Room-Temperature Phosphorescence Studies of Epoxy Resin Cured by an Aromatic Diamine

Jian Cheng Song and Chong Sook Paik Sung*

Institute of Materials Science, Department of Chemistry, University of Connecticut, 97 North Eagleville Road, Storrs, Connecticut 06269-3136

Received April 10, 1995[⊗]

ABSTRACT: The applicability of phosphorescence spectroscopy is investigated for cure characterization of epoxy resin cured by an aromatic diamine. By using a time-resolved method to separate fluorescence from phosphorescence, the room-temperature phosphorescence (RTP) behavior of a commonly used curing agent, bis(*p*-aminophenyl) sulfone (DDS), is studied. RTP emission spectra with a maximum around 500 nm are obtained. Both RTP emission and excitation intensity increase very sharply with cure time due to the increase in the rigidity of the cured epoxy. They can be correlated to the extent of cure of epoxy, when properly calibrated. The triplet lifetime (τ_T) obtained by monitoring RTP emission decay at 500 nm increases from zero to about 40 ms following cure at 160 °C for 180 min. Correlation curves of τ_T with the extent of cure and the glass transition temperature are also obtained. Thus, τ_T provides a way to estimate the cure extent without the need to calibrate the RTP emission intensity. While these RTP characteristics cannot be used for in-situ cure monitoring, they can be used as a sensitive cure estimate technique in lightly cured prepregs for composites or after a cure cycle.

Introduction

Recently, we reported on a convenient technique for epoxy cure monitoring based on the intrinsic fluorescence of a commonly used curing agent such as bis(*p*-aminophenyl) sulfone (DDS), which is used in most high-performance epoxy composites. As the curing proceeds, the fluorescence excitation spectra[1] or the UV reflection spectra[2] of the DDS curing agent exhibited spectral red shifts of about 24 nm due to the conversion of the primary amine groups in DDS to tertiary amine groups. The peak positions in the fluorescence excitation spectra or in the UV reflection spectra were shown to correlate well with the extent of DDS amine cure. Since no extrinsic fluorophore is required, this intrinsic cure sensing technique has been implemented for in-situ cure monitoring of DDS cured epoxy composites with a fiber-optic fluorimeter.[3]

Phosphorescence spectroscopy is often used as a complementary analytical technique to fluorescence spectroscopy for the analysis of organic, biological, organometallic, and polymeric materials. Because of the longer lifetimes of the triplet state, phosphorescence emission is much more subject to quenching by oxygen,[4–6] whose diffusion depends greatly on the viscosity or the physical state of the polymer. Since the phosphorescence intensity and the triplet lifetime of the nonreactive extrinsic probes are generally viscosity-sensitive, they can be used to monitor the changes in the matrix viscosity or the molecular mobility. For example, Meijer and Zwiers[7] studied the molecular mobility of a polyepoxide network by monitoring the phosphorescence emission from a photoinitiator, bis(4-*tert*-butylphenyl)-iodonium hexafluoroarsenate. Kotch et al.[8] reported that phosphorescent organometallic complexes can be used as extrinsic probes to monitor the curing reactions of epoxy or acrylate resins. The phosphorescence intensity of the probe correlated well with the rate of consumption of the acrylate monomer.

The main objective of this research is to study the intrinsic phosphorescence behavior of DDS, as a function of cure. As the curing reaction proceeds, the viscosity and the glass transition temperature increase. The matrix changes from liquid to solid at room temperature. Thus, the oxygen quenching is expected to be reduced, with cure affecting the phosphorescence emission intensities. It was of interest to see if the spectral red shifts are also observed in phosphorescence as in fluorescence. If red shifts greater than 24 mm are observed in phosphorescence, this may provide a sensitive method to determine the extent of cure.

Phosphorescence can be observed either at low temperature to reduce quenching by use of a rotating can technique or at room temperature by using a time-resolved method to separate fluorescence from phosphorescence. Sample handling and the separation of fluorescence from phosphorescence at low temperature were found to be more difficult when using a rotating can technique,[9] since the low-viscosity sample at early stages of cure had to be placed vertically in a small quartz tube. On the other hand, a time-resolved method based on room-temperature phosphorescence (RTP) was found to be more reliable after the experimental parameters such as the delay time and the gate time were optimized. Therefore, this paper will present the results based on RTP only.

Experimental Section

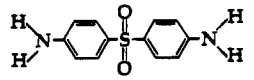
1. Model Compounds and Sample Preparation for Cure Reaction Studies. Bis(*p*-aminophenyl) sulfone (pp-DDS) (98% purity purchased from Aldrich) was used without further purification. A model compound, tt-DDS, was previously synthesized and purified from the reaction of DDS with excess monoepoxide butyl glycidyl ether.[1a] As for diglycidyl ether of Bisphenol A (DGEBA), Shell's Epon 825 was used without further purification.[8] The stoichiometric mixture of DGEBA/DDS epoxy was prepared under constant stirring at 120 °C for 2 min.[1a] In order to observe the spectral shift from pp-DDS to tt-DDS, a small amount of either compound was dissolved in chloroform solution with poly(methyl methacrylate) (PMMA), so that PMMA was about 5% by weight and the model compound concentration was around 10^{-4} M in reference to PMMA. Thin films were cast and dried before RTP was taken.

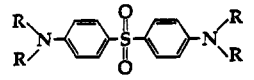
2. Instrumental Analysis. A Perkin-Elmer Model LS 50B spectrometer with a Digital Model 325C data station was used to acquire the room-temperature phosphorescence (RTP) emis-

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

0024-9297/95/2228-5581$09.00/0

Chart 1. Structures of Two DDS Model Compounds


(pp-DDS)


(tt-DDS)

R = $H_3CCH_2CH_2CH_2OCH_2CH(OH)CH_2$

sion and excitation spectra. The following experimental conditions were found to be optimal for separating fluorescence from phosphorescence and enhancing phosphorescence intensity: delay time = 0.1 ms; gate time = 50 ms; scanning speed = 120 nm/min; excitation/emission slits = 10 nm/10 nm. RTP decay curves of epoxy samples were obtained under the following conditions: λ_{ex} = 330 nm; λ_{3m} = 500 or 505 nm; gate time = 50 ms; scanning speed = 120 nm/min; excitation/emission slits = 10 nm/10 nm.

A Nicolet FTIR spectrometer with a TGS detector was used to monitor the rate of disappearance of epoxide ring around 910 cm^{-1} in thin epoxy films which were spread between two KBr disks.[1a] The thermal analyses of the epoxy resins were achieved via a Perkin-Elmer 7 Series thermal analyzer with a Model 7700 data station. Both isothermal and dynamic experiments of the samples (10–15 mg) were accomplished using an aluminum pan purged with a dry N_2 gas. The scan rate used for the dynamic experiment was 10 °C/min.

Results and Discussion

1. Phosphorescence Studies of Model DDS Compounds. Chart 1 shows the structures of two DDS model compounds studied in this work: a fully reacted DDS model compound is tt-DDS where amine groups of DDS are both tertiary, while an unreacted DDS model compound is pp-DDS, representing the case where amine groups of DDS are both primary. In order to see how much spectral shift in phosphorescence is observed when pp-DDS is converted to tt-DDS, a small amount of either DDS model compound was added in a glassy matrix of poly(methyl methacrylate) (PMMA) by casting and drying a thin film from a chloroform solution.

Figure 1a compares the room-temperature luminescence spectra of pp-DDS and tt-DDS obtained in the PMMA matrix. The fluorescence emission peaks for the pp-DDS and tt-DDS in the PMMA matrix are found to be a 341 and 362 nm, respectively, with a total spectral shift of 21 nm. The RTP emission peaks for the pp-DDS and tt-DDS in the PMMA matrix are found to be at 421 and 435 nm, respectively, with a total spectral red shift of about 14 nm, which is smaller than that for the fluorescence spectra.

Sawicki and Pfaff[10] found that the phosphorescence emission maxima of 4-nitroaniline, *N*-methyl-4-nitroaniline, and *N,N*-dimethylaniline were at 510, 522, and 525 nm, respectively, when measured in an EPA (ethyl ether–isopentane–ethanol, 5:5:2 by volume) solution at 77 K. Therefore, the total spectral shift was only about 15 nm as the primary amino groups were converted to the tertiary amino groups in 4-nitroaniline. This magnitude of the shift is similar to the DDS case observed in PMMA.

2. Phosphorescence Studies of Neat Epoxy Resins. (a) RTP Spectra of DGEBA/DDS as a Function of Cure. Figure 2 gives the RTP emission spectra of the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C, when excited at 330 nm. Before curing, the epoxy system shows very little phosphorescence emission at room temperature due to the quenching and other radiationless processes that cause the deactivation of the excited triplet state.

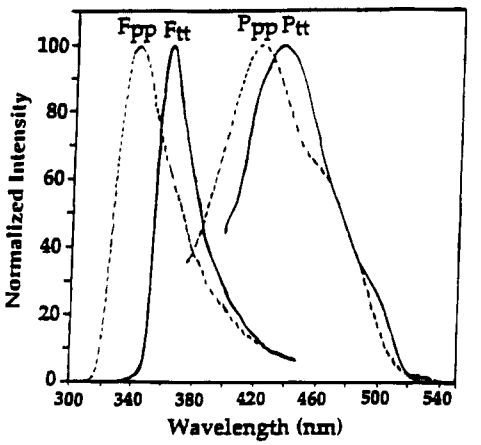


Figure 1. Comparison of the fluorescence (F_{pp} and F_{tt}) and phosphorescence (P_{pp} and P_{tt}) emission spectra of pp-DDS and tt-DDS in the PMMA matrix at room temperature (excitation at 295 or 324 nm for pp-DDS or tt-DDS, respectively).

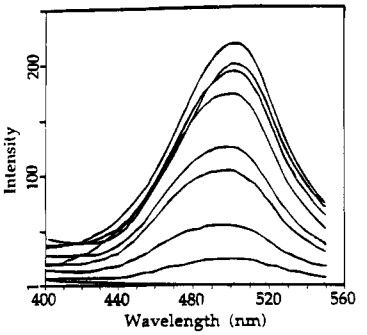


Figure 2. RTP emission spectra of the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C (cure time = 0, 10, 20, 31, 46, 60, 120, 150, 180 min, from bottom to top; excitation at 330 nm).

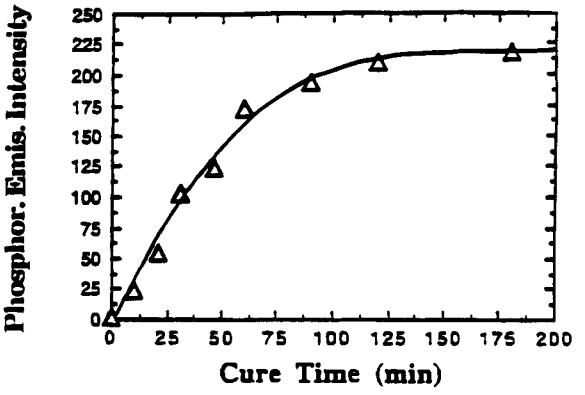


Figure 3. Plot of the RTP emission intensity at 500 nm for the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C.

However, as the curing proceeds at 160 °C, the phosphorescence emission intensity increases sharply as shown in Figure 3. The trend in the changes of RTP intensity as a function of cure time appears to be about the same as that of the changes in fluorescence excitation peak position as reported in our previous study.[1] In fact, an almost linear correlation seems to exist between the RTP emission intensity (I_p) and the fluorescence excitation peak position as shown in Figure 4a. Thus, the RTP intensity based on the DDS curing agent can also be used as an intrinsic sensor for epoxy cure characterization when the intensity is properly calibrated. A correlation plot between the RTP intensity and the extent of epoxide reaction for the stoichiometric

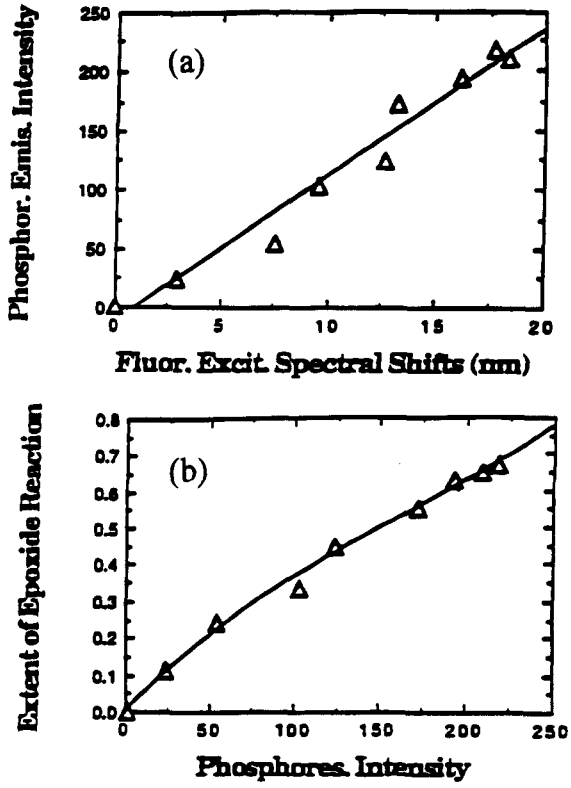


Figure 4. Correlation plots of the fluorescence excitation peak position (a) and the extent of epoxide reaction (b) vs the RTP emission intensity at 500 nm for the stoichiometric DGEBA/DDS epoxy cured at 160 °C.

DGEBA/DDS epoxy is given in Figure 4b. Since phosphorescence is not expected to be detectable at cure temperatures, its use as a cure detection method is limited only to the room-temperature measurement after cooling the cured sample or in the prepregs reinforced with fibers which have been slightly cured.[11] The extent of cure in the prepregs is generally about 15%, but it can increase due to the conditions they are exposed to. In order to optimize cure conditions, it is important to accurately measure the cure extent of the prepregs.

Another feature that can be observed from Figure 2 is that the phosphorescence peak position around 500 nm is only slightly red shifted during the cure process. The peak position occurs at a longer wavelength in the epoxy matrix than in the PMMA matrix, probably because of the more polar nature of the epoxy. The trend of a small red shift is also reasonable since the primary amine form of DDS, which is expected to appear at a shorter wavelength, is not showing much phosphorescence intensity at room temperature due to oxygen quenching in the low-viscosity matrix at the early stages of cure.

Figure 5 shows the RTP excitation spectra of the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C, when emitted at 500 nm. As expected, the excitation peak is shifted to longer wavelengths with sharp enhancement in the phosphorescent intensity as the cure time increases. The spectral positions and the red shifts observed in the phosphorescence excitation spectra are very similar to those in the fluorescence excitation spectra as reported in our previous study,[1a] indicating that the same electronic transition (S_0-S_1) is involved in both excitation spectra.

(b) RTP Lifetimes of DGEBA/DDS as a Function of Cure. Another useful parameter of phosphorescence

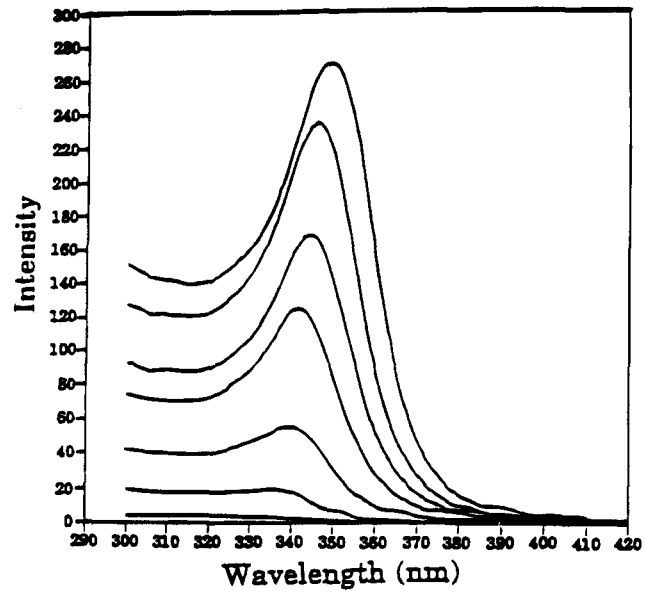


Figure 5. RTP excitation spectra of the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C (T_{cure} = 0, 10, 21, 31, 46, 60, 120, 180 min, from bottom to top; emission at 500 nm; the intensity at 0 min is zero at all wavelengths).

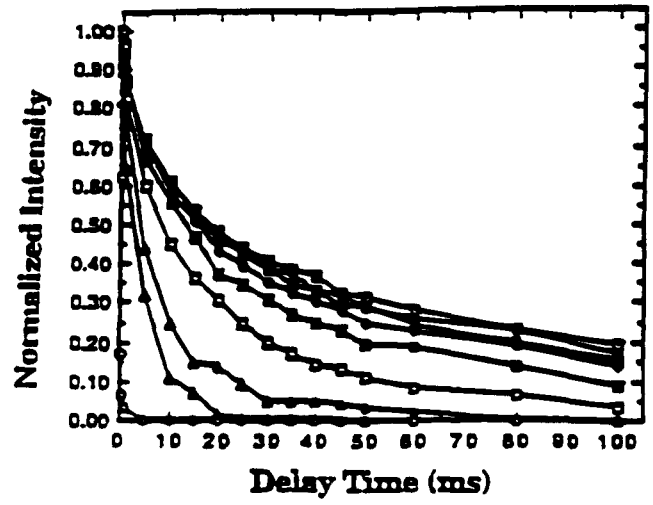


Figure 6. RTP emission decay curves of the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C (cure time = 0, 10, 20, 31, 46, 60, 90, 120, 180 min, from bottom to top; excitation at 330 nm; emission at 500 nm).

spectroscopy is the lifetime of the triplet states (τ_T) which can be obtained from the phosphorescence decay curve. The value of τ_T is equal to the time elapsed for the intensity value to decrease to 36.8% of the original value. The major advantage of using τ_T as a cure parameter is that no intensity calibration procedure is needed. The value of τ_T is mainly dependent upon the nature of the chromophore, viscosity, and temperature of the medium in which the measurement is made. Generally, τ_T increases with the local viscosity and decreases with the molecular mobility of the phosphorescence probe.[7,12] The temperature and the viscosity dependence characteristics of τ_T for a phosphorescent chromophore have been used to study the molecular mobility and the chain conformation of polymers.[7,12]

Figure 6 shows the RTP emission decay curves of the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C. The excitation and emission wave-

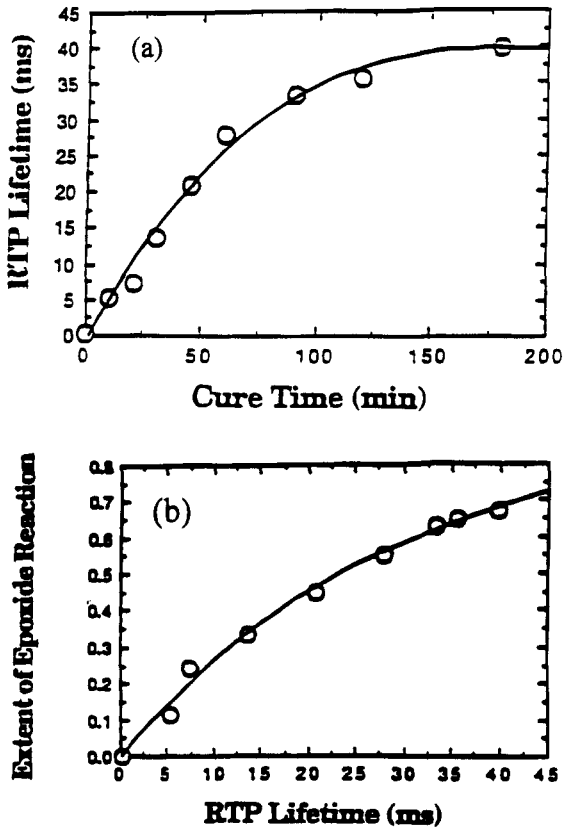


Figure 7. (a) Plot of the RTP lifetime of the stoichiometric DGEBA/DDS epoxy as a function of cure time at 160 °C (excitation at 330 nm; emission at 500 nm). (b) Correlation between RTP lifetime and extent of epoxide reaction.

lengths were set at 330 and 500 nm, respectively. It can be seen that the phosphorescence intensity decays at a very fast rate (indicating a shorter lifetime) in the early stages of the curing process and a much slower rate (indicating a longer lifetime) in the later stages of the reaction. The values of τ_T for the stoichiometric DGEBA/DDS epoxy increase from zero to about 40 ms after curing for 180 min at 160 °C, as illustrated in Figure 7a, and it can be correlated to the extent of epoxy cure by Figure 7b.

It is also useful to correlate τ_T with the glass transition temperature (T_g) which is a reflection of the degre of cross-linking in an epoxy system. Correlations plots of the triplet lifetime (τ_T) with the glass transition temperature of the epoxy resin are shown in Figure 8. Since the RTP lifetime measurement is a nondestructive method with no requirement of an internal standard for intensity calibration, it can be conveniently used to monitor the cure extent in the prepregs or after cooling the cured sample.

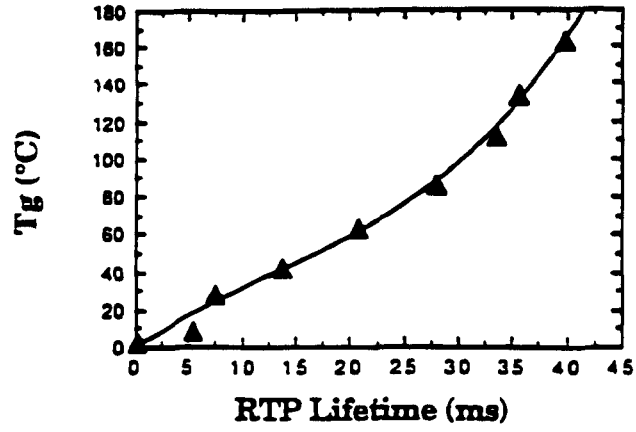


Figure 8. Correlation plots of the RTP lifetime (τ_T) with the glass transition temperature of the stoichiometric DGEBA/DDS epoxy resin.

Acknowledgment. We acknowledge the financial support of this work by the Office of Naval Research and the Army Research Office (Contract DAAL03-92-G-0267) and the National Science Foundation, Polymer Program (Grants DMR 91-08060 and 94-15385).

References and Notes

(1) (a) Song, J. C.; Sung, C. S. P. *Macromolecules* **1993**, *26*, 4818. (b) Song, J. C.; Sung, C. S. P. *Polym. Prep.* (**Am. Chem. Soc., Div. Polym. Chem.**) **1991**, *32* (3), 362.
(2) Yu, J. W.; Sung, C. S. P. *Macromolecules* **1995**, *28*, 2605.
(3) (a) Paik, H. J.; Sung, N. H.; Sung, C. S. P. *Polym. Prep.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32* (3) 669. (b) Paik, H. J.; Sung, N. H. *Polym. Eng. Sci.* **1994**, *34*, 1026.
(4) Guillet, J. E. *Polymer Photophysics & Photochemistry*; Cambridge University Press: Cambridge, U.K., 1985; Chapter 8. pp 209–212.
(5) Itagaki, H.; Horie, K.; Mita, I. *Prog. Polym. Sci.* **1990**, *15*, 361.
(6) Hurtubise, R. J. *Phosphorimetry, Theory, Instrumentation, and Applications*; VCH Publishers Inc.: New York, 1990.
(7) Meijer, E. W.; Zwiers, R. J. M. *Macromolecules* **1987**, *20*, 332.
(8) (a) Kotch, T. G.; Lees, A. J. *Polym. Prep.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32* (1), 124. (b) Kotch, T. G.; Lees, A. J.; Fueniss, S. J.; Papathomas, K.; Snider, R. *Polymer* **1992**, *33*, 657.
(9) Song, J. C.; Sung, C. S. P. *Polym. Mater. Sci. Eng.* **1992**, *67*, 497.
(10) Sawicki, E.; Pfaff, J. *Microchem. J.* **1967**, *12*, 7.
(11) Song, J. C. Intrinsic Luminescence Cure Sensors for Epoxy Resins and Fiber-Reinforced Epoxy Composites. Ph.D. Thesis, University of Connecticut, Storrs, CT, 1993, pp 178–183.
(12) Turro, N. J.; Caminati, G.; Kim, J. *Macromolecules* **1991**, *24*, 4054.

MA950487+