Macromolecules **2001,** *34,* 6202−6205

Photopolymerization of Epoxides with Platinum(II) Bis(acetylacetonato)/Silane Catalysts

Fei Wang and Douglas C. Neckers*

Center for Photochemical Sciences,[†] Bowling Green State University, Bowling Green, Ohio 43403

Received April 26, 2001; Revised Manuscript Received June 28, 2001

ABSTRACT: Photopolymerization of epoxides in the presence of silanes RSi_3H and platinum(II) bis(acetylacetonato) complexes is reported. The catalytic reactivity of the platinum complexes depended on the concentration ratio of silane/platinum complex to monomer and the molecular structure of the silanes, as well as the structure of the platinum complexes. A mechanism is proposed.

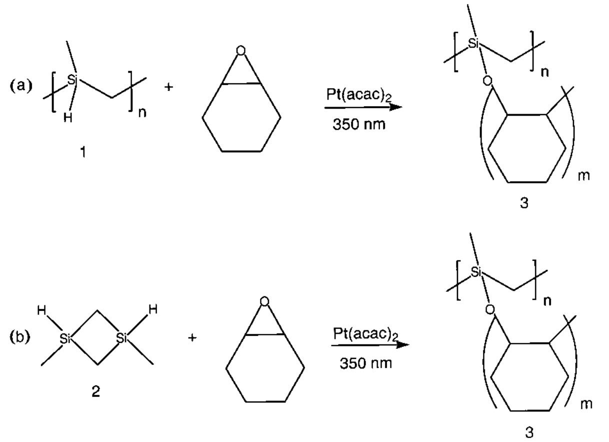
Introduction

The thermal ring-opening polymerization of epoxides using platinum-based complexes such as Ashby, Karstedt platinum catalysts or platinum salts such as $PtCl_2$, H_2PtCl_6 as the initiators and silanes has been reported.[1] Because platinum complexes bearing nonreducible ligands have previously been reported to be inactive for ring-opening polymerization, Crivello suggested that platinum metal colloids function as the active species.[1] Hayase's group had previously reported thermal polymerization of cyclohexene oxide with aluminum acetylacetonato complexes using silanols as the cocatalysts.[2−4] In these systems, catalytic activity depends markedly on the structures of both aluminum complex and the silanol. The strength of the interaction between the aluminum complex and the silanol is also important. A moderate interaction between the aluminum complex and the silanol is required for the complex to serve as an effective catalyst. The suggested mechanism is that cyclohexene oxide is polymerized cationically by a proton derived from the silanol.

There are numerous reports that onium salts containing complex metal halide anions serve as photoinitiators for epoxide polymerization.[5,6] Hayase also reported that *o*-nitrobenzyl triphenylsilyl ether/aluminum compounds can be used as catalysts in the photopolymerization of epoxides.[7,8] The photogeneration of silanols from silyl ether is the photochemical step.

In this paper, we report that platinum(II) bis(acetylacetonato) complexes are efficient photocatalysts for the polymerization of epoxides in the presence of silicon−hydrogen containing silanes. Such polymerization reactions have proven efficient both in the presence and in the absence of oxygen. A homogeneous mechanism is proposed on the basis of the results of studies in the presence of added mercury or the coordinating compound 1,7-octadiene.

Scheme 1



Experimental Section

Materials. Cyclohexene oxide (CHO), styrene oxide, 1,2-epoxy-3-phenoxycyclopentene oxide, phenylsilane, triethylsilane, and nonane were purchased from the Aldrich Chemical Co. UVR6110 was a gift from Union Carbide. 1,3,5,7-Tetramethylcyclotetrasiloxane and hexamethyltrisiloxane were purchased from Gelest Inc. Pt(acac)$_2$ was purchased from Alfa Chemical Co. Pt(hfac)$_2$ [platinum bis(hexafluoroacetylactone)], Pt(tfac)$_2$ [platinum bis(atrifluoroacetylactone)], and Pt(bac)$_2$ [platinum bis(1-phenyl-1,3-butanedione)] were synthesized.[9] 1,3-Dimethyl-1,3-disilacyclobutane and compound **1** in Scheme 1 were synthesized by Dr. Xiaosong Wu.

Instruments. Irradiations were carried out in a Rayonet photochemical reactor (350-nm lamps) equipped with a jacketed beaker (Pyrex). NMR spectra were obtained using a Varian Gemini 200 NMR spectrometer, and chemical shifts are reported in ppm relative to the corresponding deuterated solvents that serve as the internal standards. GPC was performed with a HP 1050 series HPLC equipped with a HP 1047A refractive index and a Plgel 5-μm mixed-C 300 × 7.5 mm column. THF was used as the eluent. Polystyrene standards were obtained from Polysciences. UV−vis spectra were measured on a HP 8452A diode array spectrophotometer. GC measurements were taken with a HP 5890 GC instrument (FID) detector, with a 30-m J&W DB-1 capillary column.

The quantum yield of disappearance of Pt(acac)$_2$ in the presence of $PhSiH_3$ and cyclohexene oxide was determined by measuring the amount of Pt(acac)$_2$ that had reacted at a constant light intensity in a given period of time by measuring the decrease of the 344-nm band in the absorption spectrum of the reaction mixture. Benzophenone/benzhydrol was used as the actinometer.

General Procedures for Polymerization. Polymerizations were carried out in the bulk. In a typical reaction, platinum complex, silane, and monomer were placed together in a 3-mL clear vial in the concentration ratio 10^{-4}:10^{-2}:1. The vial was inserted in a Rayonet reactor and irradiated at 350 nm. Residual cyclohexene oxide was determined by gas chromatography. Nonane was used as the internal standard in the measurement of conversion of polymerization. After polymer-

---

* Corresponding author.

[†] Contribution no. 444 from the Center for Photochemical Sciences.

10.1021/ma010727n CCC: \$20.00

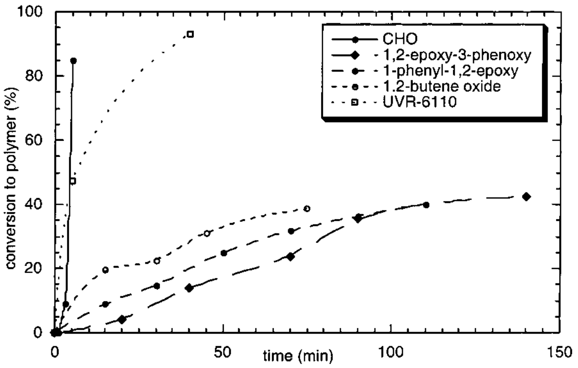


Figure 1. Plots of percent conversion to polymer as a function of irradiation time for various epoxy monomers at 350-nm irradiation. $[Pt(acac)_2]/[monomer] = 1 \times 10^{-4}$, $[PhSiH_3]/[monomer] = 2 \times 10^{-2}$.

ization, the polymer was dissolved in $CHCl_3$, precipitated with MeOH, and dried in a vacuum oven. It was then subjected to NMR and GPC analyses. Inhibition effects were studied by adding mercury or 1,7-octadiene to the reaction mixture.

Results and Discussion

The catalyzed ring-opening polymerization of epoxide monomers takes place when platinum(II) bis(acetylacetonato) complexes and silanes are irradiated with 350-nm light at room temperature ($\Phi_{\mathrm{dis\ Pt(acac)_2}} \approx 0.011$ in CHO monomer). The monomers undergo no reaction when irradiated for 2 h under similar conditions in the absence of either the platinum complex or silane. Identical mixtures remained unchanged when held in the dark for long periods. Cyclic and open-chain epoxy alkanes are more reactive than aromatic epoxides. The conversions of various epoxide monomers as functions of time are shown in Figure 1.

In a typical experiment, the polymerization of cyclohexene oxide was carried out using phenylsilane as the cocatalyst. After the polymer was precipitated with methanol and extraction in a Soxhlet extractor, the polymeric product obtained showed the major peaks attributed to polymer at 1.21, 1.57, 1.85, and 3.35 ppm, with minor peaks at 7.4 and 7.6 ppm belonging to the phenyl group of the phenylsilane (^{1}H NMR). The polymer has a M_n of 18 052 g/mol, a M_w of 30 640 g/mol, and a dispersity is 1.7 (GPC).

Our catalytic system, in contrast to that reported by Crivello,[1] does not initiate the polymerization of vinyl ether monomers. Although platinum(II) bis(acetylacetonato) complexes initiate the polymerization of 1,3,5,7-tetramethylcyclotetrasiloxanes having Si−H bonds when irradiated at 350 nm, they do not initiate the polymerization of hexamethyltrisiloxane in the presence of $PhSiH_3$.

The catalytic system (above) seems effective with any silane containing a Si−H bond. For example, the platinum complexes initiate the polymerization of cyclohexene oxide when irradiated at 350 nm in the presence of polymeric compound **1** (Scheme 1). Within 5 min, a chloroform insoluble cross-linked polymer **3** is formed (path a). 1,3-Dimethyl-1,3-disilacyclobutane also initiates the photopolymerization of cyclohexene oxide (path b) in the presence of platinum complexes. Compound **2** also undergoes ring-opening photopolymerization in the presence of platinum complexes when irradiated at 350 nm.[10] However, it is difficult to determine which process occurs first as the final product is the same as that of path a.

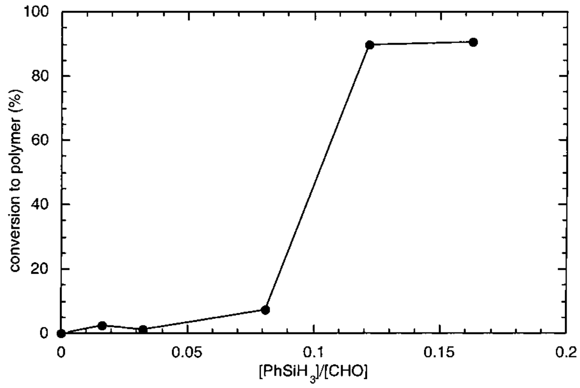


Figure 2. Effect of the relative concentration of phenylsilane on the percent conversion in the polymerization of cyclohexene oxide. Irradiation time is 5 min for each point measurement. $[Pt(acac)_2]/[monomer] = 1 \times 10^{-4}$.

Table 1. Photopolymerization of Cyclohexene Oxide in the Presence of $Pt(acac)_2$ and $HSiEt_3$ or $PhSiH_3$ with 350-nm Irradiation

silane		reaction time	M_w (g/mol)	M_n	polydispersity
Et_3SiH	O_2	1.5 h	29 423	19 532	1.51
	Ar	1.5 h	22 637	15 264	1.48
$PhSiH_3$	Ar	<5 min	30 640	18 052	1.70

The effect of oxygen on a silation reaction depends on whether the catalyst is heterogeneous (platinum metal colloid) or homogeneous (platinum complex). In a study of photoactivated hydrosilylation reactions, Lewis showed that the presence of oxygen is required to generate colloidal platinum of high catalytic activity.[11] Crivello also found that O_2 was catalytic in the thermal ring-opening polymerization in which they proposed a heterogeneous mechanism.[1] Oxygen, however, has no significant effect on the polymerization under the conditions that we report. For cyclohexene oxide, the reaction mixture was degassed and polymerization then carried out either under Ar or under O_2. Both polymerizations have the same rate, and the resulting polymers have similar, although not identical, high molecular weights (Table 1).

Although all Si−H-containing silanes exhibit a cocatalytic effect on epoxide photopolymerization, silanes with a larger number of silicon−hydrogen bonds are better cocatalysts. For instance, it took just a few minutes to complete the polymerization of cyclohexene oxide with phenylsilane as the cocatalyst (Table 1) but 1.5 h to complete the polymerization in the presence of triethylsilane.

Silane and Pt(II) Bis(acetylacetonato) Complexes. Although photopolymerizations of epoxides containing a cocatalytic concentration of silane catalyzed by $Pt(acac)_2$ are quite rapid, the concentrations of both the platinum complex and the silane affect the conversion of cyclohexene oxide to polymer (Figures 2 and 3). The efficiency of the polymerization also depends on the ratio of silane to monomer, as well as the relative concentration of the platinum complex. If [phenylsilane]/[cyclohexene oxide] is maintained at 10^{-2} and [platinum(II) bis(acetylacetonato)]/[cyclohexene oxide] is maintained at 10^{-4}, each platinum complex is identically catalytic, and polymerization is completed in 5 min. However, if [phenylsilane]/[cyclohexene oxide] is maintained at 10^{-3}, the rate of cyclohexene oxide polymerization depends on the structure of the platinum(II) bis(acetylacetonato) complex. The conversion of cyclo-

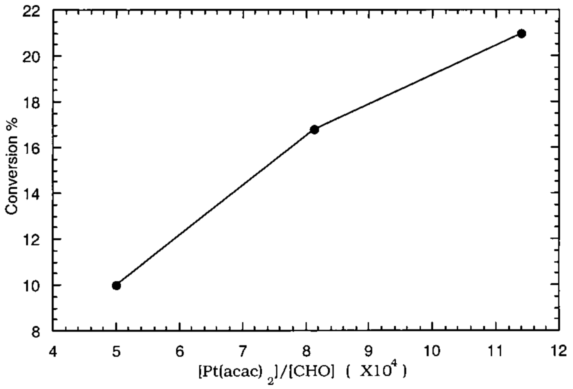


Figure 3. Effect of the relative concentration of Pt(acac)$_2$ on the percent conversion in the polymerization of cyclohexene oxide. Irradiation time is 5 min for each point measurement. [$PhSiH_3$]/[monomer] = 2 × 10^{-2}.

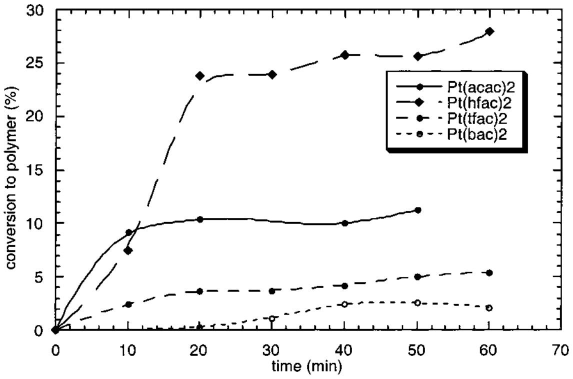


Figure 4. Effect of different platinum complexes on the polymerization of cyclohexene oxide. [$PhSiH_3$]/[monomer] = 2 × 10^{-3}, [Pt complexes]/[monomer] = 2 × 10^{-4}.

hexene oxide to polymer at fixed ratio of phenylsilane to monomer with different platinum complexes as catalysts as a function of time is shown in Figure 4. The structures of the silane and the platinum complex are also important. Pt(hfac)$_2$ is a better catalyst than Pt(acac)$_2$. Pt(bac)$_2$ is the poorest catalyst.

Mechanism. Platinum(II) bis(acetylacetonato) complexes are known to be active catalysts for photoactivated hydrosilylation reactions.[12] Hydrosilylation occurs if one irradiates the platinum complexes in the presence of hydrosilane and olefin. The same reaction results from irradiation of the platinum complexes with either hydrosilane or olefin alone, followed by the addition of the other reactant. Ring-opening polymerization of the epoxide occurs under similar conditions, that is, upon irradiation of the platinum complex with the silane and the monomer or upon irradiation of the platinum complex and silanes alone, followed by addition of the monomer. In the former case, one observes a short induction period. In the second case, a brown solution forms, and polymerization occurs without an induction period immediately after addition of monomer. This suggests, as we have previously reported,[13] that, upon irradiation of the platinum complexes in the presence of silanes, an active species is formed. In hydrosilylation reactions, this initially obtained photoproduct can be observed using both UV−vis and ^{1}H NMR spectroscopy following irradiation of platinum(II) bis(acetylacetonato) complexes with silanes or olefins.[9] We have previously isolated the photoproduct of Pt(hfac)$_2$ and ethylene.[13] Therefore, we assume that a similar reaction intermediate is formed and that the same reaction mechanism is operative in the current experiments.

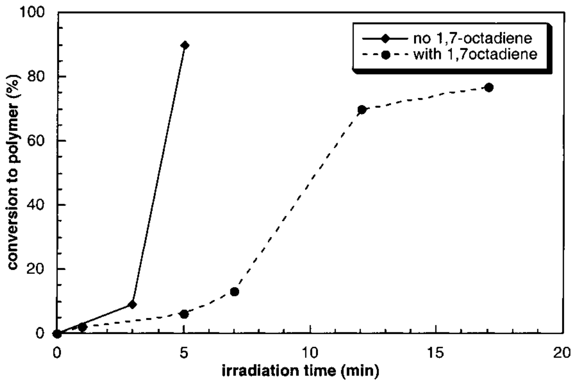


Figure 5. Effect of 1,7-octadiene on the polymerization of cyclohexene oxide with Pt(acac)$_2$ and $PhSiH_3$ as catalysts.

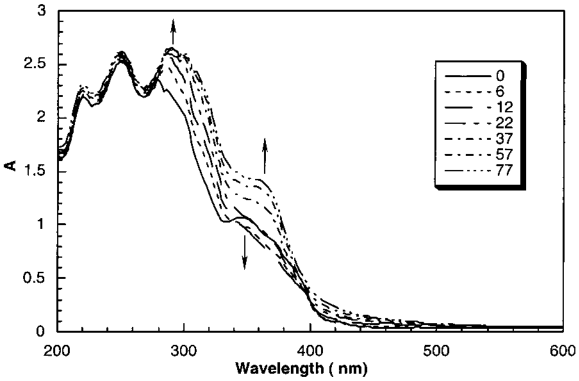


Figure 6. Photoreaction of Pt(acac)$_2$ with phenylsilane and cyclohexene oxide (time/min) followed by UV/vis spectroscopy.

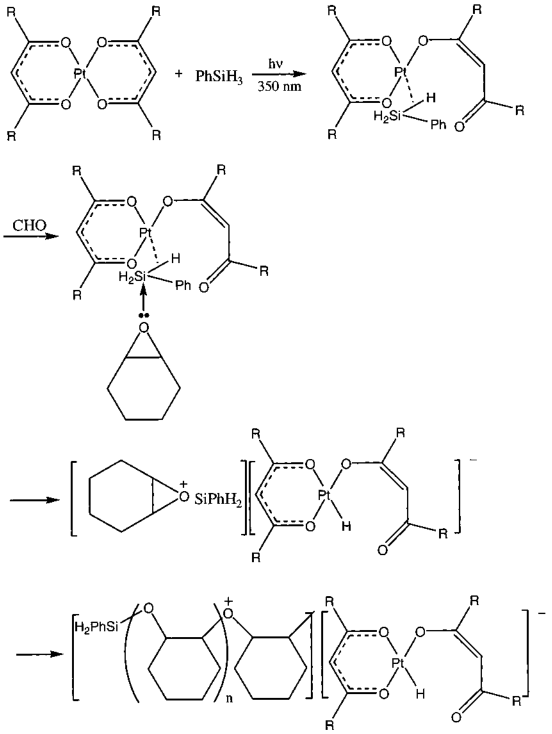
Inhibitor Experiments. A mixture of 6 mg (0.015 mmol) of Pt(acac)$_2$ and 0.2 mL (1.6 mmol) of phenylsilane was added to each of two separate glass vials. Both mixtures were irradiated at 350 nm for 1 min, and formation of a brown solution was observed. Two drops of mercury were added to one of the vials, and both reaction mixtures were stirred at room temperature for 20 h. After that, approximately 1 g. (0.01 mol) of cyclohexene oxide was added to both vials. Vigorous, exothermic polymerization was observed immediately in both cases.

1,7-Octadiene is a known inhibitor for hydrosilylation reactions occurring under homogeneous conditions.[8] When 1,7-octadiene (0.6 mmol) is added to the reaction mixture including Pt(acac)$_2$ (0.005 mmol), $PhSiH_3$ (0.8 mmol), and cyclohexene oxide (0.012 mol), the polymerization goes much more slowly than does that of a mixture that does not contain 1,7-octadiene (Figure 5). This implies that a homogeneous catalyst that reacts with the diene is being formed in the system.

The lowest-energy allowed transition for Pt(acac)$_2$ at 344 nm is assigned mainly to a ligand-localized $\pi-\pi^*$ transition. We used UV−vis spectra to follow the photochemical reaction of cyclohexene oxide, Pt(acac)$_2$, and phenylsilane in CH_2Cl_2 solution in the presence of air (Figure 6). During the irradiation, the 344-nm band disappeared, and two new bands at 350 and 300 nm appeared. After several minutes of irradiation, the baseline of the UV absorption spectrum became elevated, and the solution turned yellow.

When Lewis bases such as pyridine and ether are added to the brown solution formed upon irradiation, a

Scheme 2



vigorous reaction occurs, and the mixture releases copious quantities of gas that we presume to be hydrogen. No polymerization is observed after the prepolymer system is mixed with these Lewis bases.

^1H NMR and ^{19}F NMR spectroscopies were also used to follow the photoreaction. A mixture of $Pt(acac)_2$ and phenylsilane in $CDCl_3$ was irradiated, and the ^1H NMR spectrum was measured at 30-min intervals. Several new peaks that we could not assign appeared at 4.6, 4.9, and 5.1 ppm, and no intermediate could be isolated. After irradiation, GC/MS showed that phenylsilane was still the main constituent of the reaction mixture. Several smaller peaks belonging to diphenylsilane and 1,2-diphenyldisilane were also observed.

After irradiation of $Pt(hfac)_2$ for 5 min with phenylsilane in $CDCl_3$ $\{[Pt(hfac)]_2/[Ph_3SiH] = 1 \times 10^{-2}\}$, a brown solution again formed. Three new peaks with chemical shifts at −74.57, −79.42, and −79.67 ppm were observed by ^{19}F NMR spectroscopy. These peaks are in addition to that at −73.32 ppm belonging to starting material, $Pt(hfac)_2$. Following the addition of cyclohexene oxide, the three new peaks were high-field-shifted presumably because of the high concentration of CHO and showed chemical shifts at −75.16, −79.96, and −80.20 ppm, respectively. The peak belonging to $Pt(hfac)_2$ had disappeared, and no free ligand (hfac) was observed.

We conclude therefore that, during the irradiation of the absorbing $Pt(hfac)_2$ with phenylsilane $\{[Pt(hfac)_2]/[Ph_3SiH] = 1 \times 10^{-2}\}$, an active intermediate that cannot be isolated is formed, and it is this intermediate that initiates cyclohexene oxide polymerization. The addition of cyclohexene oxide $\{[Pt(hfac)_2]/[CHO] = 10^{-4}\}$ to the irradiated solution apparently forces the reaction to go further, and the NMR spectra show that all of the platinum complex is converted to a final product. The polymerization also resembles a living polymerization in that, if more monomer is added to the irradiated solution, polymerization continues after a time.

On the basis of these studies, we postulate that, upon irradiation, Pt(II) acetylacetonate complexes form an intermediate with phenylsilane making the silane more electrophilic. The lone electron pair of a donor is presumably donated to an empty orbital of silicon.[14−16] In the case of cyclohexene oxide, this forms a cationic center that subsequently initiates polymerization (Scheme 2). This intermediate cannot be isolated. Immediately after irradiation, the GC/MS signals of the reaction mixture show only peaks belonging to starting materials, probably because of decomposition under GC/MS conditions.

Conclusion

Platinum(II) bis(acetylacetonato) complexes have been discovered to be efficient photoinitiators for the polymerization of epoxides in the presence of silanes containing silicon−hydrogen bonds. A homogeneous, cationic polymerization mechanism is proposed. Studies of these platinum(II) bis(acetylacetonato) complexes as photoinitiators are continuing.

Acknowledgment. We thank the National Science Foundation Division of Materials Research (DMR) for financial support of this work. We also thank Dr. Huiying Li and Ms. Haiyan Gu for helpful discussions.

References and Notes

(1) Crivello, J. V.; Fan, M. J. *Polym. Sci. A: Polym. Chem.* **1991**, *29*, 1853.
(2) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *J. Polym. Sci. A: Polym. Chem.* **1982**, *20*, 3155.
(3) Hayase, S.; Ito, T.; Suzuki, S.; Wada, M. *J. Polym. Sci. A: Polym. Chem.* **1981**, *19*, 2185.
(4) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *J. Polym. Sci. A: Polym. Chem.* **1983**, *21*, 467.
(5) Manivannan, G.; Fouassier, J. P.; Crivello, J. V. *J. Polym. Sci. A: Polym. Chem.* **1992**, *30*, 1999.
(6) Crivello, J. V.; Liu, S. *Chem. Mater.* **1998**, *10*, 3724.
(7) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *J. Polym. Sci. A: Polym. Chem.* **1987**, *25*, 753.
(8) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Macromolecules* **1985**, *18*, 2777.
(9) Guo, A.; Fry, B. E.; Neckers, D. C. *Chem. Mater.* **1998**, *10*, 531.
(10) Wu, X.; Neckers, D. C. *Macromolecules* **1999**, *32*, 6003.
(11) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.
(12) Lewis, F. D.; Miller, A. M.; Salvi, G. D. *Inorg. Chem.* **1995**, *34*, 3173.
(13) Wang, F.; Wu, X.; Pinkerton, A. A.; Kumaradhas, P.; Neckers, D. C. *Inorg. Chem.* **2001**, manuscript submitted.
(14) Olah, G. A.; Li, X.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 8962.
(15) Arshadi, M.; Johnel, D.; Edlund, U.; Ottosson, C.; Crener, D. *J. Am. Chem. Soc.* **1996**, *118*, 5220.
(16) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191.

MA010727N