Dendritic Macrophotoinitiator Containing Thioxanthone and Coinitiator Amine

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Introduction. Photopolymeriztion science and technology have assumed an increasing relevance in many applications.[1−3] This technology is based on the use of photoinitiator systems suited to absorb a light to produce primary radical species, which are able to initiate polymerization. To get photoinitiator systems of high performance, one of the most important ways is to develop macrophotoinitiator,[4−12] which have two kinds of free radical photoiniaitors: photofragmentation (type I photoinitiators) and hydrogen abstracting chromophores (type II photoinitiators). Among them, thioxanthone is one of the most widely used bimolecular photoinitiators in vinyl polymerizations, and its photoinitating activity can be promoted by the presence of hydrogen donor amine.[13−20]

Low-molecular-weight amine, however, has its intrinsic disadvantages such as odor, toxicity, and migration in UV-curing technology. Dendritic poly(propyleneimine) (PPI) is a highly branched, well-defined macromolecule with a number of interesting characteristics and can be used as a hydrogen donor because of its high density of amino groups.[21−23] The introduction of thioxanthone into PPI can lead to the novel dendritic macrophotoinitiator, which has obvious advantages such as intramolecular reactions responsible for the formation of more reactive species and protecting the active species by macromolecular chain due to the macromolecular effect.[5]

In this context, we synthesized dendritic macrophotoinitiators through introducing thioxanthone moieties into PPI (generations 1.0 and 5.0). Then we studied the photopolymerization of acrylamide by these macrophotoinitiators and low-molecular-weight model compounds to evaluate the photoinitiation properties.

Experimental Section. (a) Materials. Thiosalicylic acid (from Fluka); poly(propyleneimine) (DAB-4 and DAB-64, from Aldrich); acrylamide (AM), diethylamine (DEA), and triethylamine (TEA) (from Chinese Medicine Group); 2-(2,3-epoxy)propoxylthioxanthone (synthesized according to ref 23). Epichlorohydrin was purified by refluxing with calcium hydroxide and redistilled. Other chemicals are of analytical grade except as noted.

(b) Synthesis of DAB-4-TX and DAB-64-TX. A mixture of 1.0 g (3.52 mmol) of 2-(2,3-epoxy)propoxylthioxanthone, 0.284 g (0.9 mmol) of DAB-4 or 0.40 g (0.058 mmol) of DAB-64, and 40 mL of ethanol was stirred at 40 °C for 12 h and then filtered through a thin layer of activated charcoal after cooling. The filtrate was evaporated to remove ethanol, and the residue was dissolved with diluted hydrochloric acid and washed with benzene. Ammonia was used to adjust the pH value of the aqueous solution to 8−9, and the solution was extracted with chloroform. The chloroform solution was dried over anhydrous calcium chloride and partly evaporated and then was poured into 10-fold benzinum. The precipitate was filtered to give product, which was dried in vacuo to obtain dendritic macrophotoinitiators.

DAB-4-TX: yield ratio: 91%; UV, $\lambda_{\max} = 399$ nm; $\epsilon = 4196$ L mol^{-1} cm^{-1}; melting point: 88 °C. Elemental analysis $C_{80}H_{88}N_6O_9S_4$: Calcd, C 66.11, H 6.06, N 5.78, S 8.81. Found, C 65.65, H 6.24, N 5.68, S 8.65. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.55-7.11$ (28H, aromatic), 4.20−3.98 (12H, −OCH$_2$, −OCH), 2.82−2.25 (28H, NH−CH$_2$, N−CH$_2$), 1.78−1.60 (10H, −CH$_2$−). FT-IR (KBr): 3419 (O−H, N−H), 2933, (C−H), 1630 cm^{-1} (C═O).

DAB-64-TX: yield ratio: 89%; UV, $\lambda_{\max} = 403$ nm; $\epsilon = 3895$ L mol^{-1} cm^{-1}. Elemental analysis: Calcd, C 68.21, H 6.64, N 7.65, S 8.75. Found, C 63.60, H 6.97, N 7.25, S 7.13. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.31-6.99$ (7H, aromatic), 4.20−3.98 (3H, −OCH$_2$, −OCH), 2.82−2.25 (11H, NH$_2$−CH$_2$, NH−CH$_2$, N−CH$_2$), 1.78−1.50 (5H, −CH$_2$−). FT-IR (KBr): 3419 (O−H, N−H), 2933, (C−H), 1630 cm^{-1} (C═O).

(c) Photopolymerization. Photopolymerization kinetic studies were performed dilatometerically in a recording dilatometer (according to ref 19) by irradiating about 12 mL of 1.0 M AM dimethyl sulfoxide (DMSO) solution at 30 °C. The concentration of photoinitiator is 0.001 M. The light source was a high-pressure Hg lamp (400 W), set at a distance of 40 cm from the sample. The polymerization rate (R_p) was determined below 10% conversion where R_p is almost independent of the conversion. The produced polymer was precipitated with methanol, filtered, and dried in vacuo.

(d) Analysis. The concentration of photoinitiator system is in terms of TX moieties, and the molar ratio of ETX/DEA/TEA in the low-molecular-weight photoinitiator systems is always 1:1:1 in all following measurements.

Molecular weights were determined by gel permeation chromatography (GPC) on a Perkin-Elmer Series 200 apparatus on the basis of linear polyglycol standards using water as eluent.

^{1}H NMR spectra were recorded on a Mercury Plus 400 Hz spectrometer with $CDCl_3$ as solvent.

FT-IR spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer. The samples were prepared as KBr disk.

Elemental analysis was conducted on an Elementar Varioel apparatus.

UV−vis spectra were recorded in ethanol solution by a Perkin-Elmer Lambda 20 UV−vis spectrophotometer (concentration = 5×10^{-5} mol L^{-1} in terms of thioxanthone moieties)

Fluorescence spectra were recorded in ethanol solution by a Perkin-Elmer LS50B luminescence spectrophotometer (concentration = 2×10^{-5} mol L^{-1} in terms of thioxanthone moieties, $\lambda_{ex} = 400$ nm).

Results and Discussion. DAB-4-TX and DAB-64-TX were synthesized according to Scheme 1, and the structures were confirmed by FT-IR, ^{1}H NMR spectra, and elemental analysis. Compared with ETX, the disappearance of the signals related to the epoxy group in the FT-IR and ^{1}H NMR spectra was considered as evidence of completion of the addition reaction. The

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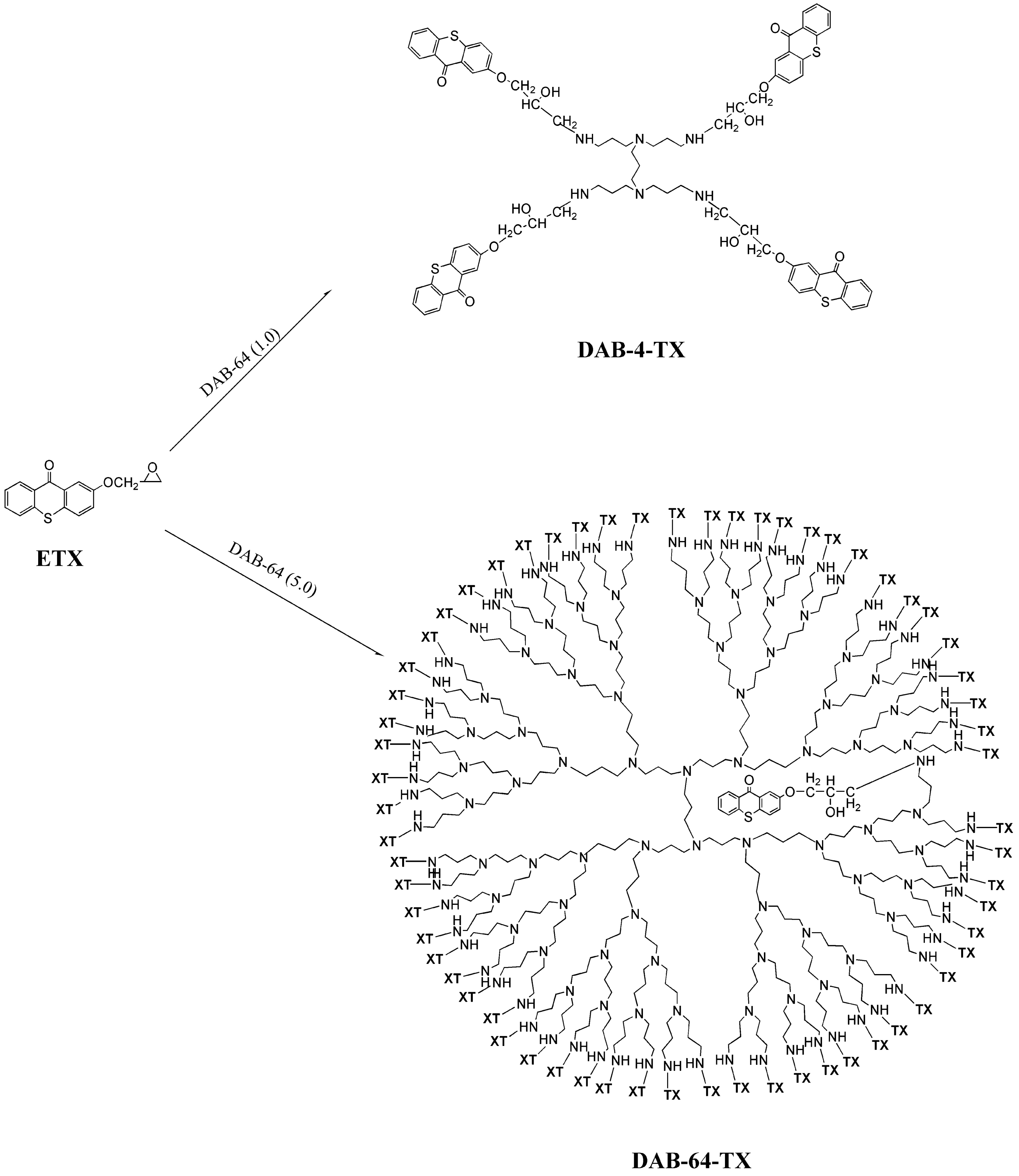
Scheme 1



component of DAB-64-TX was determined by the elemental analysis data (nitrogen content/sulfur content) and ^{1}H NMR spectrum (signal related to benzene ring/signal related to $-CH_2$). The analysis results showed that about 90% $-NH_2$ group of DAB-64 reacted with the epoxy group of ETX. Compared with DAB-4-TX, the δ values for the aromatic proton of DAB-64-TX upfield shifted (Figure 1). The upfield shift for one of the aromatic protons from 8.55 to 8.31 ($\Delta\delta = 0.24$) was observed. This may be addressed to the dendritic effect[24] of DAB-64-TX. The peripherial TX moieties of DAB-64-TX may enter into the interior of dendrimer because a DAB-64-TX molecule have cavities inside, just like a "dendritic box", and may offer possibilities for host−guest interaction [21,25,26] (seen in Scheme 1). This may lead to the surrounding of TX moieties by high intensity for electric donor of amino groups, microenvironment of the higher electronic intensity, and the upfield shift of the aromatic proton with respect to DAB-4-TX.

UV−vis absorption spectra of DAB-64-TX, DAB-4-TX, and ETX/TEA/DEA in ethanol are shown in Figure 2a. They exhibit the usual characteristic absorption of

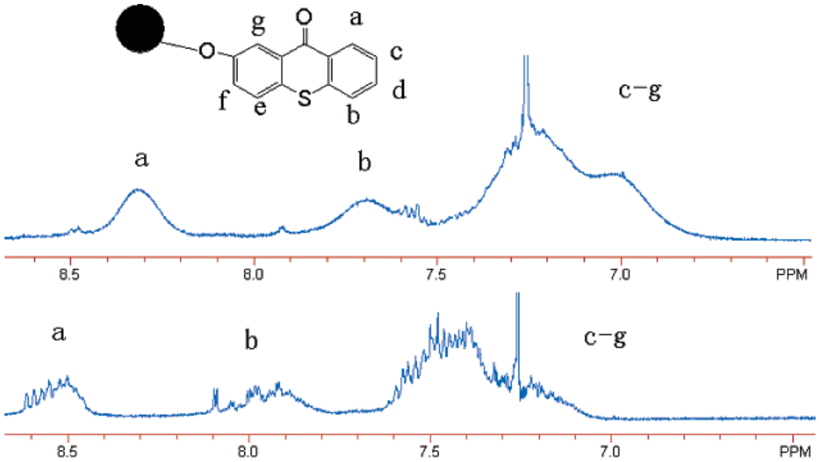


Figure 1. ^{1}H NMR spectra of DAB-4-TX and DAB-64-TX (using $CDCl_3$ as solvent).

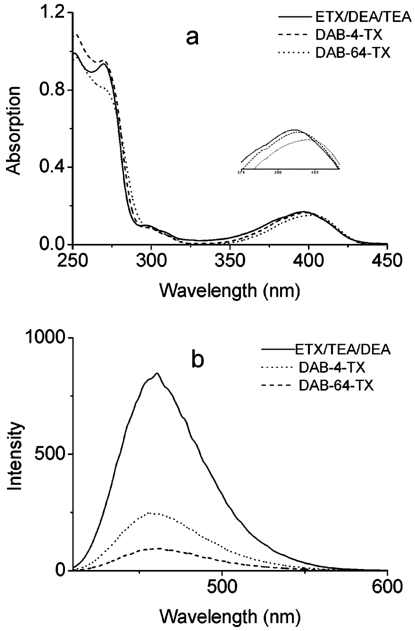


Figure 2. (a) UV−vis absorption spectra (concentration = 5 × 10^{-5} mol L^{-1} in terms of thioxanthone moieties). (b) Fluorescence spectra (concentration = 2 × 10^{-5} mol L^{-1} in terms of thioxanthone moieties, λ_{ex} = 400 nm) for ETX/TEA/DEA, DAB-4-TX, and DAB-64-TX in ethanol solution.

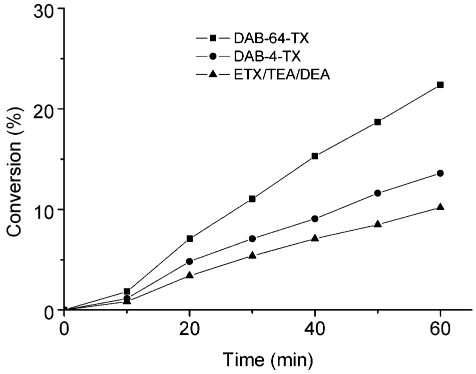


Figure 3. Conversion vs time curves for the polymerization of AM in DMSO solution photoinitiated by ETX/TEA/DEA, DAB-4-TX, and DAB-64-TX at 30 °C. The photoinitiator concentration is 0.001 M in terms of thioxanthone moieties, and [AM] is 1 M.

thioxanthone, and DAB-64-TX possesses an absorption similar to DAB-4-TX and ETX/TEA/DEA, which shows that the dendritic macromolecular structure has not significant influence on UV−vis absorption of thioxanthone moieties of DAB-64-TX. The maximum of absorption (λ_{max}) of ETX/TEA/DEA, DAB-4-TX, and DAB-64-TX, however, is different and found to be 396, 399, and 403 nm, respectively. Compared with DAB-4-TX and ETX/TEA/DEA, the intensity of fluorescence of DAB-64-TX decreases obviously according to Figure 2b. This indicates that the most effective energy transfer happens between the excited state of TX moieties and coinitiator amine in DAB-64-TX. Because of the dendritic effect, TX moieties are surrounded by the amino group of high intensity in DAB-64-TX, and the excited state of TX chromohpores is quenched by the amine most effectively and the microenvironment of TX moieties more polar. Consequently, the absorption maximum of DAB-64-TX red-shifted and the fluorescent emission is the weakest. This is in good agreement with the ^{1}H NMR measurements. The emission of DAB-4-TX is weaker than that of ETX/TEA/DEA due to the effective intramolecular quenching and antenna effect[27−29] in DAB-4-TX, which did not exist in ETX/TEA/DEA.

The photolysis of thioxanthone, in the presence of hydrogen donors such as amines and thiols, leads to the formation of a radical produced from carbonyl compound (ketyl-type radical) and another radical derived from the hydrogen donor amine.[30] The photopolymerization of vinyl monomers is usually initiated by the amine radicals, and the ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. Thus, the number of and type of active amine radical determine the photopolymerization rate. Figure 3 shows conversion of AM vs time for three types of photoinitiator systems. As can be seen, DAB-64-TX is the most efficient photoinitiator and ETX/DEA/TEA is the least. Two factors may be responsible for this result. Compared with low-molecular-weight photoinitiator systems of ETX/TEA/DEA and DAB-4-TX, the larger local concentration of coinitiator amine in the DAB-64-TX accelerates the energy transfer between the excited state of TX and amine (can also be seen in Figure 2), resulting in a larger amount of amine radical. The larger photopolymerization rate of DAB-4-TX than that of ETX/DEA/TEA may be due to quicker energy transfer.

In conclusion, DAB-64-TX is an efficient photoinitiator for free radical polymerization. This dendritic macrophotoinitiator containing in-chain thioxanthone and coinitiator amine initiates the polymerization much more efficiently than the low-molecular-weight model compound. Photophysical and photochemical properties and conformation of DAB-64-TX in aqueous solution are now under investigation.

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References and Notes

(1) Fouassier, J. P. *Photoinitiation, Photopolymerization, and Photocuring Fundamentals and Applications*; Hanser: New York, 1995.
(2) Roffy, C. *Photogeneration of Reactive Species for UV-Curing*; Wiley: New York, 1997.
(3) Decker, C. *Prog. Polym. Sci.* **1996**, *21*, 593.
(4) Angiolini, L.; Caretti, D.; Salatelli, E. *Macromol. Chem. Phys.* **2000**, *201*, 2646.
(5) Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. *J. Photochem. Photobiol. A: Chem.* **2003**, *159*, 103.
(6) Sarker, A. M.; Sawabe, K.; Strehmel, B.; Kaneko, Y.; Neckers, D. C. *Macromolecules* **1999**, *32*, 5203.
(7) Angiolini, L.; Caretti, D.; Corell, E.; Carlini, C.; Rolla, P. A. *J. Appl. Polym. Sci.* **1997**, *64*, 2247.
(8) Carlini, C.; Angiolini, L.; Caretti, D.; Corell, E.; Rolla, P. A. *Polym. Adv. Technol.* **1997**, *7*, 379.
(9) Ajayaghosh, A. *Polymer* **1995**, *36*, 2049.
(10) Degirmenci, M.; Hizal, G.; Yagci, Y. *Macromolecules* **2002**, *36*, 8265.
(11) Angiolini, L.; Caretti, D.; Carlini, C.; Corell, E.; Salatelli, E. *Polymer* **1999**, *40*, 7197.
(12) Castelvtro, V.; Molesti, M.; Rolla, P. *Macromol. Chem. Phys.* **2002**, *203*, 1486.
(13) Corrales, T.; Peinado, C.; Catalina, F.; Neumann, M. G.; Allen, N. S.; Rufs, A. M.; Encinas, M. V. *Polymer* **2002**, *41*, 9103.
(14) Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S.; Rufs, A. M.; Bueno, C.; Encinas, M. V. *Polymer* **2002**, *43*, 4591.
(15) Aydin, M.; Arsu, N.; Yagci, Y. *Macromol. Rapid Commun.* **2003**, *24*, 718.
(16) Valderas, C.; Bertolotti, S.; Previtali, C. M.; Encinas, M. V. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2888.
(17) Cokbaglan, L.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2003**, *36*, 2649.
(18) Yang, J. W.; Zeng, Z. H.; Chen, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2563.
(19) Jiang, X. S.; Yin, J. *Macromol. Rapid Commun.* **2004**, *25*, 748.
(20) Yang, J. W.; Zeng, Z. H.; Chen, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2563.
(21) Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489.
(22) Tsuda, K.; Dol, G. C.; Gensh, T.; Hofkens, J.; Latterini, L.; Weener, J. W.; Meijer, E. W.; De Schryver, F. C. *J. Am. Chem. Soc.* **2000**, *122*, 3445.
(23) Salmon, A.; Jutzi, P. *J. Organomet. Chem.* **2001**, *637*, 595.
(24) Vogtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. *Prog. Polym. Sci.* **2000**, *25*, 987.
(25) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.
(26) Morgan, M. T.; Carnahan, M. A.; Ribeiro, A. A.; et al. *J. Am. Chem. Soc.* **2003**, *125*, 15485.
(27) Kuroda, Y.; Sugou, K.; Sasak, K. *J. Am. Chem. Soc.* **2000**, *122*, 7833.
(28) Berberan-Santos, M. N.; Choppinet, P.; Fedorov, A.; Jullien, L.; Valeur, B. *J. Am. Chem. Soc.* **2000**, *122*, 11876.
(29) Sugou, K.; Sasaki, K.; Kitajima, K.; Iwaki, T.; Kuroda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1182.
(30) Anderson, D. G.; Davidson, R. S.; Elvery, J. J. *Polymer* **1996**, *37*, 2477.

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