FLUORESCENCE OF POLYUREAS BASED ON 1,5-NAPHTHALENE DIISOCYANATE

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**Abstract:**

Polyureas based on 1,5-naphthalene diisocyanate (NDI) form intramolecular excimers in dilute solution. The excimer formation is enhanced in benzene which is a relatively poor solvent for NDI based polyureas. Photolysis in dimethyl formamide solution results in a decrease in the overall intensity and a shift to the red, due most likely to photo-Fries product formation. Excimer fluorescence in the polyurea films is directly dependent on the nature of the diamine reacted with NDI. The excimer fluorescence is particularly strong for the polyurea films based on NCI and 1,12-diaminododecane.
FLUORESCENCE OF POLYUREAS

BASED ON

1,5-NAPHTHALENE DIISOCYANATE

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Introduction

Fluorescence spectroscopy has been used in a wide diversity of applications in polymer science ranging from critical evaluation of polymer blends to detection of chromophoric groups generated during the photodegradation of polymers (1).

One of the photophysical properties of polymer systems of particular importance deals with the phenomenon of excimer formation (2). Excimers are excited state complexes consisting of two identical species, one of which is excited before interacting with a ground state molecule. As a result of the increased stability of excimers, they are easily identified due to a characteristic red-shifted emission which is broad and structureless. The unexpected high degree of excimer formation in dilute solutions of 1.5-naphthalene diisocyanate and aromatic bicarbamate chromophores incorporated into the polymer backbone at regular intervals, such polyurethanes readily form both intramolecular (dilute solutions) and intermolecular (concentrated solutions and films) excimers. The unexpected high degree of excimer formation in dilute solutions of 1.5-naphthalene diisocyanate based polyurethanes in poor solvents has been attributed to a hydrogen bonding phenomenon.

Polymers and polyureas/urethanes continue to emerge as viable polymers for use in both the plastics and coatings industry. This paper describes initial results of the photophysics of polyureas synthesized from 1,5-naphthalene diisocyanate and either a polyalkylene diamine (Jeffamine® ED-2001, Texaco Chemical Co.) or a long-chain aliphatic diamine.

Experimental

1,5-naphthalene diisocyanate (NDI) was synthesized as previously described (3). The bispropyl urea of NDI (designated compound 1) was prepared by reaction of 1,5-naphthalene diisocyanate and 1,3-propylene glycol in dry p-dioxane. Spectroscopic grade dimethyl formamide (DMF-Burdick and Jackson) and benzene (Burdick and Jackson) were used as received. The polyureas were synthesized by reacting NDI with either Jeffamine ED-2001 (NDIPU-2000) from Texaco Chemical Co. or 1,12-diaminododecane (NDIPU-C12) in dry p-dioxane at 24°C for 3 hours. The polyurea NDIPU-2000 was then purified by dissolution in dichloromethane followed by precipitation in cyclohexane. This procedure was repeated 3 times. The NDIPU-C12 was dissolved in trifluoroacetic acid and then precipitated in distilled water. Fluorescence spectra were recorded on a Perkin-Elmer 650-105 fluorescence spectrometer. Peak height maxima were normalized to a constant relative intensity by a computer digitization routine to allow easy visual comparison of fluorescence emission spectra.

Results and Discussion

In order to provide a reference frame for analysis of the fluorescence of the naphthalene diisocyanate based polyurea, a simple model compound (1) was prepared.

The fluorescence spectrum (I_x = 290 nm) of a 3.0 × 10^{-4} M solution of compound 1 in nitrogen-saturated DMF is shown in Figure 1. The emission spectrum of 1 is similar to that of the emission spectrum of the bispropyl urea based on NDI (3) previously reported. Due to lack of solubility in solvents such as benzene or dichloromethane, the fluorescence spectrum of 1 in DMF must suffice for the present study.

Figure 2 shows the fluorescence spectra of the polyurea (designated NDIPU-2000) based on 1,5-naphthalene diisocyanate and Jeffamine® ED-2001. In DMF (curve a, Figure 2) which is a good solvent for polyureas, the fluorescence spectrum of NDIPU-2000 is essentially identical to that of the model 1 in DMF (Figure 1). However, the fluorescence spectrum of NDIPU-2000 in benzene (curve b, Figure 2) reveals a red-shifted emission for the polyurea. This distinctive red-shifted emission is most likely due to an intramolecular excimer emission between naphthyl urea groups in the polymer backbone. In view of the dilute solution (4.8 × 10^{-5} g/ml) employed for the fluorescence measurement in benzene, intramolecular excimer formation is expected to be very small. Similar results have been reported for naphthalene diisocyanate based polyurethanes in dilute solution where intramolecular excimer formation was significantly enhanced in poor solvents (4-10).

Interestingly, fluorescence of the NDIPU-C12 film (cast from a dilute solution of DMF) is red-shifted (curve a, Figure 3), but not to the extent one might expect in view of the significant effect of benzene (a poor solvent) on the fluorescence of NDIPU-2000 in solution. In addition, the excimer emission in Figure 3 (curve a) for the NDIPU-2000 polyurea is significantly lower than that of a similar polyurethane based on NDI and polytetramethylene oxide (10). In order to see if the degree of excimer formation in the film could be enhanced, a polyurea (NDIPU-C12) based on 1,5-naphthalene diisocyanate and 1,12-diaminododecane was synthesized. The fluorescence spectrum (curve b, Figure 3) of a film of NDIPU-C12 in solution is characterized by a high degree of excimer formation with little or no emission in the monomer region. Apparently, the increase in density of naphthyl urea groups in the backbone with the NDIPU-C12 is accompanied by a substantial increase in the degree of excimer formation.

Before presenting results of fluorescence analysis of the polyureas NDIPU-2000 polyureas, attention should be given to the fluorescence decay parameters of the two polyureas in the present study. Discussion of the fluorescence lifetime results should be prefaced by saying that analysis of the decay curves, both in the solution and film are quite difficult to interpret with the present techniques. In a long-time measurement of the degree of excimer emission, the decay curve for...
NDIPU-2000 (\(A_{ex} = 290\) nm) in the monomer region (\(A_{em} = 360\) nm) corresponds to at least a triple exponential decay function with the longest-lived component being about 11.1 ns (4.8 \(X\) \(10^{-10}\) M solution). This is comparable to a value of 13.7 ns obtained for model compounds in the same solvent. The decay curve was recorded at 420 nm in the excimer emission region and indicates some type of reversible excimer formation. Due to complications experienced to date in obtaining satisfactory fits to the decay curves at 360 nm and 455 nm, the exact mechanism for excimer formation cannot be conclusively identified. This is in marked contrast to similar polyurethanes based on NDI. In such polyurethanes, the decay profiles can clearly be interpreted in view of an “isolated monomer” scheme for excimer formation (8-10).

Figure 4 shows fluorescence spectra (\(A_{ex} = 290\) nm) of the NDIPU-2000 polymer in DMF (2.8 \(X\) \(10^{-10}\) g/ml) before (curve a) and after (curve b) photolysis. (Figure 4) is characterized by a red-shifted emission well above 400 nm which can be resolved by a curve fitting routine to give a spectrum (not shown) of the polymer on photolysis with a maximum at 420 nm. The lifetime of this red-shifted emission is around 14 ns. This is only a preliminary lifetime since the decay curve is complicated by, among other factors, excimer formation. This lifetime is, however, significantly longer than that of simple naphthyl ureas which are less than 6 ns. Similar results were obtained for photolysis of NDIPU-2000 films, although spectral resolution of the red-shifted emission was more complicated.

What can this new red-shifted emission be attributed to? The best candidate is an ortho photo-Fries product, which by analogy with aromatic polyureas is probably formed quite rapidly and efficiently (2). No doubt, as in the case of aromatic esters with an ortho substituted amino group, the emission would be substantially red-shifted to well above 400 nm, which it is. Additionally, it has been found (11) that the lifetime of ortho amino benzoates (~10 ns) are much longer than the phenyl carbamates (~5 ns depending on structure) from whence they are produced by a photo-Fries rearrangement process. The crude lifetime results obtained for the photolyzed NDIPU-2000-polyurea solution are certainly in harmony with these observations. A more exact analysis of the product(s) produced on photolysis will follow in the near future.

Conclusions

Several preliminary observations can be made. The NDI based polyureas are characterized by intramolecular excimer formation in dilute solution which is enhanced in benzene due to increased intramolecular contact. Photodegradation of the polyureas results in a new red-shifted emission extending well above 400 nm. This new emission is probably due, at least in part, to an ortho photo-Fries rearrangement product.

We are currently investigating the influence of hydrogen bonding (between the carbonyl in the urea linkage and the -NH group on nearby ureas) on excimer formation in the naphthenaline containing polyureas. Such an effect might be expected since we have previously demonstrated that hydrogen bonding is a key factor in facilitating excimer formation in similar polyurethanes (9,10). In addition, we are extending our photophysical and photochemical studies to include polyureas and polyurea/urethanes derived from conventional aromatic disiocyanates.

Acknowledgment

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References


Figures

Fig. 1. Steady state fluorescence spectrum of model compound I 
(3.0 \(X\) \(10^{-8}\) M) in DMF 
(\(A_{ex} = 290\) nm).

Fig. 2. Steady state fluorescence spectra 
(\(A_{ex} = 290\) nm) of NDIPU-2000 polyurea in DMF (--- ; 8.7 \(X\) \(10^{-7}\) g/ml) and benzene (--.-- ; 4.8 \(X\) \(10^{-7}\) g/ml) solutions.

Fig. 3. Steady state fluorescence spectra 
(\(A_{ex} = 290\) nm) of polyurea films 
(--- ; NDIPU-2000; ------ ; NDI C12).

Fig. 4. Steady State fluorescence spectra 
(\(A_{ex} = 290\) nm) of NDIPU-2000 polyurea in DMF solution (2.8 \(X\) \(10^{-10}\) g/ml). Before photolysis (---) and after photolysis (-- --).
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