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HATTIESBURG DEPT OF POLYMER SCIENCE C E HOVLE ET AL

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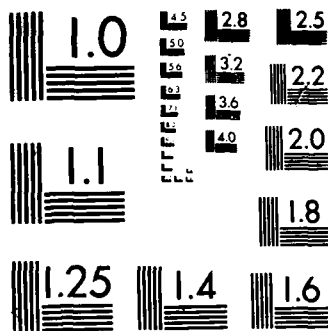
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FLUORESCENCE OF POLYUREAS BASED ON 1,5-NAPHTHALENE DIISOCYANATE

by

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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 (1) to detection of chromophoric groups generated during the photodegradation of polymers (2).

One of the photophysical properties of polymer systems of particular importance deals with the phenomenon of excimer formation (3). 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.

In the vast majority of polymers in which excimers have been reported, the interactive chromophores have been pendant to the polymer backbone (3). However, a few noted examples of excimer formation between groups incorporated into the polymer backbone have been reported (4-7). In a series of recent papers (8-10) we describe the photophysical properties of polyurethanes with aromatic biscarbamate 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.

Polyureas and polyurea/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 polyoxyalkylenediamine (Jeffamine® ED-2001; Texaco Chemical Co.) or a long-chain aliphatic diamine.

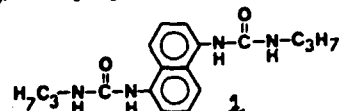
Experimental

1,5-naphthalene diisocyanate (NDI) was synthesized as described previously (10). The bispropyl urea of NDI (designated compound 1) was prepared by reaction of 1,5-naphthalene diisocyanate and 1-amino propane 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.

Fluorescence decay curves were obtained on a single-photon counting instrument from Photochemical Research Associates (PRA). Photolysis was conducted using a Spectroline ultraviolet lamp system (maximum output 302 nm).

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.

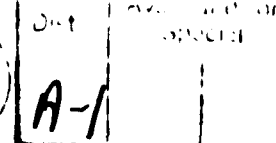


The fluorescence spectrum ($\lambda_{ex} = 290$ nm) of a 3.0×10^{-5} M solution of compound 1 in nitrogen-saturated DMF is shown in Figure 1. The emission spectrum of 1 is similar to that of the emission spectrum of the bispropyl carbamate of NDI (8-10) previously reported. Due to lack of solubility 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, intermolecular 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 (8-10).

Interestingly, fluorescence of the NDIPU-2000 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 (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 less 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 ($\lambda_{ex} = 290$ nm) 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 along the polymer backbone with the NDIPU-C12 is accompanied by a substantial increase in the degree of excimer formation.

Before presenting results of a fluorescence analysis of the photodegradation of the NDIPU-2000 polyurea, 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. In benzene, which shows a substantial degree of excimer emission, the decay curve for



NDIPU-2000 ($\lambda_{ex} = 290$ nm) in the monomer region ($\lambda_{em} = 360$ nm) corresponds to at least a triple exponential decay function with the long-lived component being about 11.1 ns (4.8×10^{-5} M solution). This is comparable to a value of 13.7 ns for the long-lived component obtained when the decay curve was recorded at 435 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 435 nm, the exact mechanism for excimer formation cannot be conclusively identified. This is in marked contrast to similar polyurethanes based on NDI. In such polymers, the decay profiles can clearly be interpreted in view of an "isolated monomer" scheme for excimer formation (8-10).

Figure 4 shows fluorescence spectra ($\lambda_{ex} = 290$ nm) of the NDIPU-2000 polymer in DMF (2.8×10^{-3} g/ml) before (curve a) and after (curve b) photolysis ($\lambda_{ex} = 302$ nm, 45 minutes) with a Spectroline ultraviolet lamp system. The spectrum after photolysis (curve a, 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 product(s) generated on photolysis with a maximum at 420 nm. The lifetime of this red-shifted emission is around 14 ns. This is only a preliminary estimate since the decay curves are 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 polyurethanes 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 those 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 polyurea 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 naphthalene 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 diisocyanates.

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Figures

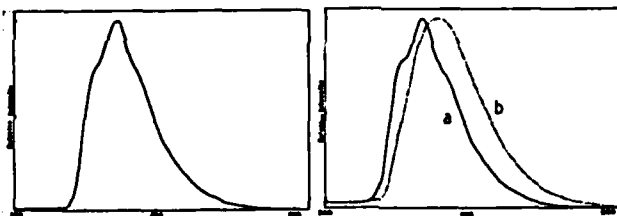


Fig. 1. Steady state fluorescence spectrum of model compound 1 (3.0×10^{-5} M) in DMF ($\lambda_{ex} = 290$ nm).

Fig. 2. Steady state fluorescence spectra ($\lambda_{ex} = 290$ nm) of NDIPU-2000 polyurea in DMF (—; 5.7×10^{-5} g/ml) and benzene (---; 4.8×10^{-5} g/ml) solutions.

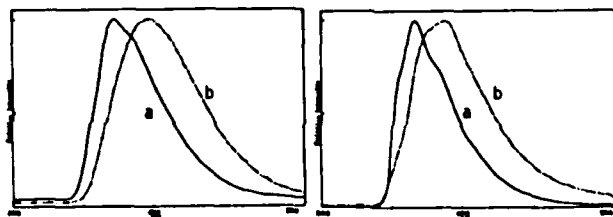


Fig. 3. Steady state fluorescence spectra ($\lambda_{ex} = 290$ nm) of polyurea films (—, NDIPU-2000; ---, NDI C12).

Fig. 4. Steady State fluorescence spectra ($\lambda_{ex} = 290$ nm) of NDIPU-2000 polyurea in DMF solution (2.8×10^{-3} g/ml). Before photolysis (—) and after photolysis (--- X 10).

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