theory if the correct band shape and width are chosen. In this paper, we have demonstrated that good agreement can be obtained between the calculated and observed circular dichroism, even under the application of exciton theory, if the absorption band shape function is utilized.

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Photophysics of a Naphthalene Diisocyanate Based Polyurethane

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ABSTRACT: A naphthalene diisocyanate based polyurethane in dilute solution is found to form intramolecular excimers between chromophores in the polymer backbone. The excimer kinetics is described by a triple exponential decay function. On the basis of comparison with model compounds, the photophysics of the polymer system is accounted for by the "isolated monomer" scheme. The relative intensity of the excimer emission depends on the solvent system employed and correlates directly with the intrinsic viscosity of the solution.

Excimers are excited-state complexes comprised of two equivalent molecules. They are formed by the interaction between an excited-state molecule (or chromophore) with a ground-state molecule (or chromophore) of the same species. Excimers are characterized by red-shifted emission spectra resulting from a stabilized excited state.

For the past two decades, excimers formed between adjacent species attached as pendant groups to polymer chains have received widespread attention. An excellent recent review of this subject is given in ref 1. The most common chromophores studied to date have been phenyl and naphthyl groups. In only a few cases have investigations been conducted on polymers in which the excimer-forming groups are located in the polymer backbone.[2-5] Incorporation of excimer-forming species in the main chain affords the opportunity to investigate the interaction of chromophores in polymer systems that are well separated as opposed to nearest neighbors in typical systems such as poly(vinylnaphthalene) or polystyrene. In this paper, we report the photophysical behavior of a 1,5-naphthalene diisocyanate based polyurethane with naphthalene chromophores periodically spaced in the polymer backbone. Investigation of the dependence of the excimer emission intensity on concentration indicates that excimer formation occurs at concentrations far below those expected for intermolecular interaction. It is demonstrated that even in quite dilute solutions excimer formation depends directly on the nature of the solvent system employed. By including lifetime results based on emission decay curves on the target polymer system, this paper constitutes one of the first detailed photophysical accounts of excimer formation involving main-chain chromophoric units.

Experimental Section

The 1,5-naphthalene diisocyanate (NDI) (mp 126–128 °C) was synthesized by reacting 1,5-diaminonaphthalene (Fluka) and trichloromethyl chloroformate (Fluka) in *p*-dioxane at the reflux temperature. The formed product was purified by sublimation. The propyl *N*-naphthalene-1-carbamate (mp 73 °C) and dipropyl *N*,*N*′-naphthalene-1,5-diylbiscarbamate (mp 203 °C) were prepared from 1-propanol and the corresponding isocyanates in ethyl

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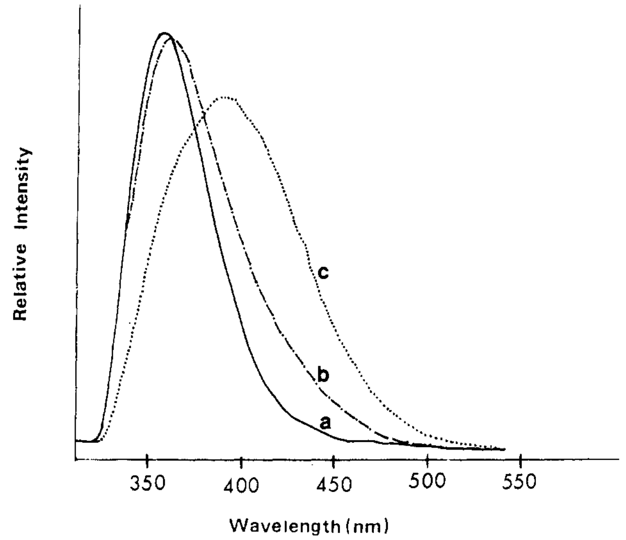


Figure 1. Steady-state fluorescence spectra (λ_{ex} = 300 nm) of PNC in dichloromethane at concentrations of 0.05 (curve a), 7.6 (curve b), and 83.8 g/dL (curve c).

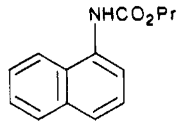
acetate and *p*-dioxane, respectively.

The NDI based polyurethane was obtained by reacting 1,5-naphthalene diisocyanate and poly(tetramethylene ether) glycol (mol wt = 650; Polysciences) with dibutyltin dilaurate and Dabco as catalysts in tetrachloroethane at 100 °C for 2.5 h. The polyurethane formed was dissolved in CH_2Cl_2 and purified by double precipitation in cyclohexane. The molecular weight was 51 000 by GPC.

Emission spectra were recorded on a Perkin-Elmer 650-10S fluorescence spectrophotometer. Fluorescence decay data were obtained on a single-photon-counting apparatus from Photochemical Research Associates (PRA). The data were analyzed by a software package obtained from PRA based on the iterative convolution method.

Results and Discussion

In order to provide a basis for interpretation of the results of the polymer system, data from a photophysical investigation of a small-molecule analogue of the naphthyl carbamate chromophore in the polymer backbone will be presented first. Figure 1 shows the steady-state fluorescence spectra of propyl *N*-naphthalene-1-carbamate (PNC) at various concentrations in dichloromethane. At the lowest concentration (0.01 g/dL, curve a), the fluorescence spectrum is characterized by a broad peak with maximum at 360 nm. The excitation spectrum obtained by monitoring the emission at 370 nm is identical with the absorption spectrum measured on a double-beam UV spectrophotometer. As the concentration of PNC is increased to 7.6 and 83.8 g/dL (curves b and c), a broadening of the fluorescence spectrum accompanied by a red shift is detected. The results in Figure 1 are indicative of excimer formation between excited and ground-state PNC molecules. In order to confirm the excimer formation, fluorescence decay curves were acquired for PNC in dichloromethane at various concentrations. In the most dilute solution (0.01 g/dL), PNC had a single-exponential decay with a lifetime of 3.59 ns (Table I) regardless of the monitoring wavelength (350 and 420 nm). In contrast, the fluorescence decay curve of a concentrated solution (33.5 g/dL) shows a marked dependence on the monitoring wavelength. Observing strictly the monomer emission at 330 nm, we obtained a double-exponential decay with a short-lived (0.3 ns) and a long-lived (15.3 ns) component (Table I). In addition, by monitoring at 480 nm in the excimer region and fitting the long-lived portion of the decay curve to a single-exponential decay function, we recorded a lifetime of 15.4 ns (Table I). A comparison of the short-lived component (0.3 ns) of the monomer decay in the concentrated solution with the lifetime (3.59 ns) in the dilute solution shows that the monomer emission is significantly quenched. Both the large decrease of the fluorescence lifetime of the monomer naphthyl carbamate and the presence of the long-lived component in the monomer emission region suggest that the monomer exists in a dynamic equilibrium with the excimer as represented by the classical Scheme I routinely used to describe excimer kinetics of small molecules in solution,[6] where k_M is the nonradiative plus radiative rate constant for excited PNC monomer M*, k_{DM} is the rate constant for excimer formation between M and M*, k_{MD} is the rate constant for dissociation of excimer E* into component species M and M*, k_E is the nonradiative plus radiative rate constant for excimer E*, M is ground-state PNC, M* is excited-state PNC, and E* is PNC excimer.



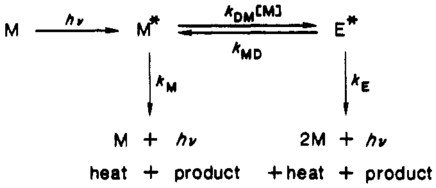
PNC

Table I
Fluorescence Lifetimes of Model Compounds and NDI-650 Polyurethane in Dichloromethane

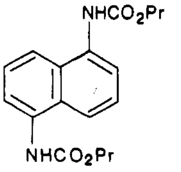
compd	concn, g/dL	τ_1,[a] ns	τ_2,[b] ns	τ_3,[c] ns
PNC	0.01	3.59		
PNC	33.5		0.33	15.3 (15.4)[d]
DNB	0.01	1.84		
NDI-650	0.01	2.04	1.20	19.2 (21.4)[d]

[a] τ_1 is unquenched monomer lifetime in each case. [b] τ_2 is quenched monomer lifetime in each case. [c] τ^3 is excimer lifetime in each case. [d] The value designates the lifetime of the long-lived component in the excimer region.

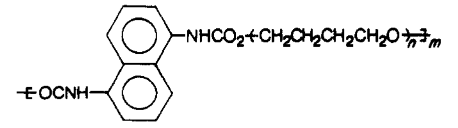
Scheme I



Having considered the monocarbamate model system, our investigation is extended to the fluorescence properties of the biscarbamate model compound, dipropyl *N*,*N*′-naphthalene-1,5-diylbiscarbamate (1,5-DNB), and the polyurethane [designated NDI-650 and prepared from 1,5-naphthalene diisocyanate and poly(tetramethylene ether) glycol (average mol wt = 650] in a dilute solution (0.01 g/dL). It should be noted that 1,5-DNB can only be studied in dilute solution due to solubility considerations.



1,5-DNB



NDI-650

Figure 2 shows the steady-state fluorescence spectra (λ_{ex} = 310 nm) of dilute solutions of 1,5-DNB (0.01 g/dL, curve a) and NDI-650 (0.01 g/dL, curve b). The two spectra are similar in shape; however, there is a distinct red-shifted tail above 400 nm in the NDI-650 spectrum (curve b). The

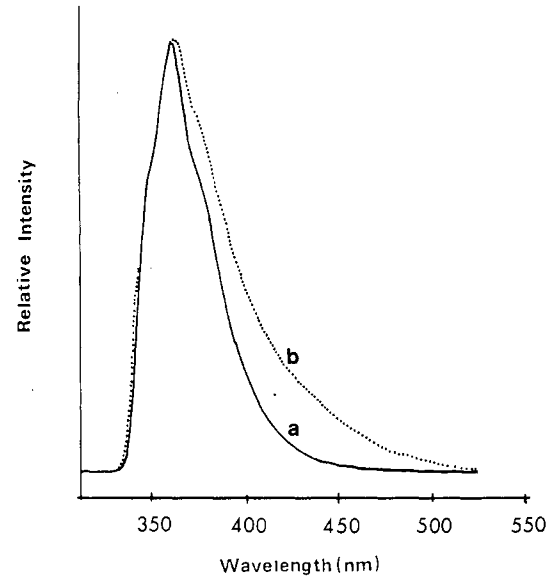


Figure 2. Steady-state fluorescence spectra (λ_{ex} = 310 nm) of 1,5-DNB (curve a, 0.01 g/dL) and NDI-650 (curve b, 0.01 g/dL) in dichloromethane.

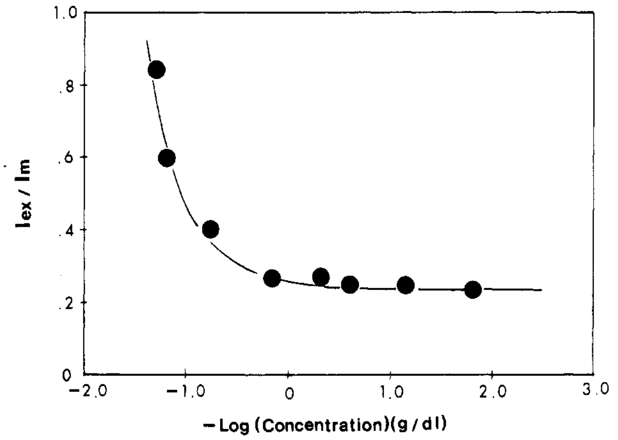


Figure 3. Ratio of excimer (I_{ex}) to monomer (I_m) fluorescence intensity (λ_{ex} = 310 nm) as a function of NDI-650 concentration in dichloromethane.

excitation spectrum of the NDI-650 fluorescence with the emission monochromator set at 430 nm is identical within the limits of our current instrumental setup to the absorption spectrum obtained independently. These observations suggest the formation of intramolecular excimers in the dilute NDI-650 solution. In order to clarify the mechanism of excimer formation, the ratio of excimer to monomer emission intensity was plotted as a function of polymer concentration (Figure 3) in dichloromethane. Up to a polymer concentration of about 1.0 g/dL, the ratio of excimer (I_{ex}) to monomer (I_m) emission intensity recorded at 430 and 355 nm, respectively, remains unchanged, presumably due to the fact that the excimer formation is strictly intramolecular in this concentration range. Above a polymer concentration of 1.0 g/dL, the polymer chains begin to interact to generate intermolecular excimers and I_{ex}/I_m increases. Since the fluorescence emission spectrum for NDI-650 in Figure 2 was obtained at a polymer concentration of almost 2 orders of magnitude (0.01 g/dL) less than the concentration (1.0 g/dL) required for intermolecular excimer formation, it is reasonable to conclude that the excimers responsible for the fluorescence of NDI-650 in Figure 2 are formed intramolecularly. Characterization of the intramolecular excimers formed in NDI-650 solutions requires careful analysis of appropriate decay curves.

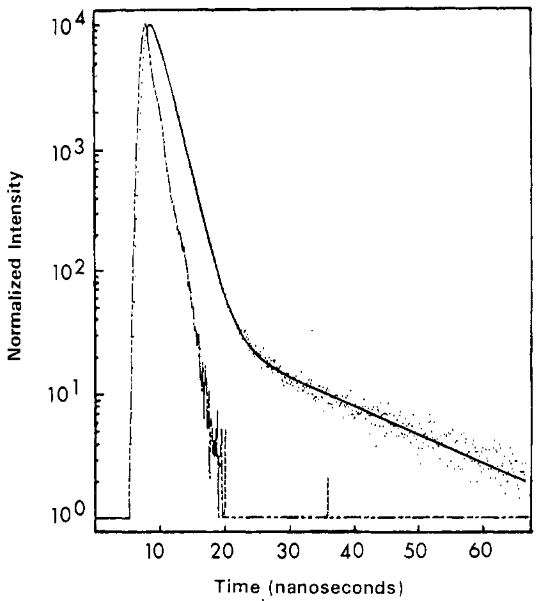
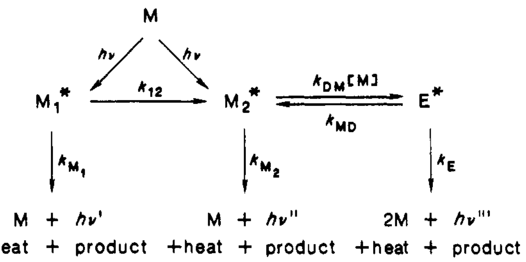


Figure 4. Fluorescence decay curve (λ_{ex} = 310 nm, λ_{em} = 330 nm) of NDI-650 (0.01 g/dL) in dichloromethane.

Scheme II



The decay profile of the monomer fluorescence (λ_{ex} = 310 nm; λ_{em} = 330 nm) of a dilute solution of NDI-650 (0.01 g/dL) in dichloromethane is given in Figure 4. Neither a single- nor a double-exponential decay function can account for the experimental decay curve; however, a triple-exponential decay function gave an excellent fit with lifetimes of 1.20, 2.04, and 19.2 ns (Table I). These results are consistent with the recent findings of Phillips et al.,[7,8] who reported that the fluorescence decay curves of polymers with excimer-forming naphthyl type groups pendant to the polymer chain were best fit to triple-exponential decay functions. The presence of the long-lived component (19.2 ns) in the monomer emission region indicates that the excimer is formed reversibly and exists in a dynamic equilibrium with an excimer-forming monomer species. A similar lifetime of 21.4 ns was also obtained from the decay curve recorded at 500 nm by fitting a single-exponential decay function to the long-lived portion of the decay curve.

The short-lived decay in Figure 4 consists of two components with lifetimes of 1.20 and 2.04 ns. The longer of these two lifetimes, 2.04 ns, corresponds to the lifetime of the model biscarbamate compound 1,5-DNB, which is 1.84 ns (Table I) in dichloromethane and probably results from an isolated monomer that does not participate directly in excimer formation. The quenched monomer emission that exists in equilibrium with the excimer can then be assigned to the 1.20-ns component. A similar argument, the isolated monomer concept, has recently been advanced by Phillips et al.[7,8] and Holden et al.[9] to account for the excimer kinetics in polymers containing pendant (side-chain) naphthalene moieties. Thus, Scheme II adequately accounts for the triple-exponential decay obtained for the NDI-650 polymer in dichloromethane. This, of course, differs from

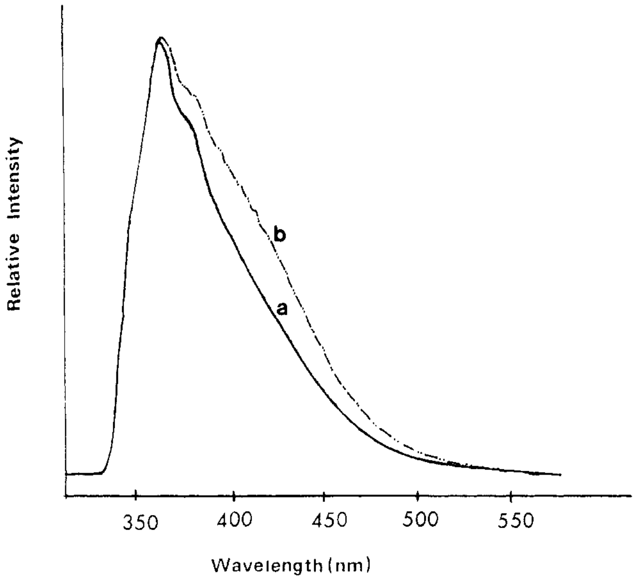


Figure 5. Steady-state fluorescence spectra (λ_{ex} = 310 nm) of NDI-650 (0.01 g/dL) in benzene (curve a) and xylene (curve b).

the mechanism presented in Scheme I used to account for the excimer of the PNC model system since Scheme II includes the isolated monomer M_1^*. In Scheme II k_{M_1} is the nonradiative plus radiative rate constant for excited isolated naphthyl monomer M_1^*, k_{M_2} is the nonradiative plus radiative rate constant for excited excimer-forming naphthyl monomer M_2^*, k_{DM} is the rate constant for excimer formation between M_2^* and M, k_{MD} is the rate constant for dissociation of excimer E^* into component species M_2^* and M, k_E is the nonradiative plus radiative rate constant for excimer E^*, k_{12} is the rate constant for formation of excited excimer forming naphthyl monomer M_2^* from the excited isolated naphthyl monomer M_1^*, M is the ground-state naphthyl monomer, M_1^* is the excited isolated naphthyl monomer, and M_2 is the excited excimer forming naphthyl monomer.

Note that M_1^* and M_2^* in the present paper are defined as the isolated excited-state naphthyl monomer and the excited excimer forming naphthyl monomer, respectively. This allows all of the lifetime data for the model compounds and polymer to be displayed in a concise manner in Table I for quick reference. In the case of the NDI-650 polyurethane, we favor the mechanism in Scheme II over an altenative second mechanism reported by Phillips[8] in which the isolated monomer M_1^* is allowed to form a nondissociative excimer directly. This is based on our observation that the 2.04-ns lifetime is essentially identical, within our error limits, with the lifetime of the model compound 1,5-DNB (1.84 ns). It is worthwhile noting that the isolated monomer concept was employed by Holden et al.[9] in order to explain the results for polymers with naphthyl chromophores separated by greater than three carbon atoms. In the present case, the naphthyl groups in NDI-650 certainly fit this criterion. They proposed, as we do for the NDI-650 polymers in solution, that the rate constant k_{12} for conversion of the excited isolated monomer M_1^* into the excited excimer forming monomer M_2^* is low compared to the rate constant k_{M_1} for deactivation of M_1^*.

Since the excimer-forming naphthyl carbamate sites are located in the backbone of the NDI-650 polyurethane, an excellent opportunity exists to study the effect of solvent on the polymer chain conformation in solution. Figure 5 shows the fluorescence spectra of NDI-650 in dilute solutions of both benzene and xylene (mixture of *o*- and *p*-xylene). In comparison with the results in Figure 2 (curve b) for NDI-650 in dichloromethane, it is obvious that the red-shifted excimer emission in benzene and xylene is significantly increased. The excimer to monomer intensity ratio (I_{ex}/I_m) recorded at 430 nm (I_{ex}) and 355 nm (I_m) in Table II for the three solvents under consideration shows an increase in the order I_{ex}/I_m (dichloromethane) < I_{ex}/I_m (benzene) < I_{ex}/I_m (xylene). Apparently, as the solvent goes from a good solvent like dichloromethane where the polymer is somewhat extended to a poor solvent such as benzene or xylene the polymer chain becomes compact and the chance for intramolecular excimer formation increases. These results are confirmed by the higher intrinsic viscosity, $[\eta]$, for NDI-650 (Table II) in dichloromethane compared to that of benzene and reflects the relatively contracted nature of the polymer in benzene. Unfortunately, xylene is such a poor solvent for NDI-650 that obtaining a reliable value for the intrinsic viscosity was not possible, although the intrinsic viscosity must certainly be less than that measured in dichloromethane or benzene.

Table II
I_{ex}/I_m Ratio and Intrinsic Viscosity of NDI-650 Polyurethane in Various Solvents

solvent	$I_{ex}{}^a/I_m{}^b$	intr visc,[c] dL/g
dichloromethane	0.21	0.30
benzene	0.35	0.22
xylene[d]	0.47	*e*

[a] The emission intensity at 430 nm. [b] The emission intensity at 355 nm. [c] Measured at 30 °C. [d] Mixture of *o*- and *p*-xylene. [e] Not available due to low solubility.

Conclusions

This paper presents one of the first detailed steady-state fluorescence and emission decay studies of intramolecularly formed excimers in which the excimer-forming sites comprise the polymer backbone. A triple-exponential fit to the fluorescence decay curve of the naphthalene diisocyanate based polyurethane in solution was interpreted by an isolated monomer model scheme. Recording the steady-state fluorescence spectra in dilute solutions with decreasing solvent power demonstrated that excimer formation can be directly correlated with the intrinsic viscosity of the solution. This suggests that excimer formation can be used as a sensitive probe of polyurethane conformation in solution and may be employed to provide valuable information on solubility characteristics.

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Registry No. PNC, 25216-27-7; 1,5-DNB, 106139-38-2; NDI-650, 66218-10-8.

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