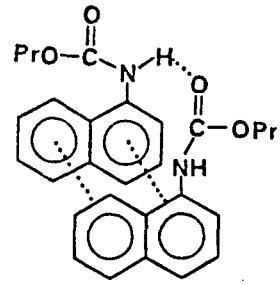
ref 10). Apparently, the methyl group on the nitrogen of the carbamate chromophore hinders excimer formation. To contrast the results for PNC and PNMNC directly, we give plots of the excimer to monomer intensity ratio (I_{ex}/I_m) versus concentration in Figure 2 for PNC, PNMNC, and naphthalene (for reference). From the results for PNC and PNMNC, it is quite obvious that methyl substitution greatly inhibits excimer formation. The high degree of excimer formation for PNC versus naphthalene is particularly surprising when considered in light of the short monomer lifetime (3.8 ns) of PNC in 1,2-dichloroethane.

Scheme I



One other piece of information must be considered before attempting to rationalize the high degree of excimer formation for PNC: the rate of excimer formation. It has been established previously[10] that the PNC excimer in dichloromethane solution is formed according to the standard Birks scheme for excimer formation (Scheme I), where k_M = nonradiative plus radiative rate constant for excited PNC monomer M*, k_{DM} = rate constant for excimer formation between M and M*, k_{MD} = rate constant for dissociation of excimer E* into component species M* and M, k_E = nonradiative plus radiative rate constant for excimer E*, M = ground-state PNC, M* = excited-state PNC, and E* = PNC excimer. The reciprocal of the decay constants for PNC monomer ($\lambda_2 = 1/\tau_2$) and excimer ($\lambda_3 = 1/\tau_3$) emission as a function of monomer concentration [M] have been calculated. Birks has shown that a plot of $\lambda_2 + \lambda_3$ versus [M] should yield a straight line with slope equal to k_{DM}. The value of k_{DM} thus deduced from such a plot in Figure 3 is substantial (2.0×10^9 s^{-1} M^{-1}).

In analyzing the results from Figures 2 and 3, one is forced to conclude that excimer formation for PNC is quite efficient. In comparing the results for PNC and PNMNC in Figure 2, a first analysis might attribute the low degree of excimer formation in PNMNC to steric hindrance afforded by methyl substitution. However, the carbamate group is already quite bulky before methyl substitution. One explanation for the efficiency of PNC excimer formation can be deduced by consideration of the well-known hydrogen-bonding phenomena[18] exhibited by aliphatic and aromatic urethanes. This is illustrated for PNC at high concentrations by the structure



where the hydrogen connected to the central nitrogen of the urethane moiety of a PNC molecule forms a hydrogen bond to the carbonyl of the urethane group of a second PNC molecule. Such a preexisting structure prior to excitation of one of the PNC molecules could account for the efficiency of excimer formation.

Evidence for hydrogen bonding in PNC solutions can be obtained by FT-IR analysis of the N–H stretching region. The unbonded N–H stretching in typical aryl urethanes has a strong IR band at ~3400 cm^{-1}, while hydrogen-bonded N–H stretching has a somewhat red-shifted band (~3300 cm^{-1}) resulting from a decrease in the resonant stretching frequency. Figure 4 shows a series of

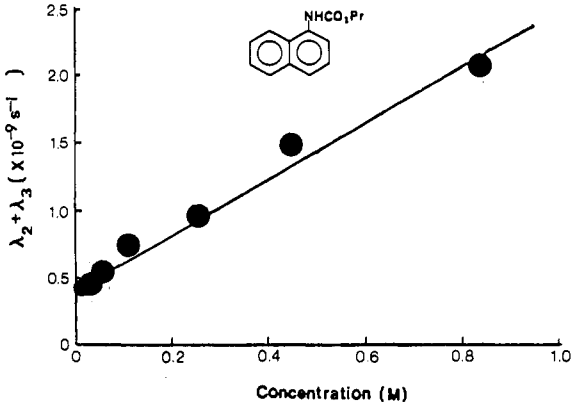


Figure 3. Plot of $\lambda_2 + \lambda_3$ of PNC as a function of concentration in 1,2-dichloroethane.

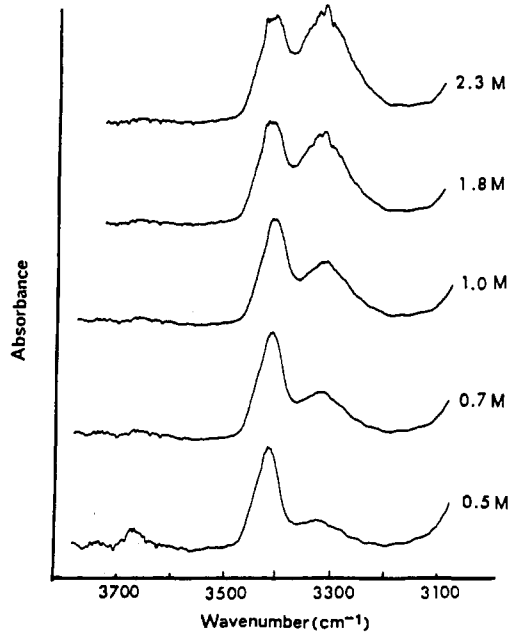


Figure 4. IR spectra of PNC at various concentrations in 1,2-dichloroethane.

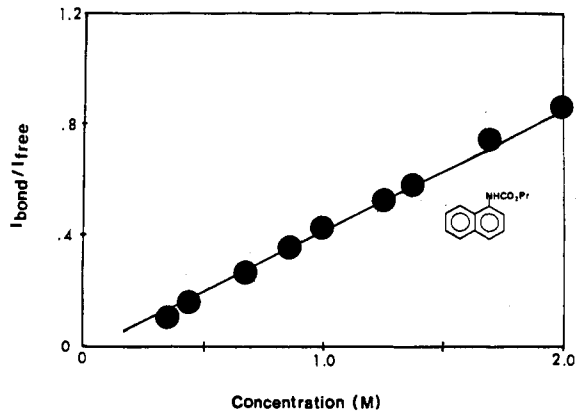


Figure 5. Plot of I_{bond}/I_{free} as a function of PNC concentration in 1,2-dichloroethane.

FT-IR spectra of PNC in 1,2-dichloroethane ranging from 0.5 to 2.3 M. Both a nonbonded N–H (3410 cm^{-1}) and a hydrogen-bonded N–H (3320 cm^{-1}) absorbance are present in each spectra. The relative intensity of the hydrogen-bonded peak (I_{bond}) increases linearly (Figure 5) with respect to the intensity of the free or nonbonded N–H (I_{free}) as the PNC concentration increases. The increase in the I_{bond}/I_{free} ratio (Figure 5) over the same concentration range as the I_{ex}/I_m ratio (Figure 2) increase leads to the postulation that excimer formation is enhanced by hydrogen bonding.

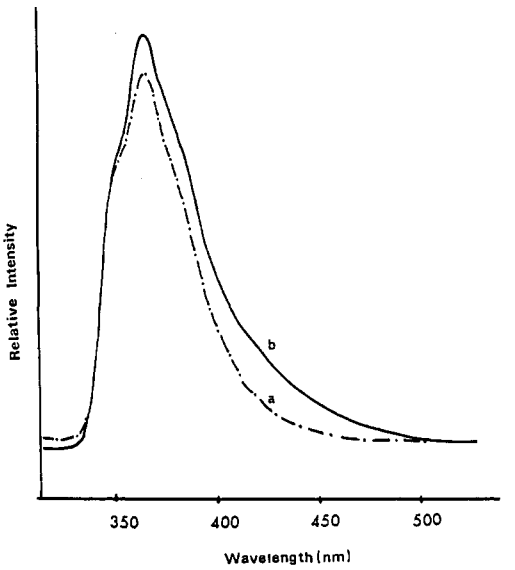


Figure 6. Steady-state fluorescence spectra (λ_{ex} = 300 nm) of 1,5-DNB (curve a, 9.1×10^{-5} M) and NDI-650 (curve b, 0.01 g/dL) in 1,2-dichloroethane.

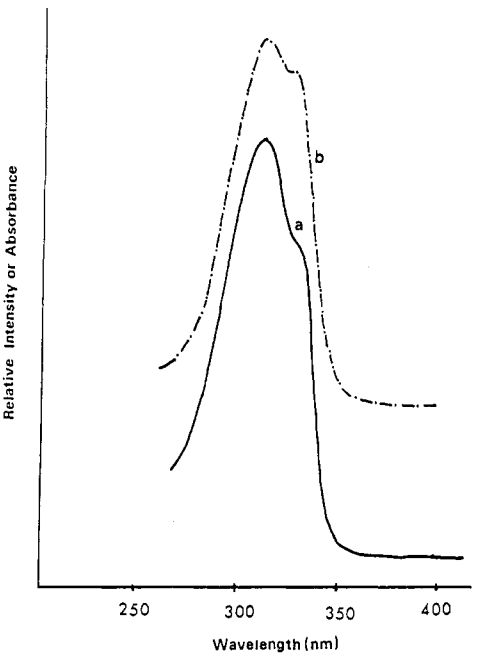


Figure 7. Absorption spectrum (curve a, 0.01 g/dL) and excitation spectrum (curve b, 1.7×10^{-3} g/dL, λ_{em} = 430) of NDI-650 in 1,2-dichloroethane.

Excimer Fluorescence of Naphthalene Diisocyanate Based Polyurethanes. Having shown that small-molecule naphthylcarbamates form excimers quite efficiently, we turn to the more complex situation where naphthylbiscarbamate groups are spaced at regular repeating intervals on the backbone of a polymer chain. Figure 6 (curve b) shows the fluorescence spectrum of a very dilute 1,2-dichloroethane solution (0.01 g/dL) of a polyurethane (designated NDI-650) made from 1,5-

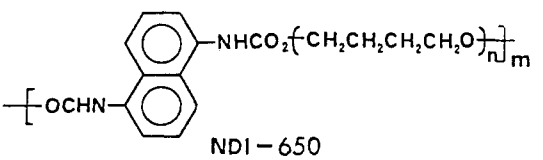
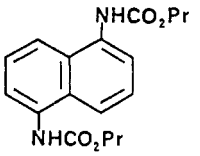


Table II
Fluorescence Decay Parameters of NDI-650 in Various Solvents[a]

solvt	τ_1, ns	A_1	τ_2, ns	A_2	τ_3, ns	A_3	τ_{DNB}[f]	10^{-3} × solubility parameter[g]
DMF[b]	2.38	4.92	1.41	5.43	13.4 (12.8)[e]	0.035	2.36	24.8
DMF/H_2O (70/30)[c]	2.60	0.71	0.44	5.46	18.1 (23.9)	0.018	2.58	32.0
toluene[b]	2.30	1.81	1.13	5.73	32.6 (27.8)	0.025	2.20	18.3
DMF/H_2O (80/20)[c]	2.56	0.48	0.62	1.22	16.1 (21.6)	0.039	2.47	29.0
1-butanol[b]	2.41	6.28	1.22	4.58	22.9 (22.3)	0.033	2.48	23.3
1,2-propanediol[d]	2.67	2.72	0.84	1.70	18.8 (18.1)	0.018	2.57	26.0
benzene[b]	2.43	4.76	1.25	16.95	22.3 (24.9)	0.041	2.30	18.8
dichloromethane	2.04	2.14	1.20	8.05	19.2 (21.4)	0.015	1.84	19.8

[a] λ_{ex} = 310 nm; λ_{em} = 330 nm; nitrogen atmosphere. [b] 0.01 g/dL. [c] 1.5×10^{-3} g/dL. [d] Less than 0.01 g/dL; the fluorescence emission spectrum was obtained from the solution that was filtered after heating at 60 °C for 30 min. [e] The value in parentheses signifies the lifetime of the long-lived component when monitored at 480 nm. [f] Lifetime of 1,5-DNB. [g] Units of $(J/m^3)^{1/2}$.

naphthalene diisocyanate and poly(tetramethylene ether glycol) (average MW 650). Comparison of the fluorescence from NDI-650 to that of a biscarbamate model compound dipropyl *N,N'*-naphthalene-1,5-diylbiscarbamate (1,5-DNB) in Figure 6 (curve a, 9.1×10^{-5} M) reveals a red-shifted



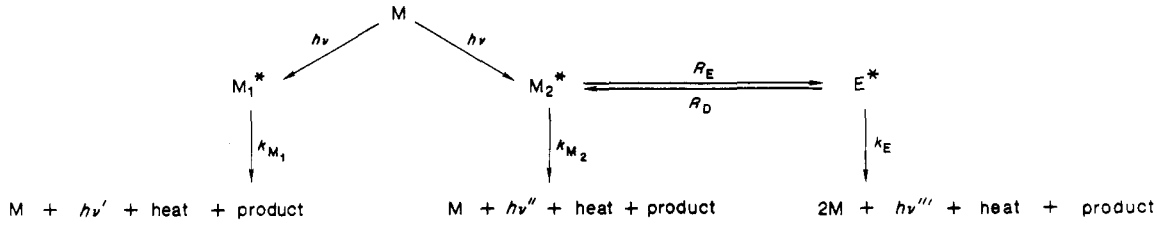
1,5-DNB

tail for NDI-650. The absorption spectrum of NDI-650 (Figure 7, curve a) recorded on a conventional UV spectrometer and the excitation spectrum (λ_{em} = 430 nm) for NDI-650 (curve b in Figure 7) indicate that the emitting and absorbing species are derived from the same basic type of ground-state chromophore. (Note that the small difference in the absorption and excitation spectrum in Figure 7 can be attributed to the fact that the absorption spectrum was recorded on a corrected dual-beam UV spectrometer, while the excitation spectrum was recorded on a single-beam fluorescence spectrometer uncorrected for wavelength response.) Additionally, it is probably safe to conclude that the excimer is formed intramolecularly at the low concentrations employed (0.01 g/dL; see ref 10 for discussion).

The fluorescence decay curve for a dilute solution of 1,5-DNB in 1,2-dichloroethane can be fit to a single-exponential decay curve with a lifetime of 1.81 ns (Table I). We recently reported a similar value of 1.84 ns for 1,5-DNB in dichloromethane.[10,11] In contrast to the concentrated PNC solution, the decay curve for a dilute solution (0.01 g/dL) of NDI-650 monitored at 330 nm in the monomer emission region cannot be fit to a double-exponential decay function. Rather, the NDI-650 decay curve (330 nm) is fit by a triple-exponential decay function with decay constants of 1.18, 2.04, and 15.5 ns. A value for the long-lived component of 17.9 ns was calculated by fitting a single-exponential function to the long-lived portion of the decay curve obtained at 480 nm in the excimer region. Identical behavior has been reported in a recent paper[10] for NDI-650 in dichloromethane and can be interpreted by the "isolated monomer" scheme first reported by Phillips et al.[19] and Holden et al.[20] to account for the excimer kinetics in naphthalene-containing polymers. This photophysical mechanism is reproduced in Scheme II, where k_{M_1} = nonradiative plus radiative rate constant for excited isolated naphthyl monomer M_1*, k_{M_2} = nonradiative plus radiative rate constant for excited-state excimer-forming naphthyl monomer M_2*, R_E = rate of excimer formation by two processes, prompt excimer formation involving excited naphthyl monomers that are in immediate proximity of a ground-state monomer and excimer formation between excited naphthyl monomers that are remote from ground-state monomers, R_D = total rate of excimer disassociation, k_E = nonradiative plus radiative rate constant for excimer E*, M = ground-state naphthyl monomer, M_1* = excited isolated naphthyl monomer, and M_2* = excited-state excimer-forming naphthyl monomer, which may be either remote from or hydrogen bonded to a ground-state monomer. Since this scheme is well documented, only a brief synopsis will be given here. Basically a ground-state monomer (M) upon excitation forms either (1) excited noniteractive monomers M_1* that decay to the ground state by a radiative/nonradiative decay process or (2) excited interactive monomers that combine with ground-state monomers to give the excimer E*. In the present case for NDI-650, the isolated monomer lifetime (τ_1) is 2.04 ns, in close agreement with the monomer lifetime of 1.81 ns for the 1,5-DNB model compound. Fluorescence decay curves were recorded and analyzed for 1,5-DNB and NDI-650 in several solvent systems to provide additional evidence for the mechanism in Scheme II. The results shown in Table II illustrate the strong agreement between the isolated monomer lifetime (τ_1) and the lifetime of the model compound 1,5-DNB (τ_{DNB}) in each solvent system employed. Such a correlation between τ_1 and τ_{DNB} in eight solvents lends support to the "isolated monomer" scheme for the NDI-650 polymer in dilute solution.

Since the excimer fluorescence of NDI-650 in dilute solution can be attributed to an intramolecular process, it should be responsive to solvent-induced changes in the conformational geometry of the polymer backbone. A preliminary paper[13] confirms this postulation for NDI-650 in dichloromethane, benzene, and xylene, where it was reported that the excimer (I_{ex}) to monomer (I_m) intensity ratio increases in the order I_{ex}/I_m (dichloromethane) < I_{ex}/I_m (benzene) < I_{ex}/I_m (xylene), parallel with the decrease in the solvent solubility parameter and the intrinsic viscosity of the solution. To extend these results, we recorded the ratio I_{ex}/I_m for each of these three solvents (Figure 8) as a function of the NDI-650 polymer concentration. For each solvent, there is a rapid rise in I_{ex}/I_m at a critical concentration (C_{crit}) that is directly dependent on the solvent system used. The value for C_{crit} increases with an increase in the solvent solubility parameter and solution intrinsic viscosity. Thus, in dichloromethane, which is a "good" solvent for NDI-650, a much higher polymer concentration (1.0 g/dL) must be employed before the occurrence of intermolecular interaction between naphthylcarbamate groups on different polymer chains. Conversely, in xylene and benzene (relatively poor solvents) intermolecular chain association takes place at much

Scheme II



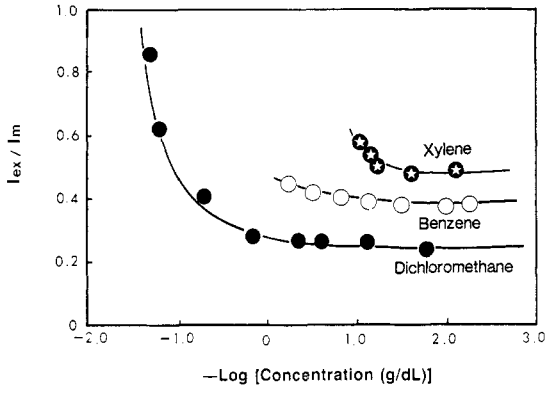


Figure 8. Ratio of excimer to monomer intensity as a function of NDI-650 concentration in various solvents.

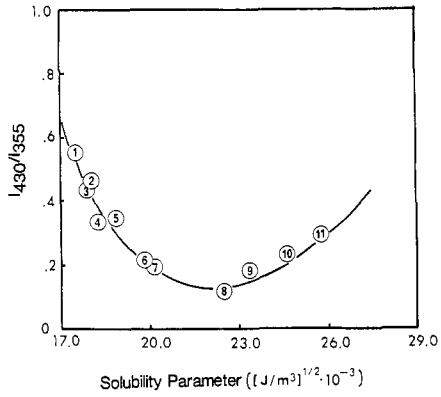


Figure 9. Ratio of excimer to monomer of NDI-650 as a function of solvent solubility parameter: 1, propylbenzene; 2, xylene; 3, ethylbenzene; 4, toluene; 5, benzene; 6, dichloromethane; 7, 1,2-dichloroethane; 8, 2,3-butanediol; 9, 1-butanol; 10, 1,4-butanediol; 11, 1,2-propanediol.

lower polymer concentrations. However, in both xylene and benzene the extent of intermolecular excimer formation, as indicated by the ultimate I_{ex}/I_m ratio, is quite low since precipitation occurs almost simultaneously with intermolecular contact. For NDI-650 in dichloromethane, even though high concentrations are required to reach the point for intermolecular association, the extent of intermolecular excimer formation is much larger as reflected by the I_{ex}/I_m ratio.

To expand the solvent studies, we recorded NDI-650 fluorescence spectra in a large number of pure solvents with varying solubility parameters. The resulting I_{ex}/I_m versus solvent solubility parameter plot is shown in Figure 9. The highest I_{ex}/I_m value is in propylbenzene, which has the lowest solubility parameter. The I_{ex}/I_m ratio reaches a minimum in 2,3-butanediol, which has a solubility parameter of 22.7×10^3 $(J/M^3)^{1/2}$. A minimum value of $(\sim 21 \pm 2) \times 10^3$ $(J/m^3)^{1/2}$ can be construed as the polymer solubility parameter. Plots of I_{ex}/I_m versus solvent solubility parameter have been previously used[21,22] to determine solubility parameters of 1-vinyl-

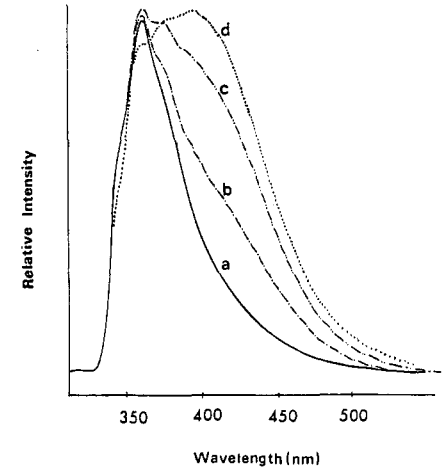


Figure 10. Steady-state fluorescence spectra (λ_{ex} = 300 nm) of NDI-650 in the mixed CH_2Cl_2/cyclohexane solvent systems (5×10^{-5} g/dL): curve a, 100% dichloromethane; curve b, cyclohexane/dichloromethane (70/30 vol %); curve c, cyclohexane/dichloromethane (80/20 vol %); curve d, cyclohexane/dichloromethane (90/10 vol %).

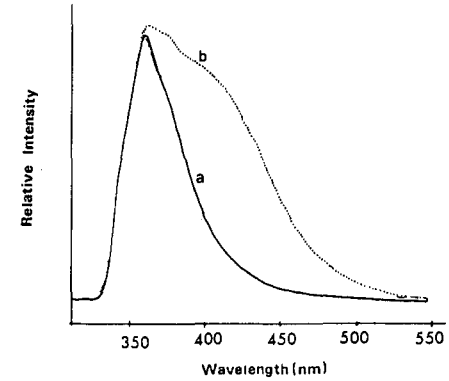


Figure 11. Steady-state fluorescence spectra (λ_{ex} = 300 nm) of NDI-650 in DMF (curve a) and DMF/H_2O (70/30 vol %; curve b) solvent systems (1.5×10^{-3} g/dL).

naphthalene-based polymers in host polymer matrices and solvent systems.

Results similar to those obtained for the pure solvent systems can also be derived from fluorescence spectra of NDI-650 in mixed or cosolvent systems. For this study, two dual solvent systems were selected, each comprised of a good solvent and a nonsolvent. The first dual solvent system consists of a good solvent (dichloromethane) and a nonpolar nonsolvent (cyclohexane). The second system consists of a good solvent (*N*,*N*-dimethylformamide) (DMF) and a polar nonsolvent (water). Fluorescence spectra of NDI-650 in selected dichloromethane/cyclohexane and DMF/H_2O solvents are shown in Figures 10 and 11. In each case as the percentage of nonsolvent (cyclohexane in Figure 10 and H_2O in Figure 11) is increased, the relative excimer fluorescence increases. (The spectra in Figures 10 and 11 are all normalized to maintain a constant intensity for the monomer emission.) A plot

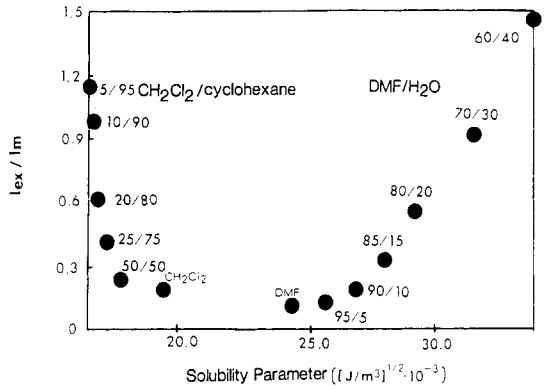


Figure 12. Ratio of excimer to monomer intensity in NDI-650 as a function of the solubility parameter of the mixed solvent systems.

(Figure 12) of I_{ex}/I_m versus solvent solubility parameters for a series of dichloromethane/cyclohexane and DMF/H_2O solvent systems results in a minimum value for I_{ex}/I_m of approximately $(22 \pm 2) \times 10^3$ $(J/m^3)^{1/2}$. This value agrees within experimental error with the minimum value obtained from Figure 9 for the pure solvent systems and confirms a polymer solubility parameter for NDI-650 of about $21-22 \times 10^3$ $(J/m^3)^{1/2}$.

Conclusions

This paper deals with excimers formed between naphthylcarbamate groups spaced along the backbone of a polyurethane prepared from 1,5-naphthalene diisocyanate and poly(tetramethylene ether glycol) (average MW = 650 g/mol). Model compounds have been extensively investigated to provide a basis for interpretation of the polymer systems. Specific findings reported in this paper are summarized as follows:

(1) Propyl *N*-(1-naphthyl)carbamate (PNC) exhibits strong excimer emission at higher concentrations. By contrast propyl *N*-methyl-*N*-(1-naphthyl)carbamate (PNMNC), which has a methyl group substituted on the central nitrogen atom of the carbamate group, has little excimer emission even at very high concentrations.

(2) The degree of excimer formation of PNC correlates directly with the extent of hydrogen bonding in the system.

(3) The NDI-650 polyurethane forms solvent-dependent intramolecular excimers between carbamate groups on the same polymer at low concentrations.

(4) The critical NDI-650 concentration required for intermolecular excimer formation is dependent on the "goodness" of the solvent medium, i.e., the critical concentration is 1–2 orders of magnitude larger for a good solvent such as dichloromethane.

(5) The photophysical results support an "isolated monomer" scheme for intramolecular excimer formation in the NDI-650 polyurethane.

(6) The variation of the excimer (I_{ex}) to monomer (I_m) intensity ratio with the solvent solubility parameter leads to an estimation of the polymer solubility parameter of $21-22 \times 10^3$ $(J/m^3)^{1/2}$.

This is one of the first detailed accounts of the photophysics of a polymer with interacting excimer forming chromophores in the backbone. It suggests that a wealth of critical information concerning polymer structure can be obtained by careful investigation of intramolecular excimer photophysics. Future work in this area will contrast the photophysics of polyurethanes and polyureas.

Acknowledgment. This work was sponsored by the Office of Naval Research.

Registry No. (NDI)(polytetramethylene ether glycol) (block copolymer), 84515-75-3; NDI, 3173-72-6; PNC, 25216-27-7; PNMNC, 114090-34-5; 1,5-DNB, 106139-38-2; 1,5-diaminonaphthalene, 2243-62-1; trichloromethyl chloroformate, 503-38-8; 1-naphthylisocyanate, 86-84-0; 1-propanol, 71-23-8.

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