Macromolecules **2003,** *36,* 9775−9783

Photocleavage of Pyridyl-Based Aromatic Polyureas

Jeremiah Mwaura,[†] Baocheng Yang,[†] Rongfu Li, Martha Morton, and Fotios Papadimitrakopoulos*

Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269

Received January 18, 2003; Revised Manuscript Received September 15, 2003

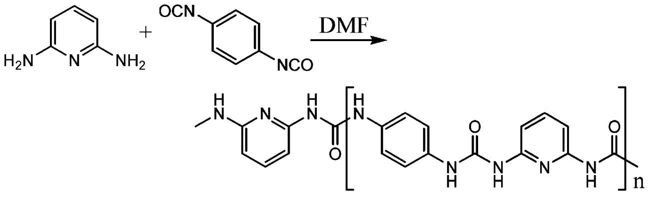
ABSTRACT: The photophysical properties of a metal chelating pyridyl-based aromatic ureas and poly(1,4-phenylene-2,6-pyridylurea) were investigated. In their solution state and upon exposure to 365 nm UV radiation, these low and high molecular weight compounds were found to cleave the urea linkage nearly quantitatively, generating the corresponding amine-terminated subunits and CO_2. Through a series of model compounds along with nuclear magnetic resonance (NMR), UV/vis absorption, and fluorescence spectroscopy characterization, the photocleavage process was delineated as a function of UV dose, O_2, and water. The presence of water was found crucial to this photocleavage process with O_2 playing a role only in subsequent oxidation of resulting amine functionalities. The experimental results support a light-assisted hydrolysis of the urea bond as the most plausible photocleavage mechanism. The photocleavage of such pyridyl-based ureas can potentially find usages in light-assisted base generation and/or for releasing metal cations.

Introduction

Much attention has been recently focused on a variety of conjugated polymers with good stability and high electroluminescence efficiency.[1−5] Besides improving charge transport and quantum efficiency, prolonging device lifetime presents also a major challenge. Unlike inorganic light-emitting devices, which are very stable under photoirradiation, polymers often tend to degrade when exposed to long periods of absorptive radiation in the presence of species such as O_2, CO_2, and moisture.[6−9] To improve upon the stability of organic light-emitting devices, a good molecular level understanding of the degradation processes is of great importance.[10,11] A variety of spectroscopic methods have been used to study such photodegradation processes with photooxidation and photorearrangements dominating these light-assisted degradation mechanisms.[12−14] Certain photodegradation mechanisms of such polymers, although undesirable for device configurations, can find alternate usage in the field of micro/nanolithography, where light and/or ionizing radiation patterning[15−17] along with photoacid[18,19] and photobase[19,20] generation are utilized in polymer resist development.

In conjunction with conjugated polymers, various metal chelates have been utilized as charge injectors and emitters in the field of organic light-emitting diodes (OLEDs).[21−23] 8-Hydroxyquinoline aluminum (Alq_3) has been the most widely used metal chelate in OLEDs, with demonstrated bright green emission and good electron transport properties.[24,25] Recently, metal chelates based on platinum and iridium complexes have been successfully employed in electrophosphorescent applications.[26,27] One drawback with these materials (polymeric and small molecule chelates) is that they have broad emission and hence difficult to obtain pure colors in EL devices. This has led to an increase in research on organo-lanthanide chelates due to their characteristic sharp emission bands.[28−30] Typically, thin films incorporating these chelates have been realized via vacuum evaporation and spin-coating techniques.

Scheme 1. Synthesis of Poly(1,4-phenylene-2,6-pyridylurea) I



(I)

Recently our group has reported on a novel layer-by-layer film growth methodology where highly fluorescent polyurethane−urea/lanthanide metal chelates (based on 2,6-diaminopyridine) thin films were assembled.[31] A related fully conjugated lanthanide chelating polymer (poly(1,4-phenylene-2,6-pyridylurea)) (**I**) was synthesized to improve charge mobility for OLED devices (see Scheme 1).[32] Surprisingly enough, this polymer was found to undergo some interesting photophysical changes upon exposure to 365 nm UV irradiation. In this paper, we report on a detailed spectroscopic characterization of these photophysical processes, where through a series of model urea compounds the photocleavage mechanism is elucidated. Although polymer **I** might prove unsuitable for OLED applications, photocleavage of 2,6-diaminopyridine-based ureas and their respective metal chelates can potentially find usages in light-assisted base generation and/or for releasing metal cations, respectively.

Experimental Section

General Methods. Solvents and starting materials were acquired from J.T. Baker and Aldrich, respectively, and used without further purification unless otherwise stated.

UV absorptions of dilute solutions (10^{-4} M) of **I** and model compounds were measured using a Perkin-Elmer Lambda 6 spectrometer with 1 cm quartz cells. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS-50 spectropho-

---

[†] Authors made equal contributions.

* Corresponding author. Tel 860-486-3447; Fax 860-486-4745; e-mail papadim@mail.ims.uconn.edu.

10.1021/ma034058k CCC: $25.00

tometer. UV irradiation was performed using a high-pressure long wave mercury UV lamp (UVP model B 100 AP) (21 700 μW/cm^2), with emission envelope from 363 to 370 nm, peaking at 365 nm (filtered UV light). The entire amount of the UV irradiation of the lamp was directed into a highly reflective enclosure that contained the sample, which was located at the center, about 5 cm from the lamp. No provisions were made to prevent the samples from heating, and temperature increased no more than 80 °C after prolonged irradiation. ^{1}H, ^{13}C, 1D, and 2D NMR spectra were acquired using a Bruker DRX 400 instrument. Both deuterated *d*-DMF and *d*-DMSO solvents (Aldrich) (with water concentration on the order of 0.037% as measured for DMSO with GC-MS) were used to make solutions ($\sim$0.05 M) of **I** and other model compounds for the NMR measurements. The solutions were UV-irradiated with 365 nm filtered light (with UV light passing through the glass NMR tubes) for 10, 20, 30, and 60 min durations followed by recording both ^{1}H and ^{13}C NMR spectra. Samples of terbium/polyurea **I** chelate were prepared by adding $TbCl_3$ to dilute solutions ($\sim 10^{-4}$ M, based on polymer repeat unit) of **I** in DMF to result in chelate solutions with a 1:2 (Tb^{3+}/polymer) molar ratio (based on polymer **I** repeat). UV irradiation was performed, as described above for 10, 30, and 60 min, and PL spectra were recorded for each sample. A variety of methods like casting (slow drying), dip-coating, and spin-coating were used to prepare solid samples of the polymer **I**. Following UV irradiation, the films were redissolved in *d*-DMSO, and their NMR spectra were collected.

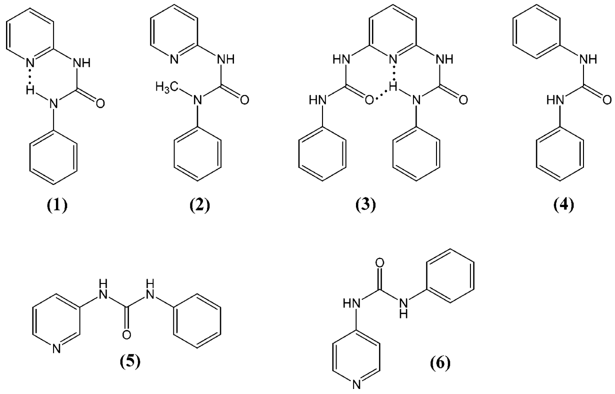
GC-MS Characterization of the UV Photocleaved Products of Compound 1. 6 mg of **1** was dissolved in 2 mL of DMSO, sealed in a screw-cap glass vial, and UV-irradiated for given amount of times as described above. Following irradiation, sample aliquots were quickly withdrawn and injected into a Hewlett-Packard 5890 series II gas chromatograph equipped with a Hewlett-Packard 5971A mass selective detector. Samples were analyzed immediately after irradiation as well as after they were allowed to stand unsealed overnight. Typical GC-MS experimental conditions involve the following: injection port temperature, 225 °C; detector port temperature, 280 °C; initial time, 2 min; injector ON time, 0.5 min; injector OFF time, 0.01 min; oven temperature ramp, 35−325 °C at 15 °C/min. Control experiments involve the GC-MS analysis of the solvent (DMSO) as well as dilute solutions of phenyl isocyanate and 2-aminopyridine under similar operating conditions.

Synthesis of I. 2,6-Diaminopyridine and 1,4-phenylene diisocyanate were sublimed before use. 10 mmol of each was dissolved in 10 mL of freshly distilled DMF, and the solutions were bubbled with N_2 for 30 min. Then the 2,6-aminopyridine solution was cannulated into the diisocyanate solution, and the mixture was stirred for 2 h while continuing bubbling N_2. The turbid suspension was then poured into 400 mL of methanol to yield a white precipitate. This was then filtered, washed several times with methanol, and vacuum-dried overnight. The polymer molecular weight of this product was found to be 18.7 kDa (with a polydispersity index of 1.15) as determined by size exclusion chromatography in DMF using polystyrene standards.

General Procedure for the Synthesis of Model Urea Compounds 1, 3, 4, 5, and 6 (shown in Scheme 2). A stirred solution of the corresponding amine (10 mmol) in dichloromethane (DCM) was cooled to 0 °C. Phenyl isocyanate (10 mmol) in DCM was added dropwise over 20 min. The solution was then allowed to warm to room temperature and stirred for 1−3 h. Subsequently, the solvent was then evaporated in vacuo, and the residue was recrystallized from ethanol. All compounds are known, and the analytical data were in accordance with literature values.[33]

Synthesis of 1-Methyl-1-phenyl-3-(2-aminopyridyl)-urea (2). 940 mg (10 mmol) of 2-aminopyridine was dissolved by warming in 2 mL of pyridine. 1.7 g (10 mmol) of *N*-methyl-*N*-phenylcarbamoyl chloride was dissolved in 3 mL of pyridine, but very soon crystals of the pyridine−acyl halide complex began to separate, and in a few minutes the mixture had set to a solid mass of crystals. The solid was reduced to powder, and 2 mL of dioxane was added; the suspension was then mixed with the 2-aminopyridine solution. The resulting mixture was warmed over a steam bath until a clear solution was obtained and then set aside for 24 h. The solvent was removed in vacuo, 20 mL of water added, and the suspension stirred for 30 min. Then the aqueous solution was extracted with 3 × 10 mL of DCM. The organic phase was washed with brine and dried over Na_2SO_4, and the solvent was removed in vacuo. The crude product was purified by preparative TLC using 5% MeOH in DCM eluting solvent. The final yield was 40%. All analytical data of compound **2** are in accordance with literature values.[34]

Scheme 2. Low Molecular Weight Model Urea Compounds Employed To Assist with NMR Peak Assignments and Elucidate the Photocleavage Process of I



Results and Discussion

The polyurea **I** used in this study was synthesized by a simple condensation of 2,6-diaminopyridine and 1,4-phenylene isocyanate as shown in Scheme 1. To investigate the photochemistry of polymer **I**, solutions (10^{-4} M) in DMF were irradiated (365 nm UV) for increasing durations while measuring their UV−vis absorbance and the corresponding photoluminescence (PL) spectra as illustrated in Figure 1. As shown in Figure 1A, the absorbance peak at 325 nm of **I** decreases during the course of irradiation, while a broad absorption peaking at 460 nm emerges (see inset). The decrease in absorption intensity of **I** and the corresponding blue-shifting (from 325 to 315 nm after 60 min of irradiation) is reminiscent of reduced conjugation that might be associated with a possible breakdown of the polymer chain to smaller molecules. As it will become apparent later on in the discussion, the progressive increase of the broad peak at 450 nm is associated with photooxidization of the polymer's photocleaved byproducts.

The photoluminescence behavior of a dilute DMF solution of **I** shows a more complex behavior as shown in Figure 1B. The PL intensity first increases, and its peak maximum shifts from 360 to 385 nm within 30 min of irradiation. Such behavior can be explained by the continuous formation of chemical species that exhibit red-shifted emission and higher photoluminescent quantum efficiencies compared to **I**. Irradiation of the polymer beyond 30 min results in a decrease of PL intensity. This PL intensity decrease along with the corresponding blue shift of the peak maximum from 385 to 380 nm might originate from photooxidation of the photocleaved byproducts of **I**, as noted before in UV−vis spectra of Figure 1A.

The photocleavage mechanism was studied through the use of several model urea compounds **1**−**6**. These compounds exhibit similar UV absorption and PL

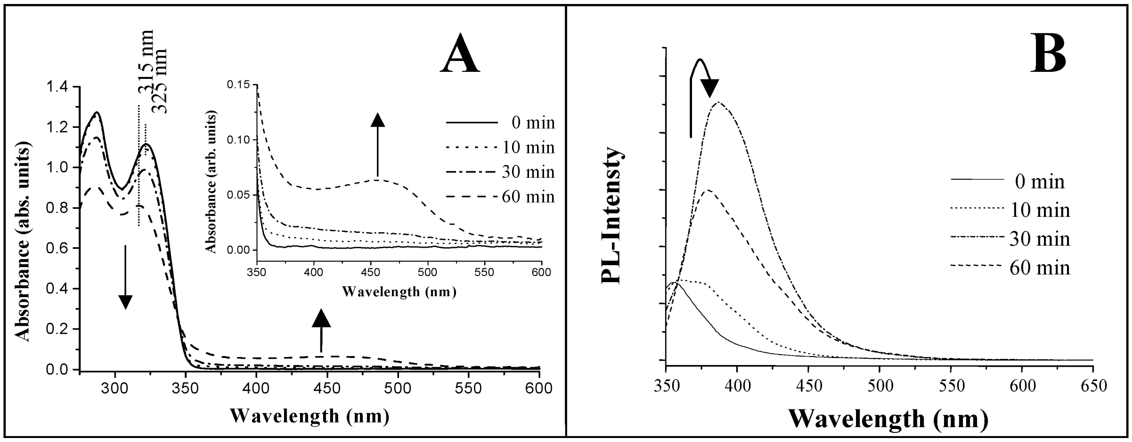


Figure 1. Solution UV−vis (A) and photoluminescence (PL) (B) spectra of **I** (10^{-4} M solutions in DMF) upon exposure to 365 nm UV irradiation for varying durations. The PL spectra were obtained from 340 nm excitation.

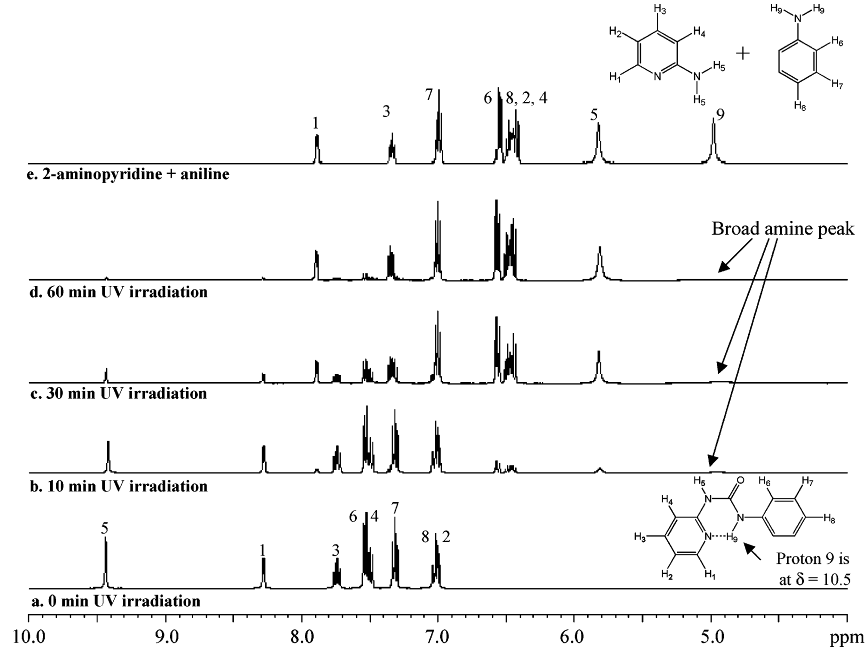


Figure 2. ^{1}H NMR of model compound **1** (2-aminopyridylphenyl urea, 0.05 M in *d*-DMSO) before (a) and after (b−d) UV irradiation for the indicated duration. The top spectrum (e) is the ^{1}H NMR of an equimolar mixture of 2-aminopyridine and aniline.

characteristics as polymer **I**. Figures 2 and 3 illustrate the ^{1}H and ^{13}C NMR spectra of model compound **1,** respectively, before and after 10, 30, and 60 min of UV irradiation.

As seen in Figure 2, the photocleavage of **I** is evident from the dramatic change in the chemical shifts upon UV exposure. After 10 min irradiation, several peaks at $\delta = 5.8$, 6.4, 6.5, and 7.9 ppm and a broad peak at 5.0 ppm (indicated with arrows) develop which, with the exception of the 5.0 ppm peak, all increase in intensity upon longer UV exposure.

In addition, from the ^{13}C NMR spectra (Figure 3), we observed the disappearance of the peak at 153 ppm (carbonyl carbon) after an hour of UV irradiation, implying the complete elimination of the carbonyl group during the photocleavage process. The upfield shift of aromatic protons on both pyridyl ring and phenyl ring suggests a change in electron density of aromatic rings. After carefully studying these NMR spectra, the possibility of urea bond breaking up to form two amines, i.e., aniline and pyridine, became evident. This was confirmed by comparing the proton and carbon NMR spectra of pure amines (aniline and pyridine), shown as the top spectrum in Figure 2 and Figure 3, respectively, to the spectra obtained from UV-irradiated **1** model compound. The closely matched spectrum of the 60 min irradiated **1** to the corresponding amines indicates the near complete breakdown of the urea linkage. Here it is noteworthy to mention that the proton peak at 5.0 ppm for the irradiated model compound **1** is very broad compared to the sharp peak of aniline proton shown in Figure 2. This could be due to the different water content in the NMR solvent, consequentially leading to a different environment, causing a variance in exchange rate between the amino proton and water in the solvent. From the ^{1}H NMR spectra (Figure 2), we can also see that the photocleavage process was completed within 1 h. This photocleavage process was found to be much faster in *d*-DMSO than in *d*-DMF, and consequently all the other NMR experiments were carried out in *d*-DMSO.

Ureas have been shown to photocleave through free radical mechanism.[14,35] Unlike the photo-Fries cleavage mechanism, which usually gives several products,[36,37] the urea system based on 2-aminopyridine as shown above gives only two clearly definable products with

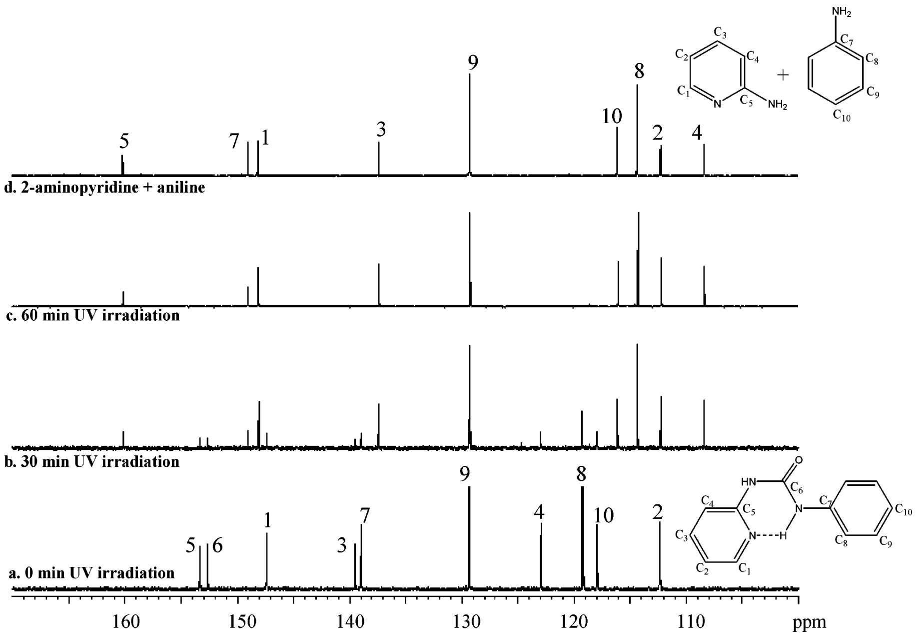


Figure 3. ^{13}C NMR of model compound **1** (0.05 M in *d*-DMSO) before (a) and after (b, c) UV irradiation for the indicated duration. The top spectrum (d) is the ^{1}H NMR of an equimolar the mixture of 2-aminopyridine and aniline.

nearly 100% conversion. The pyridine moiety seems to play an important role in the photocleavage process. When the presence of the pyridine ring is removed as in model compound **4**, even after 6 h of UV irradiation, no photocleavage products (amines) are obtained (data not shown). This could be due to the fact that, without the pyridine ring, the diphenylurea **4** absorbs at 320 nm, far below the wavelength (365 nm filtered light) at which all the model compounds were irradiated. In addition, photocleavage of model compound **2**, which has a methyl substitution on a phenylamino group, gave 2-aminopyridine and *N*-methylaniline while model compound **3** gave 2,6-diaminopyridine and aniline (^{1}H NMR shown in Supporting Information, Figures S1 and S2). Furthermore, their photocleavage rates were on the same order of magnitude with model compound **1**.

To determine whether external reagents such as O_2 and H_2O played any significant role in the photocleavage of these ureas, NMR experiments were also carried out using oxygen degassed (via multiple freeze−thaw−pump cycles followed by vacuum-sealing) *d*-DMSO solutions. No significant differences in photocleavage rate between the degassed and nondegassed samples were observed, which suggests that oxygen plays no obvious role in the process. This is contrary to the reported photooxidative degradation of aromatic polyurethanes to quinoids.[12,13] On the other hand, the amount of water in the *d*-DMSO was found to be crucial in this photocleavage process. NMR samples with different water content (0.5, 1.5, 2.5, and 5 equiv to the model compounds) were prepared, sealed in NMR tubes, and similarly irradiated for different durations while recording NMR spectra. Figure 4 illustrates the percent conversion of disappearing **1** for different water content as a function of UV exposure duration. The percent conversion was calculated by comparing integrated proton NMR peak values (specifically the proton α to the pyridyl nitrogen) from the starting compound with those from the photocleavage products. From the initial slope of Figure 4, it is evident that the photocleavage rate increased with water content. It should also be noted that for the sample with the lowest water content (0.5 mol equiv of H_2O to **1**) the photocleavage reaction stopped nearly at 50% after all water was consumed, as indicated by the disappearance of water peak in the NMR spectra, even after prolonged exposure to UV irradiation. This implies that water acts as a reactant and not as a catalyst, in this cleavage process. With samples containing more water, the photocleavage reaction proceeded to completion with prolonged exposure to UV irradiation. The kinetics of this process is under investigation and will be the study of a separate paper.

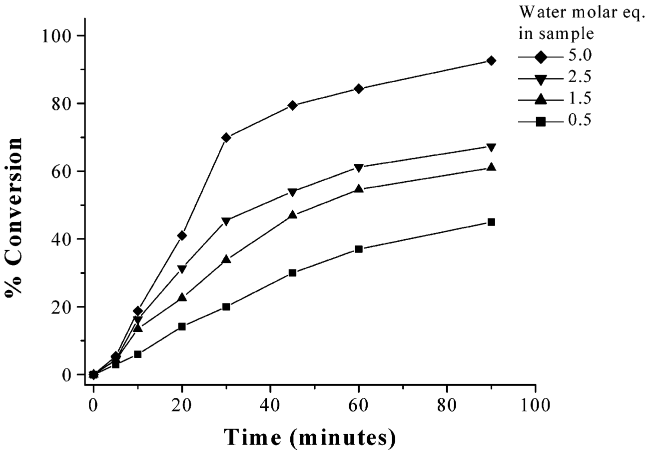


Figure 4. Percent conversion vs irradiation duration for model compound **1** (0.05 M in *d*-DMSO) as a function of different water contents.

To study in more details the effect of the neighboring pyridyl moiety to the photocleavage, model compounds **5** and **6** (shown in Scheme 2) were synthesized and their NMR spectra (*d*-DMSO solutions) also investigated as a function of exposure to UV irradiation. Here, as compared to **1**, model compounds **5** and **6** have their amino groups on 3-position and 4-position of the pyridine rings, respectively. Shown in Figure 5 are the ^{1}H NMR spectra of **5** and **6** before and after 1 h of UV irradiation. Figure 5A indicates that for the 3-aminopyridylphenylurea (**5**) little change was observed as indi-

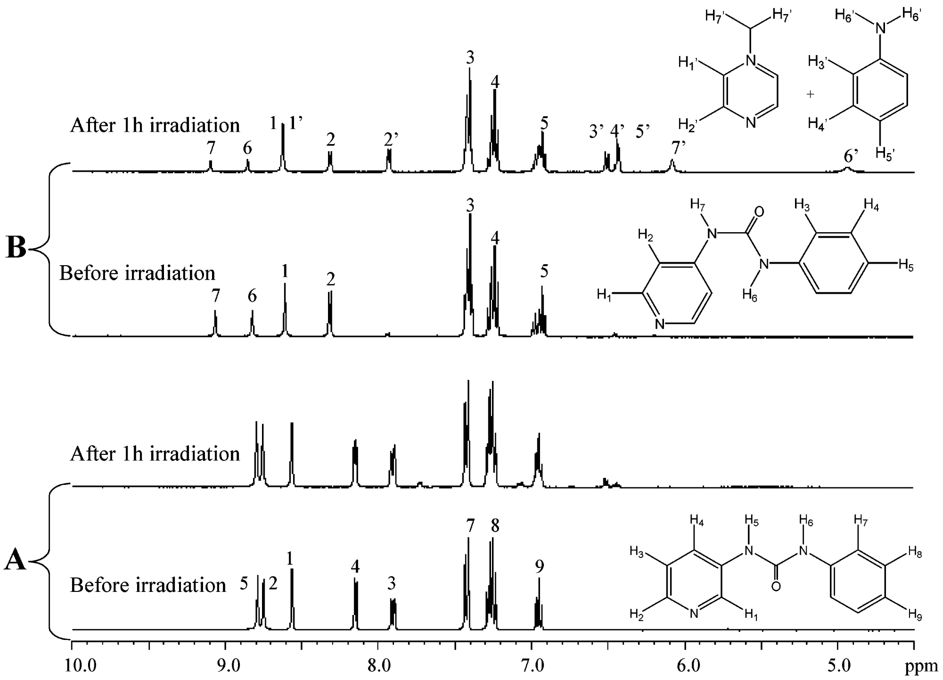
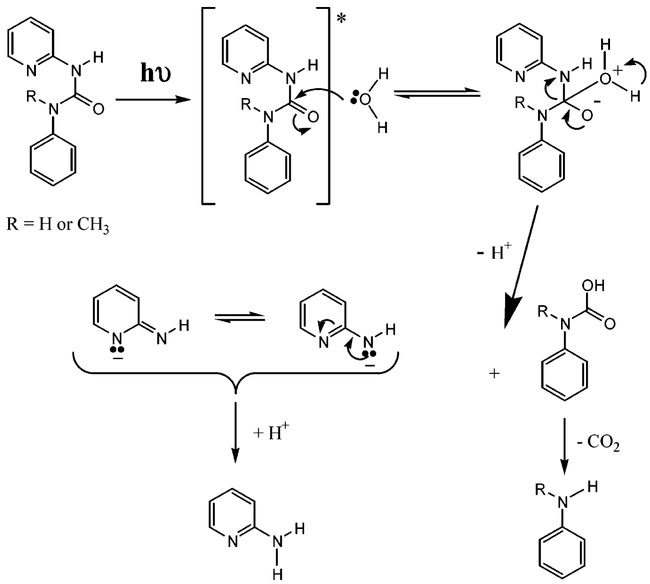


Figure 5. ^{1}H NMR of (A) model compound **5** (3-aminopyridylphenyl urea) and (B) model compound **6** (4-aminopyridylphenyl urea) before and after 1 h irradiation (0.05 M in *d*-DMSO).

cated by the appearance of small intensity peaks at δ 6.5, 7.1, and 7.7 ppm. In contrast to **5**, **6** (4-aminopyridylphenylurea) exhibited an almost 50% conversion. Upon UV irradiation, the new set of chemical shifts (peaks marked in primed numbers) generated closely match the corresponding pure amines, i.e., 4-aminopyridine and aniline. From these observations it can be concluded that compounds with the urea groups ortho and para to the pyridyl nitrogen are much more prone to water-assisted photocleavage as opposed to the meta-substituted ones.

It has been proposed that intramolecular hydrogen bonding plays an important role in photoinduced proton-transfer processes.[38] In addition, Fiksdahl et al.[39] reported that *N*-(2-pyridyl)amides can go through a concerted proton-transfer mechanism involving a six-membered intermediate to form 2-aminopyridines and ketenes. Compounds **1** and **3** in Scheme 2 exhibit this kind of intramolecular hydrogen bonding.[40,41] This was also confirmed by NMR where a NOE was detected between protons 1 and 9, indicating the presence of a hydrogen bond (see Supporting Information, Figure S3). To study the role of this intramolecular hydrogen bond, during the photoirradiation process, compound **2**, which does not possess such hydrogen bond, was synthesized and exposed to UV irradiation in a manner similar to the other model compounds. As shown in the Supporting Information, Figure S1, compound **2** exhibited similar water-assisted photocleavage behavior to **1**, clearly suggesting that intramolecular H-bonding is not mandatory for this photocleavage process. This is also reinforced by the photocleavage behavior of **6**, which also is not capable of intramolecular hydrogen bonding. On the basis of the results described above, a photoassisted hydrolysis mechanism of the ortho- and para-substituted pyridyl ureas (shown only for the ortho position) is proposed in Scheme 3. When such pyridyl ureas are exposed to UV irradiation, it appears that their excited states results in weakened amide bond, probably due to resonance with the electron-withdrawing pyridine nitrogen. A trace amount of water in the system nucleophilically attacks the carbonyl carbon to initiate such hydrolysis process. The equilibrium state is determined by the stability of the leaving groups. For the phenyl amide moiety, the leaving group is the carbamic acid, which most of the time is quite unstable and yields the corresponding amine (Ph−NHR) plus CO$_2$. For the pyridylamine moiety, the 2-aminopyridine anion is stabilized through tautomerization[42,43] which leads to efficient electron delocalization and further assists in shifting the equilibrium to the right. Tautomerization of the 2-aminopyridine anion explains the profound reactivity deference between the ortho- and para-pyridyl-based model ureas, **1**, **2**, **3**, and **6**. Similarly, the meta-substituted pyridylurea (i.e., **5**) cannot be stabilized through tautomerization, a fact that adds weight to the proposed photocleavage mechanism.

Scheme 3. Proposed Photocleavage Mechanism of the Urea Compounds



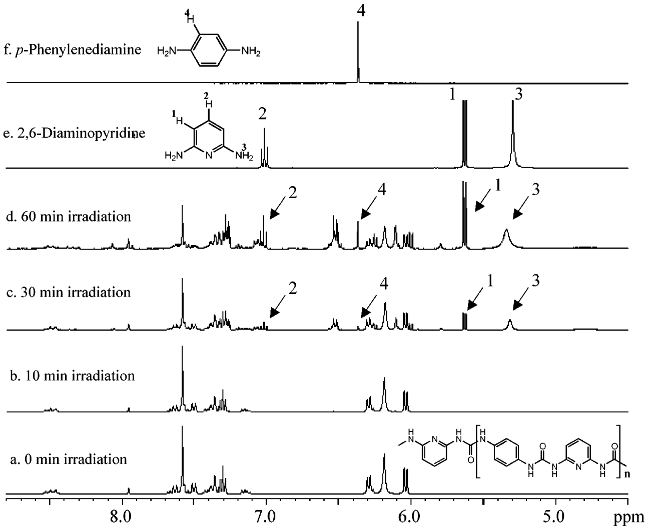


Figure 6. H NMR spectra of polymer (**I**) (a) before irradiation and (b, c, d) after 10, 30, and 60 min irradiation, respectively. The top two spectra are the H NMR traces of pure (e) 2,6-diaminopyridine and (f) phenylenediamine for comparison purposes (0.05 M in *d*-DMSO).

To further reinforce this mechanism, we have conducted a series of GC-MS experiments on the photoirradiated compound **1** along with two additional model compounds (phenyl isocyanate and 2-aminopyridine). Figure S4 in the Supporting Information depicts the GC traces of photocleavage products of compound **1**, injected from its DMSO solution immediately after irradiation (A), and after they were allowed to stand unsealed overnight (B), along with the respective MS assignment (C) of the corresponding elution peaks of the total ion chromatogram (TIC). As evident, CO_2 was abundantly detected in the samples immediately after irradiation. However, for the same samples that were allowed to stay unsealed overnight, only a very weak CO_2 signal was detected in the TIC, while the remaining byproducts remain unchanged. This might arise from (a) weak solubility of CO_2 in DMSO, (b) rapid decomposition of the phenylcarbamic acid, and (c) weak basicity of the byproduct phenylamine and 2-aminopyridine (also observed in the TIC trace of Figure S4). To test (a) and (c), GC-MS traces of CO_2-bubbled DMSO in the presence and absence of phenylamine and 2-aminopyridine, respectively, after having been left unsealed overnight, confirmed that the solubility of CO_2 in these media is negligible. Moreover, immediately after addition of water to a DMSO solution of phenyl isocyanate (known to produce the unstable phenylcarbamic acid), the GC-MS trace recorded abundant CO_2 and phenylamine. Upon letting that solution to stay unsealed overnight, only phenylamine was detected, which confirms that the phenylcarbamic acid is not stable at room temperature, let alone the elevated heating within the GC oven. In accordance to the proposed mechanism, no CO was detected in all GC-MS experiments, and the very small peak (near the prominent CO_2 peak) results from air, whose MS shows two prominent peaks at 28 and 32 Da with intensity ratio always near 3/1 (i.e., N_2 and O_2).

As shown in Figure 6 and Scheme 4, on the basis of the described detailed study on various urea model compounds, it became apparent that polymer **I** photocleaves in a manner similar to form, among other photocleavage products, amine-terminated aromatic moieties and ultimately 2,6-diaminopyridine and *p*-phenylenediamine along with releasing of CO_2. Several new peaks (labeled by 1, 2, 3, and 4 in the ^1H NMR spectra of Figure 6) emerged upon UV irradiation. By comparing the NMR spectra of pure diamines (i.e., 2,6-diaminopyridine and *p*-phenylenediamine), a clear match between peaks 1, 2, and 3 and protons from 2,6-diaminopyridine is evident. In addition, peak 4 was at exactly the same chemical shift as the phenyl protons in *p*-phenylenediamine. However, the plurality of additional peaks generated during prolonged UV radiation may arise from oligomeric fragments along with further photoassisted processes that take place in parallel to photocleavage. These processes have been linked to photooxidation of the amine-terminated moieties as well as the two low molecular weight diamine byproducts mentioned above.

On the basis of the above-described NMR investigation, we now shift our attention to explain the UV–vis and PL behavior of polymer **I** upon irradiation, shown in Figure 1A,B. Figure 7A show the UV–vis absorption spectral change of a mixture of the polymer **I** photocleave amine products, 2,6-diaminopyridine, and *p*-phenylenediamine as a function of UV irradiation (365 nm). The UV irradiation was carried out on DMF solutions of the diamines mixture. The absorption at 310 nm decreases slightly while a broad absorption peak around 410 nm increases with prolonged exposure to

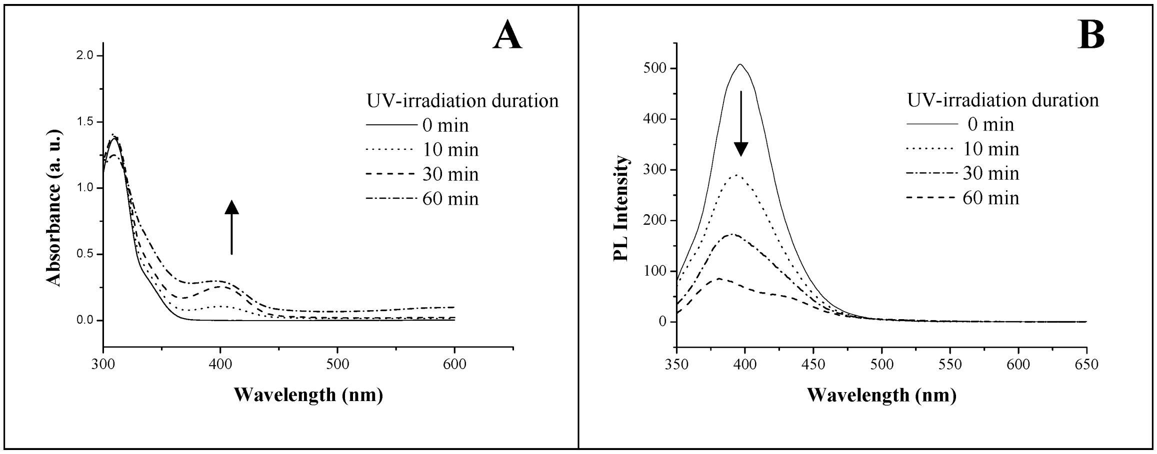
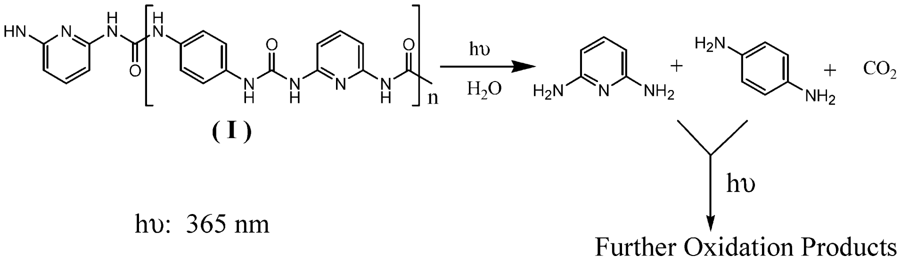


Figure 7. UV–vis (A) and PL (B) spectra of mixture of pure 2,6-diaminopyridine and 1,4-phenylenediamaine upon exposure to UV irradiation (365 nm) for varying periods of time. The PL spectra were obtained from 340 nm excitation for 10^{-4} M solutions of each compound in DMF.

Scheme 4. Proposed Photocleavage Process for the Polymer I



Scheme 5. Possible Photooxidation Products from *p*-Phenylenediamine[44]

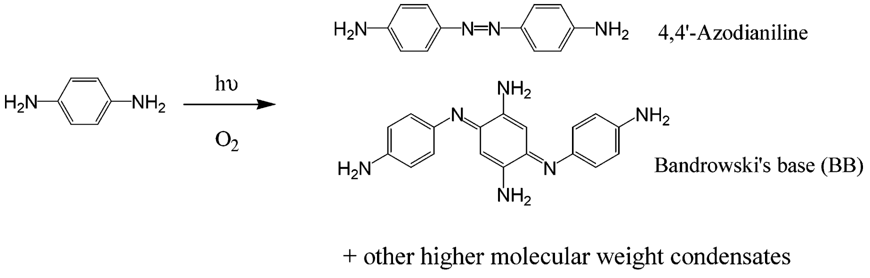
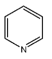
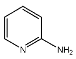
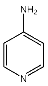
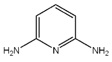
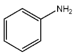
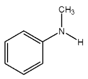


Table 1. Reported pK_a Values in CH_3CN and H_2O along with Relative Basicity with Respect to Pyridine of Various Amines Generated from the Photocleavage of Model Compounds 1, 2, 3, and 6

Amines	Pyridine*	2-Amino pyridine	4-Amino Pyridine	2,6-Diamino Pyridine	Aniline	N-Methyl Aniline
						
pKa (in CH_3CN)	12.33	14.26	17.40	14.56		
pKa (in H_2O)	5.25	6.82	9.11		4.63	4.85
Relative Basicity#	4	3	1	2	6	5

* Due to insolubility of urea compounds in water, pyridine is selected to show the basicity of starting urea compounds. The actual basicity of urea compounds in this study is much less than that of pyridine because of the strong acidity and electron withdrawing ability of urea group.

\# Relative basicity strength is shown by number. The smaller the number, the stronger the base.[47,48]

UV irradiation. Aromatic diamines, especially *p*-phenylenediamine, have been shown to form dimerized and trimerized quinoids when photooxidized.[44] The formation of such quinoid-type compounds as illustrated in Scheme 5 would explain the evolution of the broad red-shifted absorption peak, which could also be a result of formation of charge-transfer complexes between the amines (donor) and quinoids (acceptor). From reports in the literature[45] and our own experiments with photoluminescence of mixture of the diamines, it was found they exhibit intense emission centered ~390 nm (when excited at 315 nm). As can be seen from PL spectra in Figure 7B, of a mixture of 2,6-diaminopyridine and *p*-phenylenediamine, emission intensity decreases as a function of duration of exposure of the mixture to UV irradiation. This can be explained by the fact that formation of quinoid compounds, which are nonemissive, progressively quenches the PL.

Incorporating the photophysical results from the diamines described above, we can explain the polymer behavior illustrated in Figure 1. As the polymer photocleaves, less conjugated, smaller molecular weight moieties are formed, and this explains the decrease in absorption at ~325 nm in Figure 1A. The photocleaved products, especially *p*-phenylenediamine, get photooxidized on prolonged irradiation to form quinoids (see Scheme 5), among other products, that account for the increasing broad absorption centered at 450 nm. The initial relative increase and red shift (from 360 to 390 nm) in PL intensity observed (Figure 1B) is attributed to the steady formation of the photocleavage products, i.e., 2,6-diaminopyridine and *p*-phenylenedamine, as illustrated in Figure 7B. Subsequent reduction in PL intensity as the polymer sample is irradiated beyond 30 min is attributed to quenching by the nonemissive photooxidation products formed on prolonged irradiation, as also illustrated in Figure 7B. These observations, combined with the described NMR data from model compounds, strongly support the proposed photocleavage mechanism.

All the described results presented so far were for liquid samples. Here we shift our attention to solid samples of polymer **I**. Films of the polymer were photoirradiated for similar durations as in solution experiments and then solubilized in *d*-DMSO for proton NMR analysis. The resulting chemical shifts pattern did not change, and no generation of peaks was observed (data not shown), suggesting that such a photocleavage process is not favored in thin films of **I**. This could be due to the fact that in solids no water is available for the photocleavage reaction to occur, and this is consistent with the high degree of hydrogen bonding which leads to a very crystalline structure.[46] In solution, particularly in polar solvents, the hydrogen bonding is

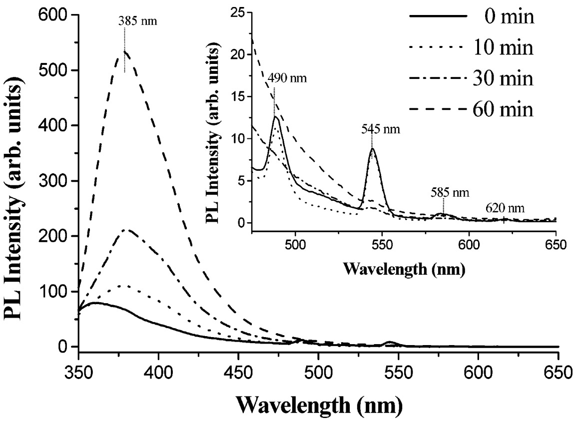


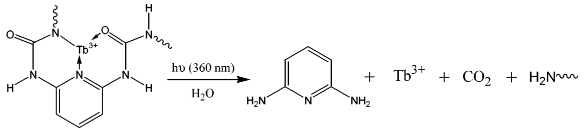
Figure 8. PL spectra (excited at 340 nm) of terbium/polyurea **I** chelate for various exposure times to UV irradiation. Inset depicts a closer view of the PL spectra between 400 and 650 nm, where the characteristic Tb^{3+} emission peaks at 490, 545, 585, and 620 nm gradually disappear with prolonged exposure time [1:2 (Tb^{3+}/polymer **I**) molar ratio in DMF (10^{-4} M of **I** based on its monomer repeat)].

disrupted, providing water with adequate volume to successfully allow the nucleophilic attack at the excited urea linkage.

The ease of formation of amine moieties upon irradiation of these type of ureas, in the presence of H_2O, opens up the opportunity for exploiting these compounds as (i) photobase generators and (ii) photoassisted metal releasing agents. As shown in Table 1, the reported pK_a values and relative basicity of the various photocleaved amines,[47,48] stronger bases are formed after the severance of the urea linkage. Here, because of the insolubility of urea compounds in water, pyridine is selected to compare the basicity of the starting urea compounds. The actual basicity of the starting urea compounds is much less than that of pyridine due to the fact that the relatively acidic nature and electron-withdrawing ability of the urea moiety reduces the basicity of the nearby pyridine group. It is interesting to note that the basicity of the photogenerated amines can be controlled by utilizing different isocyanate compounds for synthesis of the aminopyridyl-based ureas and polyureas. Also, the solubility of these kinds of polyureas (in the current study, soluble only in solvents like DMF and DMSO due to high crystallinity) can be improved by using monomers with bulky side chain substitutes (preferably ethylene oxide based, to further increase water uptake) This is expected to make such polyureas more amorphous, leading to higher solubility in solvents amenable for spin-coating thin films.

The metal chelating ability of 2,6-diaminopyridine-based ureas to lanthanide (terbium in particular) has previously been demonstrated by our group.[31] Figure 8 shows the PL spectra of dilute solutions of terbium/polymer **I** chelate in DMF as a function of exposure time to UV irradiation. Initially, these solutions luminesce noticeably green due to the characteristic $^5D_4 \rightarrow {}^7F_j$ (j = 6, 5, 4, and 3) electronic transitions of Tb^{3+} peaking 490, 545, 585, and 620 nm, respectively. However, upon irradiation, these quickly disappear, replaced with a strong blue emission peaking at 385 nm. This is consistent with the steady photocleavage of **I** where, in the absence of the 2,6-diureidopyridinyl chelating cavity, the Tb^{3+} ions are released (as shown in Scheme 6). As previously described, when the urea linkage cleaves, the steady formation of diamine moieties accounts for the increase in PL intensity at 385 nm.

Scheme 6. Release of Tb^{3+} Ions after Photocleavage of the Metal-Chelating Urea Ligand



In conclusion, the photocleavage of poly(1,4-phenylene-2,6-pyridylurea) under 365 nm UV irradiation has been spectroscopically studied through the use of several urea compounds. The photocleavage was found to occur through a photoassisted hydrolysis mechanism in ortho- and para-substituted pyridine ureas. The amount and chemical accessibility (solution vs solid phase) of water to these pyridyl urea moieties were found crucial for this photocleavage process, with O_2 playing a role only in subsequent oxidation of the resulting amine functionalities. Polymeric or oligomeric analogues of this system might find a number of possible applications where light-induced generation of bases and/or release of certain metal cations are desired.

Acknowledgment. The authors thank Dr. Theodore Goodson, III (Wayne State University), and his research group for investigating the ultrafast dynamics of this system (subject of a separate paper) that motivated us to study the photoinduced transformations of this class of compounds. We also thank Dr. Xiangqun Xie (University of Connecticut) for additional help with the NMR experiments. Financial support by AFOSR (Wayne State PO # Y-30173), NSF CAREER Grant DMR-970220, and Connecticut Innovations Inc., Critical Technologies Program, State of Connecticut, is greatly appreciated.

Supporting Information Available: Figures S1, S2, S3, and S4. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Yang, C.; He, G.; Wang, R.; Li, Y. *Thin Solid Films* **2000**, *363*, 218–220.
(2) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121–128.
(3) Friend, R. H. *Pure Appl. Chem.* **2001**, *73*, 425–430.
(4) Bradley, D. D. C. *Adv. Mater.* **1992**, *4*, 756–758.
(5) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 403–428.
(6) Berntsen, A. J. M.; Van De Weijer, P.; Croonen, Y.; Liedenbaum, C. T. H. F.; Vleggaar, J. J. M. *Philips J. Res.* **1998**, *51*, 511–525.
(7) Cumpston, B. H.; Jensen, K. F. *Synth. Met.* **1995**, *73*, 195–199.
(8) Papadimitrakopoulos, F.; Konstandinidis, K.; Miller, T.; Opila, R.; Chandross, E.; Galvin, M. *Chem. Mater.* **1994**, *6*, 1563–1568.
(9) Lee, T.-W.; Park, O. O.; Kim, J.-J.; Hong, J.-M.; Kim, Y. C. *Chem. Mater.* **2001**, *13*, 2217–2222.
(10) Cumpston, B. H.; Parker, I. D.; Jensen, K. F. *J. Appl. Phys.* **1997**, *81*, 3716–3720.
(11) Ettedgui, E.; Davis, G. T.; Hu, B.; Karasz, F. E. *Synth. Met.* **1997**, *90*, 73–76.
(12) Hoyle, C. E.; Kim, K.-J. *J. Polym. Sci., Part A* **1986**, *24*, 1879–1894.
(13) Hoyle, C. E.; Kim, K.-J.; No, Y. G.; L, G.; Nelson *J. Appl. Polym. Sci.* **1987**, *34*, 763–774.
(14) Kim, H.; Urban, M. W. *Langmuir* **2000**, *16*, 5382–5390.
(15) Yoshino, K.; Kuwabara, T.; Manda, S.; Kawai, T. *Jpn. J. Appl. Phys.* **1990**, *29*, L1716.
(16) DeAro, J. A.; Gupta, R.; Heeger, A. J.; Buratto, S. K. *Synth. Met.* **1999**, *102*, 865–868.

(17) Tada, K.; Onoda, M. *J. Appl. Phys.* **1999**, *86*, 3134−3139.

(18) Yu, J.; Holdcroft, S. *Chem. Mater.* **2002**, *14*, 3705−3714.

(19) Shirai, M.; Tsunooka, M. *Prog. Polym. Sci.* **1996**, *21*, 1−45.

(20) Jensen, K. H.; Hanson, J. E. *Chem. Mater.* **2002**, *14*, 918−923.

(21) Hamada, Y. *IEEE Trans. Electron Devices* **1997**, *44*, 1208−1217.

(22) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161−174.

(23) Sapochak, L. S.; Padmaperuma, A.; Washton, N.; Endrino, F.; Schmett, G. T.; Marshall, J.; Fogarty, D.; Burrows, P. E.; Forrest, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 6300−6307.

(24) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913−915.

(25) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610−3615.

(26) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4−6.

(27) O'Brien, D. F.; Giebeler, C.; Fletcher, R. B.; Cadby, A. J.; Palilis, L. C.; Lidzey, D. G.; Lane, P. A.; Bradley, D. D. C.; Blau, W. *Synth. Met.* **2001**, *116*, 379−383.

(28) Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, *102*, 2357−2368.

(29) Christou, V.; Salata, O. V.; Ly, T. Q.; Capecchi, S.; Bailey, N. J.; Cowley, A.; Chippindale, A. N. *Synth. Met.* **2000**, *111*−*112*, 7−10.

(30) Edwards, A.; Claude, C.; Sokolik, I.; Chu, T. Y.; Okamoto, Y.; Dorsinville, R. *J. Appl. Phys.* **1997**, *82*, 1841−1846.

(31) Mwaura, J. K., III; D. L. T.; Phely-Bobin, T.; Taher, M.; Theodoropoulos, S.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2000**, *122*, 2647−2648.

(32) Mwaura, J. K.; Mathai, M.; Chen, C.; Papadimitrakopoulos, F. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2003**, *40*, 1253−1262.

(33) Tomazic, A.; Tisler, M.; Stanovik, B. *Tetrahedron* **1981**, *37*, 1787−1793.

(34) Ohsawa, A.; Arai, H.; Igeta, H. *Chem. Pharm. Bull.* **1980**, *28*, 3570−3575.

(35) Guaoguang, L.; Xiangning, J.; Xiaobai, X. *J. Agric. Food Chem.* **2001**, *49*, 2359−2362.

(36) Ninomiya, I.; Naito, T. *Photochemical Synthesis*; Academic Press: London, 1989; Vol. 1.

(37) Pitchumani, K.; Warrier, M.; Ramamurthy, V. *J. Am. Chem. Soc.* **1996**, *118*, 9428−9429.

(38) Nunes, T.; Eichen, Y.; Bastos, M.; Burrows, H. D.; Trommsdorff, H. P. *J. Phys. D: Appl. Phys.* **1999**, *32*, 2108−2117.

(39) Fiksdahl, A.; Plug, C.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1841−1845.

(40) Ge, Y.; Miller, L.; Ouimet, T.; Smith, D. K. *J. Org. Chem.* **2000**, *65*, 8831−8838.

(41) Singha, N. C.; Sathyanarayana, D. N. *J. Chem. Soc., Perkin Trans. 2* **1997**, 157−162.

(42) Kolehmainen, E.; Osmialowski, B.; Nissinen, M.; Kauppinen, R.; Gawinecki, R. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2185−2191.

(43) Pietrzycki, W.; Sepiol, J.; Tomasik, P.; Brzozka, L. *Bull. Soc. Chim. Belg.* **1993**, *102*, 709−717.

(44) Dolinsky, M.; Wilson, C. H.; Wisneski, H. H.; Demers, F. X. *J. Soc. Cosmet. Chem.* **1968**, *19*, 411−422.

(45) Fujimoto, A.; Inozuka, K. *Spectrochim. Acta* **1988**, *44A*, 1035−1043.

(46) Papadimitrakopoulos, F.; Hsu, S. L.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4671−4681.

(47) Weast, R. C.; Astle, M. J. *CRC Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981; pp D139−141.

(48) Kaljurand, I.; Rodima, T.; Leito, I.; Koppel, I. A.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 6202−6208.

MA034058K