Anionic Photopolymerization of Methyl 2-Cyanoacrylate and Simultaneous Color Formation

Viktor V. Jarikov and Douglas C. Neckers*

Center for Photochemical Sciences,[1] Bowling Green State University, Bowling Green, Ohio 43403

Received July 11, 2000

ABSTRACT: Anionic polymerization of methyl 2-cyanoacrylate initiated by photoinduced heterolysis of crystal violet leuconitrile (CVCN) and of malachite green leucohydroxide (MGOH) is demonstrated. Polymerization is accompanied by color formation.

Introduction

The past two decades have seen dramatic advances in the application of photochemical processes in the preparation of materials for coatings, surface modification and combinatorial processes, integrated circuits, data storage, digital optical recording, stereolithography, holography, and chemical sensors based on fiber optics.[2−4] Many systems used in such processes involve radiation curing. The most common monomers are acrylates, and these are polymerized by radical chain reactions.[5] Though photoinduced cationic polymerizations[6] now contribute ∼10% market share, reports of photoinduced anionic polymerizations are rare.[7−10] Photoinitiated anionic polymerizations have been briefly reviewed.[11−14]

For some years we have been interested in concomitant polymerization and selective coloration.[4,15] The notion is to selectively color individual volumes of photopolymers concomitantly with their formation. As in the case of a 2D color photograph, the idea is to produce an authentic color replica but to do so in three dimensions. Our initial objective was to selectively color volumes in stereolithography models so that they could be specifically identified.

Simultaneous free radical polymerization of acrylates and color formation from leucolactones of triarylmethane (TAM) dyes has already been successfully demonstrated with oxidizing agents such as iodonium salts[15−17] and is commercial. In such reactions, the photon-absorbing lactone becomes an electron donor in the excited state, and the initial reaction is electron transfer to the iodonium salt. Subsequent reactions convert the reduced iodonium salt to radicals and the lactone radical cation to the colored cation. A similar process, which forms color and radicals, can be accomplished via oxidation of TAM leuco dyes by halogenated hydrocarbons.[18−20] Leucolactones have also been reported to be opened photochemically by irradiating an acid generator such as anthracene-bound sulfonium salt and 2,6-dinitrobenzyl tosylate[21] in their presence.[15] Resins that can be colored and cured in a single photoinduced step may find numerous applications. The formation of a colored shaped plastic is especially desirable in those applications where color visualization is critical.[22−24]

It is well-known that TAM dyes can be prepared by direct irradiation of colorless leuconitriles, leucocarbinols, and leucoethers since this leads to heterolysis (ionization).[20,25,34] This is a ubiquitous phenomenon in that structurally similar xanthene and acridine leuco dyes undergo a similar process. We surmised, therefore, that the photoinduced heterolytic cleavage of the dye-leaving group (dye-LG) bond in colorless nitriles, carbinols, thiols, ethers, esters, azides, ammonium salts, phosphonium salts, and the like could be employed in the simultaneous generation of color and a reactive nucleophilic species:

$$\mathrm{Ar_3C{-}LG} + h\nu \rightarrow \mathrm{Ar_3C^+} + \mathrm{LG^-}$$

or

$$\mathrm{Ar_3C{-}LG^+X^-} + h\nu \rightarrow \mathrm{Ar_3C^+X^-} + \mathrm{LG}$$

where Ar_3C^+ = R_2N-substituted TAM, xanthene, or acridine dye and LG^- = CN^-, $^-CH_2COR$, HO^-, HS^-, RO^-, RS^-, $RCOO^-$; LG = pyr, NR_3, SR_2, PR_3 and X^- = BF_4^-, AsF_6^-, ClO_4^-.

Nucleophiles such as CN^-, RO^-, NR_3, and PR_3 are known to polymerize cyanoacrylates, cyanoacetylene, acrolein, acrylonitriles, formaldehyde, *N*-phenylmaleimide, propiolaldehyde, isocyanates, epoxides, methacrylates, nitrostyrene, *N*-alkenamide, methacrylamide, crotonaldehyde, dialkylmethylenemalonate, *N*-acylethylene imine, cyanoformamidyl, etc.[26] Thiolates and malonates act as initiators for the polymerization of *n*-butyl acrylate.[27] Since most of the nucleophiles that can be generated by the heterolysis of TAM leuco dyes are known to initiate anionic polymerization with appropriate monomers, we thought this is a route to photoinitiated anionic polymer formation.[20]

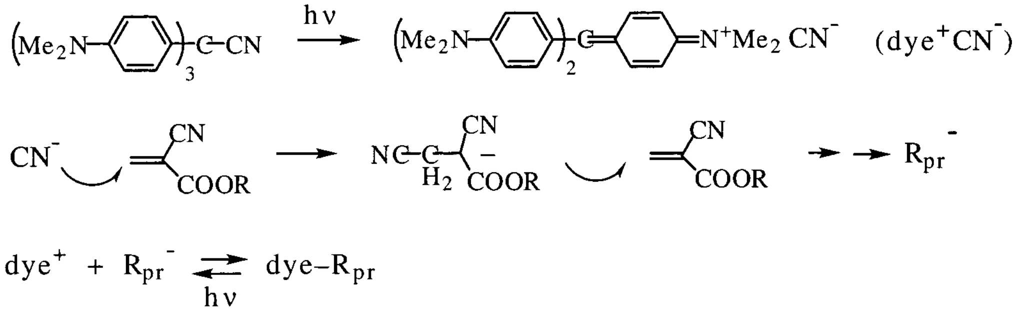
As we have indicated, literature reports of anionic photopolymerization are rare. It was reported that photogeneration of thiocyanate[8] from $K^+[Cr(NH_3)_2(NCS)_4]^-$, pyridine[10] from $W(CO)_5py$, PPh_3 and 2-methylpyridine from heterolytic decomposition of phosphonium and *N*-ethoxy-2-methylpyridinium salts, respectively,[7] and $acac^-$ from $Pt(acac)_2$[9] led to a rapid polymerization of neat cyanoacrylate monomer. Photogeneration of bases such as amines has been utilized for base-catalyzed polymerizations and cross-linking.[28] There are no commercial applications of anionic photopolymerization of which we are aware. Scheme 1 exemplifies how the anionic polymerization of cyanoacrylate might be induced via photoheterolysis of a leuco dye such as CVCN.

Results and Discussion

Photogeneration of CN^- and OH^- in Methyl 2-Cyanoacrylate (M-2-CA). Photolysis was conducted

10.1021/ma0012090 CCC: $19.00

Scheme 1. Anionic Polymerization of Cyanoacrylate via the Photoionization of CVCN (NB: in the Absence of H$^+$ Donors Such as Water, Alcohol, etc.)



in NMR tubes in a Rayonet photoreactor (λ_{exc} = 280−320 nm, Pyrex glass filter) and was followed by NMR with TMS as an internal standard. Irradiation of a solution of M-2-CA, CVCN, and SO_2 in $CDCl_3$ (0.09, 4.5 × 10^{-3}, and 4 × 10^{-5} M, respectively; 5 h) led to total conversion of CVCN into CV$^+$. Since the monomer concentration decreased only by one-quarter and all of CVCN was converted to CV$^+$CN$^-$ (5 mol % with respect to the monomer), this implied that 25% of the M-2-CA was converted, on average, into pentamers. On the other hand, photolysis of M-2-CA and CVCN (0.1 and 5 × 10^{-3} M) in $CDCl_3$ in the presence of CD_3OD (0.28 M) led to the conversion of half of the monomer, indicating formation, on average, of decamers. In this case, the initiating species could be either CN$^-$ or CD_3O^-. It is well-known that leuco dyes such as CVCN undergo photooxidation in the presence of halogenated solvents,[18,20] so $CDCl_3$ was a poor choice of solvent since one generates CV$^+$Cl$^-$ in lieu of CV$^+$CN$^-$. With Cl$^-$ being substantially less nucleophilic/basic than CN$^-$, polymerization is sure to be less efficient.

Similar experiments with malachite green leucohydroxide instead of CVCN produced rapid thermal polymerization (~5 min) upon addition of MGOH (5 × 10^{-3} M) to the 0.1 M solution of M-2-CA in $CDCl_3$. However, a similar solution in benzene-d_6 was thermally stable. Subsequent 2 h photolysis led to complete disappearance of both monomer and the leucohydroxide and extensive dark-green precipitate. Presumably, MG$^+$-dyed cyanoacrylate polymer was formed. The yield of the polymer was 97 wt %, and it had a MW of 2 × 10^3 (PDI ~ 3.5) as determined by GPC. The main peak had a broad shoulder centered at ~6 × 10^3. Complete conversion of the monomer may be attributed to the greater nucleophilicity of OH$^-$. In control reactions carried out under identical conditions in the absence of CVCN or MGOH, there was no significant decrease of M-2-CA concentration. The intensely colored dark-green precipitate was filtered, and the color did not exhibit any visual fading for a few weeks while stored in room atmosphere in the absence of light. The fading of color was notably accelerated when the precipitate was exposed to room light, which is consistent with poor light fastness of malachite green dye. The color of the polymer disappeared even faster upon dissolution in acetone or acetonitrile. This is expected on the basis of the known thermal and photoinduced reactions of MG$^+$ with nucleophiles and oxygen.

Homolysis of the dye−LG bond competes with heterolysis, and both are singlet excited-state reactions.[20,25] The relative amount of each reaction is solvent-dependent because heterolysis is strongly affected by the polarity of the environment. Thus, M-2-CA might have been polymerized by both radical[29] and anionic mechanisms in less polar solvents. However, our previous work suggested that homolysis is either inefficient or followed by a rapid in-cage recombination of the singlet radical pair.[20,30] Hence, the radical mechanism is likely to be of decreased importance.

Effect of CV$^+$ on Polymerization of M-2-CA. Na$^+$ and Li$^+$ are generally the countercations in anionic thermal polymerizations. Since both the free anion and the ion pair are thought to contribute to chain propagation, one anticipates that the countercation plays an important role.[31] This is confirmed by the work of Warmkessel, who showed that the relative rate of termination of anionic polymerization (the ratio of rate constants of termination and propagation) decreases from Li$^+$ to Cs$^+$.[32] In another recent investigation, metal-free anionic polymerization of MMA initiated in the presence of the bulky countercation tetraphenylphosphonium produced excellent results.[31] In our case TAM, xanthene, or acridine dye cation would be expected to be noninterfering. Because these cations are electrophilic but large and bulky, the additional termination route provided via reaction with propagating anions would be likely of decreased importance. The adduct of countercation to polymer chain is expected to be photoreactive in its own right and could contribute to the photoionization reaction as well (Scheme 1). Therefore, the nucleophiles generated in our system would effectively initiate polymerization, and the dye cations would ineffectively quench the propagating anions. The last postulate was tested as follows.

Several poly(cyanoacrylate) polymers were synthesized in the presence or absence of CV$^+$BPh$_4^-$ in order to compare their MW's and MWD's. The starting monomer mixture consisted of M-2-CA, THF (solvent), *p*-TsOH (inhibitor), and SO_2 (stabilizer) (Table 1). Tributylamine was used as initiator. The same synthetic scheme was repeated without inhibitor, without stabilizer, and with the monomer being added to THF or THF added to the monomer. In control experiments the glassware and stirrers were washed with acid (acidified), or not washed with acid, to test the results. Analysis (GPC) showed that the presence of CV$^+$BPh$_4^-$ had a negligible effect on MW and MWD of the poly(cyanoacrylate) polymers in all the cases. Both with and without dye present, the polymer was formed repeatedly and reproducibly in three fractions with MW = 3.5 × 10^6 (~20%), 1.5 × 10^4 (~10%), and 4.5 × 10^3 (~70%). Polydispersities of all the fractions varied from 2 to 4. In the absence of the initiator the starting monomer mixture started to solidify in about a week when kept on the benchtop in a closed vial.

Table 1. Synthesis of Cyanoacrylate Polymers 1−4 in THF[a]

component	1	2	3	4
M-2-CA	0.066 M	0.067 M	0.22 M	0.22 M
SO_2 (stabilizer)	2.9×10^{-5} M, 0.044%	3.0×10^{-5} M, 0.044%	9.6×10^{-5} M, 0.044%	9.6×10^{-5} M, 0.044%
p-TsOH (inhibitor)	6.29×10^{-5} M, 0.095%	6.5×10^{-5} M, 0.096%	9.81×10^{-6} M, 0.0045%	9.79×10^{-6} M, 0.0045%
NBu_3 (initiator)	6.27×10^{-4} M, 0.95%	6.5×10^{-4} M, 0.96%	1.02×10^{-3} M, 0.47%	1.01×10^{-3} M, 0.47%
$CV^+BPh_4^-$ (additive)	0	6.65×10^{-4} M, 0.99%	0	1.05×10^{-3} M, 0.49%

[a] Absolute concentrations; percent molar with respect to the monomer.

Control Experiments: Stability of M-2-CA. NMR experiments revealed that nonirradiated M-2-CA is not stable at room temperature in dry $CDCl_3$:CD_3CN = 3:1 (by weight) or in dry $CDCl_3$:CD_3COCD_3 = 4:1. Under these conditions the monomer disappeared in several minutes. In neat acetonitrile, cyanoacrylate was completely consumed in 5−7 min. The monomer, however, is stable for a week in chloroform and in $CDCl_3$:CD_3CN = 5:1 and much longer in C_6D_6. It appears that polarity of the environment determines thermal stability of the monomer. However, traces of water might have played a role also, although we kept the conditions as anhydrous as possible. Also, one should keep in mind that $CDCl_3$ contributes DCl impurity, which further inhibits spontaneous thermal polymerization. Another possible conclusion for systems containing acetonitrile has to do with weak basicity of this solvent: acetonitrile may not be basic enough to initiate polymerization in less polar solvents but is basic enough to initiate polymerization in more polar ones.

We also found that nonirradiated *N*,*N*-dimethyl-*p*-toluidine, Michler's ketone $(p\text{-}Me_2NPh)_2CO$, and CVCN do not initiate polymerization of the monomer dissolved in $CDCl_3$. The presence of CVCN does not lead to polymerization of M-2-CA in THF-d_8 either. On the other hand, tributylamine and triethylamine initiate the thermal polymerization process instantaneously even in nonpolar solvents.

CVCN and M-2-CA. Upon addition of crystalline powder of CVCN to neat M-2-CA (stabilized with 4×10^{-3} M SO_2), polymer formed instantaneously on the surface of the CVCN. The dimethylanilino groups of CVCN are likely basic enough to initiate polymerization in the polar monomer environment. Since this could be prevented by the addition of an inhibiting acid, colorless polymer was only produced when a solution of *p*-TsOH or HCl:CVCN = 2:1 (molar) in the neat monomer (CVCN:monomer = 1:100 by weight) was irradiated for 20 min. The same colorless polymer resulted from irradiation of a similar mixture in 1:1 cyanoacrylate and THF, but in this case there was an initially formed violet color of moderate intensity that disappeared during further irradiation.

In attempt to prevent the spontaneous thermal polymerization of M-2-CA, we prepared a TAM dye leuconitrile containing less nucleophilic amino groups. Conversion to amides, carbamates, sulfonamides, 2,5-dimethylpyrrole, or attaching bulky protective groups (can be photolabile) reduces basicity and nucleophilicity of an amino group.[33] The trityl group was chosen as one of the most promising sterically hindered protective groups. Reaction of rhodamine 6G leuconitrile with trityl bromide in anhydrous THF in the presence of NEt_3 at 60 °C failed to yield the ditritylated adduct. However, basic fuchsin leuconitrile and leuco trityl ether, both protected with three trityl groups $(p\text{-}TrNHPh)_3CCN$ and $(p\text{-}TrNHPh)_3COTr$, were successfully prepared. These were shown to generate an intense red-blue color as efficiently as basic fuchsin leuconitrile itself both in solution and even in polymerizing viscous epoxy resin. Unfortunately, the spontaneous thermal polymerization of neat M-2-CA persisted, and additional investigation is required to clarify the reasons. Possibly, water was present in the trace amounts and was deprotonated by the trityl-protected amino groups. This released the initiating species, OH^-. Therefore, we expect electron-withdrawing protective groups to enhance thermal stability better than sterically demanding protective groups.

Conclusions

We have demonstrated that anions produced by the photoheterolysis of crystal violet leuconitrile (CVCN) and malachite green leucohydroxide (MGOH) show significant potential for the controlled anionic polymerization of cyanoacrylates such as methyl 2-cyanoacrylate. Having the colored polymer obtained from irradiation of a solution of MGOH in benzene in the presence of M-2-CA, we have demonstrated the principle of simultaneous photoinduced anionic polymerization and color formation. Thermal anionic polymerization of M-2-CA initiated by trialkylamines is indifferent to the presence of CV^+ in the polymerizing monomer. Polymerizations with neat monomer have presented difficulties in that it was hard to control the dark reaction and coloration. Currently work to resolve these issues is underway.

Experimental Section

Monomer was purchased from Polysciences, Inc., and used without further purification. CVCN [tris(4-*N*,*N*-dimethylaminophenyl)acetonitrile] and BFCN [tris(4-aminophenyl)acetonitrile] were prepared previously.[30] Pure MGOH [bis(4-*N*,*N*-dimethylaminophenyl)phenylmethyl alcohol] was prepared according to the known procedure.[34] Both the compounds and deuterated solvents were kept in a chamber with P_2O_5, and their NMR spectra were taken prior to experiments to ensure total absence of water peaks. Benzene and THF were distilled from sodium/benzophenone. NMR spectra were taken with a Varian Gemini 200 NMR spectrometer. GC/MS and DIP/MS were taken on an HP 5988 mass spectrometer coupled to an HP 5880A GC and interfaced to an HP 2623A data processor. UV−vis spectra were obtained using an HP 8452 diode array spectrophotometer. Infrared spectrometry was performed using a Mattson Instruments 6020 Galaxy series FT-IR spectrometer. Melting points were determined using a capillary melting point apparatus (Uni-melt, Arthur H. Thomas Co., Philadelphia, PA) and were uncorrected. HPLC and GPC were performed with an HP 1050 series instrument equipped with multiple wavelength diode-array and refractive index detectors. For GPC, the instrument was equipped with 300 × 7.5 mm PLgel 5 μ-mixed C column. Acetone or acetonitrile was used as the mobile phase, and the flow rate was 0.8 mL/min. Polystyrene samples of known MW were used for MW calibration.

Photolyses of air-saturated solutions were performed in a Rayonet RPR-100 photoreactor (a merry-go-round apparatus) equipped with 14 filter-coated GE (21 W), low-pressure mercury UV bulbs ($\lambda_{exc} = 280-320$ nm). Vials, quartz test tubes (10 mL), Pyrex NMR tubes, and microscope glass plates all dried were used as photolysis vessels (tubes sealed with a rubber septum). Compounds were characterized by ^1H and ^{13}C NMR, mass, IR, and UV−vis spectroscopy, elemental analysis, and TLC. The disappearance of the starting materials and appearance of products was monitored by HPLC and NMR.

Tris(4-*N*-tritylaminophenyl)acetonitrile. BFCN was dissolved in anhydrous THF, and triethylamine was added followed by the solution of trityl bromide in THF, BFCN:TrBr:NEt_3 = 1:3:10. THF was partially evaporated, and triethylammonium bromide was filtered. Hexanes were added to the mother liquor, and the precipitate was cold-recrystallized from dichloromethane−methanol and then from dichloromethane−hexanes.[33] $(p\text{-TrNHPh})_3CCN$ (95% yield): ^1H NMR (200 MHz, $CDCl_3$) δ 7.36−7.10 (m, 45H), 6.43 (d, $J = 8.8$ Hz, 6H), 6.17 (d, $J = 8.8$ Hz, 6H), 4.95 (s, 3H); ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 145.6, 145.2, 129.8, 129.1, 128.4, 127.8, 126.7, 124.4-(CN), 115.8, 71.6, 54.7; IR (KBr) cm^{-1} 3398, 3055, 3022, 2233 (CN), 1608, 1509, 1489, 1446, 1321, 1302, 1255, 1184, 1030, 900, 818, 761, 750, 700, 636; MS (EI, MW is 1040, instrumental maximum is 900) 797 (−Tr), 554 (−2Tr), 479, 466, 390, 314, 298, 243 (b), 228, 215, 165 (b), 119; mp = 176−178 °C. Anal. Calcd for $C_{77}H_{60}N_4$: C, 88.81; H, 5.80; N, 5.38. Found: C, 88.51; H, 5.67; N, 5.45.

Poly(cyanoacrylate). Vial and stirrer were soaked in hydrochloric acid and dried. THF solution of *p*-TsOH was placed in the vial and diluted. Solution of $CV^+BPh_4^-$ was added where needed followed by fresh M-2-CA. The vial was sonicated for 10 min. Solution of amine was quickly delivered with intensive stirring. After 30 min, THF was evaporated, and the residue was dissolved in the minimal amount of acetonitrile. Either chloroform or diethyl ether was added, and the white solid was filtered and dried in vacuo.

Acknowledgment. We thank Drs. George S. Hammond and Thomas H. Kinstle for insightful discussions. This research was supported by the McMaster Endowment, the National Science Foundation (DMR-9526755), and the Office of Naval Research (Navy N00014-97-1-0834).

References and Notes

(1) Contribution 419 from the Center for Photochemical Sciences.
(2) Thompson, L. F.; Willson, G. C.; Bowden, M. J. *Introduction to Microlithography*; American Chemical Society: Washington, DC, 1994.
(3) Reiser, A. *Photoreactive Polymers: the Science and Technology of Resists*; Wiley: New York, 1989.
(4) Shou, H.; Neckers, D. C. *J. Imag. Sci. Technol.* **1995**, *39*, 18.
(5) Fouassier, J. P. *Prog. Org. Coat.* **1990**, *18*, 229.
(6) Kelly, J. M. *Photochemistry and Polymeric Systems*; Royal Society of Chemistry: London, 1993.
(7) Onen, A.; Arsu, N.; Yagci, Y. *Angew. Makromol. Chem.* **1999**, *264*, 56.
(8) Kutal, C.; Grutsch, P. A.; Yang, D. B. *Macromolecules* **1991**, *24*, 6872.
(9) Palmer, B. J.; Kutal, C.; Billing, R.; Hennig, H. *Macromolecules* **1995**, *28*, 1328.
(10) Paul, R. B.; Kelly, J. M.; Pepper, D. C.; Long, C. *Polymer* **1997**, *38*, 2011.
(11) Ito, H. *ACS Symp. Ser.* **1998**, *696*, 218.
(12) Fouassier, J. P. *Eur. Coat. J.* **1996**, *6*, 412.
(13) Schabel, W. *Macromol. Eng.* **1995**, 67.
(14) Hayashi, K.; Irie, M.; Yamamoto, Y. *Photogr. Sci. Eng.* **1979**, *23*, 193.
(15) Ren, Y.; Jager, W. F.; Neckers, D. C. *Macromolecules* **1996**, *29*, 3751.
(16) Kaneko, Y.; Neckers, D. C. *J. Phys. Chem. A* **1998**, *102*, 5356.
(17) Zhou, W.; Liu, J.; Wu, Z.; Wang, E. *Photochem. Photobiol. A: Chem.* **1998**, *112*, 173.
(18) MacLachlan, A. *J. Phys. Chem.* **1967**, *71*, 718 and references therein.
(19) Bertelson, R. C. In *Photochromism*; Brown, G. H., Ed.; Techniques of Chemistry; Wiley-Interscience: New York, 1971; Vol. 3; Chapters 3 and 10.
(20) Jarikov, V. V. Ph.D. Dissertation, Bowling Green State University, Bowling Green, OH, 1999.
(21) Oldring, P. K. T. *Chemistry and Technology of UV and EB Formulations for Coatings, Inks, and Paints*; Selective Industrial Training Associates Limited: London, 1994; Vol. 5, pp 70−76.
(22) Neckers, D. C.; Jager, W.; Ren, J. A Method for Forming Highly Colored Polymeric Bodies. U.S. Patent #5,942,554, 1999.
(23) Neckers, D. C.; Wright, R. F. Production of Three-Dimensional Objects. U.S. Patent #5,514,519, 1996.
(24) Neckers, D. C. Production of Three-Dimensional Bodies by Photopolymerization. U.S. Patent #5,137,800, 1992.
(25) Jarikov, V. V.; Neckers, D. C. *Adv. Photochem.* **2000**, *26*, in press.
(26) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983; pp 15−65.
(27) Reetz, M. J. *Chem. Soc., Chem. Commun.* **1988**, 213.
(28) Frechet, J. M. J.; Leung, M.-K.; Urankar, E. J.; Willson, C. G.; Cameron, J. F.; MacDonald, S. A.; Niesert, C. P. *Chem. Mater.* **1997**, *9*, 2887.
(29) Yamada, B.; Yoshioka, M.; Otsu, T. *Makromol. Chem.* **1983**, *184*, 1025.
(30) Jarikov, V. V.; Neckers, D. C. *J. Org. Chem.* **2000**, in press.
(31) Baskaram, D.; Muller, A. H. E. *Macromolecules* **1997**, *30*, 1869 and references therein.
(32) Warmkessel, J. *Polym. Preparation* **1994**, *35*, 589.
(33) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*; Wiley: New York, 1991; p 309.
(34) Holmes, E. O., Jr. *J. Phys. Chem.* **1966**, *70*, 1037.

MA0012090