Macromolecules **2004,** *37,* 41−44

A Novel Approach to the Preparation of Dissociative Electron Transfer Photoinitiators for Free Radical Polymerization

Andrzej Wrzyszczyński,* Marek Pietrzak, and Jerzy Pączkowski

University of Technology and Agriculture, Faculty of Chemical Technology and Engineering, Seminaryjna 3, 85-326 Bydgoszcz, Poland

Received November 12, 2002; Revised Manuscript Received September 3, 2003

ABSTRACT: A new approach to the design of the electron transfer free radical photoinitiating system (ETPS) is presented in the paper. The system applying a light absorber (dye), and an electron donor (sulfur-containing aromatic carboxylic acid, SCCA), possessing the structure allowing the formation of the leaving group that forms a neutral free radical, is described. The experimental results show that after the transformation of the SCCA into its ammonium salt a substantial increase of the polymerization photoinitiation ability of the system is observed. The mechanism of the photoinitiated polymerization for the tested photoredox pairs is clarified on the basis of the laser flash photolysis experiments obtained from the neutral dye (5,7-diiodo-3-pentoxy-6-fluorone, DIPF) serving as electron acceptor and (phenylthio)-acetic acid (Ph−S−CH_2−COOH, PTAA) and its tetrabutylammonium salt (PTAA AS) as electron donors in MeCN solution. It is documented that the photoreduction of DIPF in the presence of (phenylthio)-acetic acid and its tetrabutylammonium salt occurs via the photoinduced electron transfer process. On the basis of the known photochemistry of sulfur-containing aromatic carboxylic acids, it is postulated that the existence of the carboxyl group in an ionic form allows a rapid decarboxylation, yielding a neutral α-alkylthio-type radical (R−S−$CH_2^{\bullet}$). The system described in this paper applies the dissociative electron transfer process for an effective production of very reactive free radicals able to initiate a radical polymerization.

Introduction

There have been a number of studies on the dyeing photoinitiators forming a free radical via the photoinduced electron transfer process. These include acridines, xanthenes, and thiazines, first reported by Oster,[1] a wide group of the fluorone dyes,[2] the cyanine dyes,[3] pyrene,[4] safranine T,[5] the dyes based on quinaxolin-2-one residue,[6] and many others.[7] However, it is necessary to emphasize that the research related to the photochemistry of dyeing photoinitiators is mostly focused on the development of new light absorbers, while there are only few papers describing the effect of an electron-donating molecule structure on the efficiency of photoinitiation process.[8]

In this presentation, we have compared the reactivity of several photoinitiation systems composed of xanthene dye acting as light absorber and a series of sulfur containing aromatic carboxylic acids and their tetrabutylammonium salts functioning as the electron donors. For comparison, ethyl (phenylthio)acetate (PTAA EE), phenoxyacetic acid (PAA), and its tetrabutylammonium salt (PAA AS) were tested as well.

Experimental Section

The substrates used for the preparation of the dye and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) were purchased from Aldrich. 5,7-Diiodo-3-pentoxy-6-fluorone (DIPF) was synthesized according to the method of Shi and Neckers.[2a,b] The tetrabutylammonium salts of sulfur-containing aromatic carboxylic acids were obtained by the treating of the corresponding acid dissolved in boiled water with a molar equivalent of tetrabutylammonium hydroxide. After the evaporation of water, the clammy residue was dried in a vacuum desiccator, yielding transparent crystals. Ethyl (phenylthio)acetate (PTAA EE) was prepared using standard organic chemistry. The final products were identified by ^1H NMR spectroscopy. The spectra obtained were the evidence that the reaction products were of the desired structures.

The kinetics of the polymerization measurements were carried out by measuring the polymerization heat evolution of a sample, irradiated with a laser beam through an optical system, in a homemade microcalorimeter.[8a,b] The irradiation of the polymerization mixture was carried out using the emission of an Omnichrome model 543-500 MA argon ion laser. The light intensity was measured by a Coherent model Fieldmaster power meter.

The kinetics of free radical polymerization was studied using a polymerization solution composed of TMPTA and a photoinitiating photoredox pair. The concentration of 5,7-diiodo-3-pentoxy-6-fluorone (DIPF) was 1×10^{-3} M. The concentrations of acids and their salts studied in the tested formulations were 0.1 M.

Nanosecond laser flash photolysis experiments in part were performed using the apparatus previously described[2d] and in part using a LKS.60 laser flash photolysis apparatus (Applied Photophysics), applying a laser irradiation at 355 nm from the third harmonic of the Q-switched Nd:YAG laser from a Lambda Physik/model LPY 150 operating at 65 mJ/pulse (pulse width about 4−5 ns). The rate DIPF triplet decay and the transient spectra of short-lived photoreaction products were measured for 3×10^{-4} M solution in acetonitrile.

Results and Discussion

The mechanism for the photoinitiation of polymerization by dye−sulfur (oxygen)-containing aromatic carboxylic acid in its ionic form may be suggested on the basis of the transient absorption spectra recorded for 5,7-diiodo-3-pentoxy-6-fluorone (DIPF) in the presence of (i) sulfur-containing aromatic carboxylic acid ((phenylthio)acetic acid, PTAA), (ii) tetrabutylammonium salt of sulfur-containing aromatic carboxylic acid (PTAA AS), and (iii) *n*-butyltriphenylborate (BTPB) in MeCN solution and compared to the transient spectra recorded for the tested dye in 2-propanol. The spectra illustrating the behavior of DIPF in the presence of the above-mentioned triplet state quenchers are shown in Figure 1.

10.1021/ma021679p CCC: $27.50

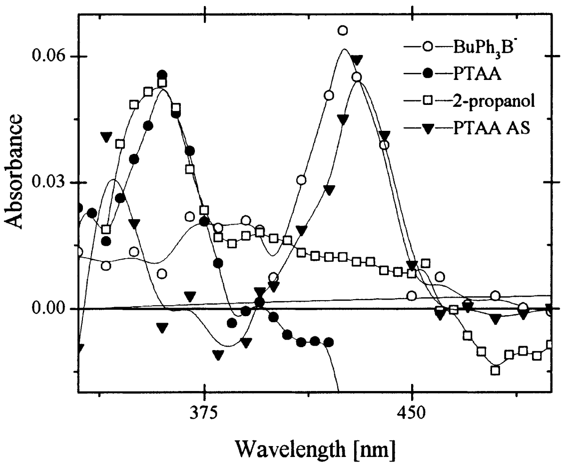


Figure 1. Transient absorption spectra of 5,7-diiodo-3-pentoxy-6-fluorone in MeCN in the presence of various electron donors and hydrogen atom donors (marked in the figure).

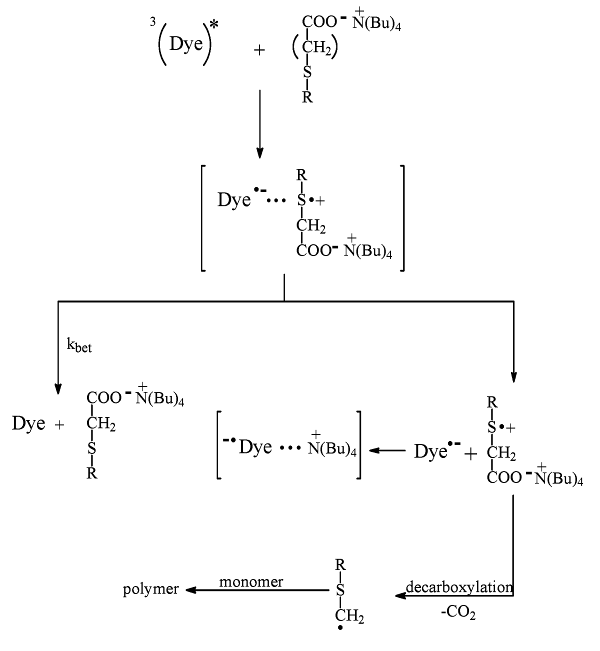
The photoreduction of the dye by PTAA AS yields stable DIPF radical anion (DIPF$^{\bullet -}$, transient at 420 nm) and no presence of neutral radical of DIPF$^{\bullet}$ (transient at 360 nm) can be detected. On the other hand, the photoreduction of the dye by PTAA gives only the neutral radical (DIPF$^{\bullet}$) as a product.[2d] The photolysis of DIPF in a 2-propanol solution also gives as a transient typical for the neutral radical of the dye (DIPF$^{\bullet}$).

During the study of DIPF−PTAA photoredox pair we were not able to detect DIPF$^{\bullet -}$. The dye radical anion has a negative charge centered on the oxygen at the 6-position. This intermediate acts as a base and promotes a rapid proton transfer from the carbon α to the sulfur of the sulfur-centered radical cation. Since the proton transfer within a radical ion pair occurs on the picosecond time scale, the above-described processes cannot be detected on the nonosecond time scale.[9]

All of the presented spectroscopic investigations of the photoreduction of the tested xanthene dye allow to suggest the mechanism of the photooxidation of PTAA AS. Proposed mechanisms are consistent with one proposed for the photooxidation of sulfur-containing amino acids[10] and one accepted for one-electron oxidation of similar types of molecules.[11]The flash photolysis results confirms that the photoreduction of the dye in the presence of PTAA and PTAA AS acting as the electron donors is one electron transfer process. The electron transfer from the PTAA AS salt results in the formation of radical cation (PTAA$^{\bullet +}$) and DIPF radical anion (DIPF$^{\bullet -}$) pair. This type of the reaction is confirmed by the comparison of the photoreduction process of the dyes in the presence of tetrabutylammonium triphenylborate, the well-known one-electron photoreducing agent.[5] The transient spectra in the PTAA AS case show that DIPF$^{\bullet -}$ is the only product obtained after the triplet quenching of the tested dye. On the basis of the well-established mechanism of the photooxidation of sulfur-containing amino acids or one-electron oxidation of similar types of molecules, one can easily predict that under these circumstances the α-alkylthio-type radical (R−S−CH$_2^{\bullet}$) is produced from the radical cation of the sulfur-containing carboxylic acid as a result of decarboxylation that occurs in the nanosecond time scale.[12]

A different picture of the process is observed when PTAA is applied as an electron donor. On the basis of the pioneer works of Davidson[13] and the more current

Scheme 1



of Bobrowski, Hug, and Marciniak,[10,11] one can predict that in organic solvent from PTAA$^{\bullet +}$ the α-(alkylthio)-carboxylic radical (R−S−CH$^{\bullet}$−COOH) radical is formed.

There are also noteworthy facts: (i) The insertion of an additional amount of tetraalkylammonium cation (as ClO$_4^-$ salt) into the reaction medium (both PTAA and PTAA AS) has no effect on the mechanism of the process. However, it slightly decreases the rate of the triplet state quenching.[14] The observed results suggest that the presence of electron donor as tetraalkylammonium salt is a basic prerequisite for the reaction with no deprotonation of radical cation. (ii) The change of the solvent polarity does not affect the mechanisms of the processes. (iii) An extension of an investigation on laser flash photolysis of ethyl (phenylthio)acetate photooxygenation showed the presence of DIPF$^{\bullet}$ that is the evidence of α-deprotonation reaction.

In our most recent paper,[15] exploring the mechanism of benzophenone photoreduction in the presence of both PTAA and PTAA AS, it is documented that steady state irradiation of the BP-TPAA AS photoredox system in MeCN causes decarboxylation with the quantum yield $\Phi_{CO_2} = 0.45 \pm 0.09$ and benzophenone consumption with the quantum yield being equal $\Phi_{BP} = 0.42 \pm 0.05$. The equality of Φ_{CO_2} and Φ_{BP} is evidence that the potential formation of benzophenone ketyl radical via deprotonation reaction can be neglected because this reaction does not lead to the formation of CO$_2$. This observation allows to conclude that the quantum yield of electron acceptor disappearance is equal to the quantum yield of α-alkylthio radical (R−S−CH$_2^{\bullet}$) formation. During the steady state irradiation of the DIPF-TPAA AS photoredox pair the quantum yield for DIPF consumption was determined to be $\Phi_{DIPF} = 0.37 \pm 0.05$. The quantum yield of benzophenone triplet state formation is equal $\Phi_T = 1$, and DIPF is approximately similar to that observed for tetraiodohydrofluorescein ($\Phi_T = 0.87$).[16] Taking this into account, one can state that the quantum yields of both photoreduction reactions are practically identical. Thus, on the basis of this comparison, one can state that the quantum yield of α-alkylthio radical (R−S−CH$_2^{\bullet}$) formation by DIPF is equal to $\Phi_R = 0.37$. The above-discussed similitude clearly indicates

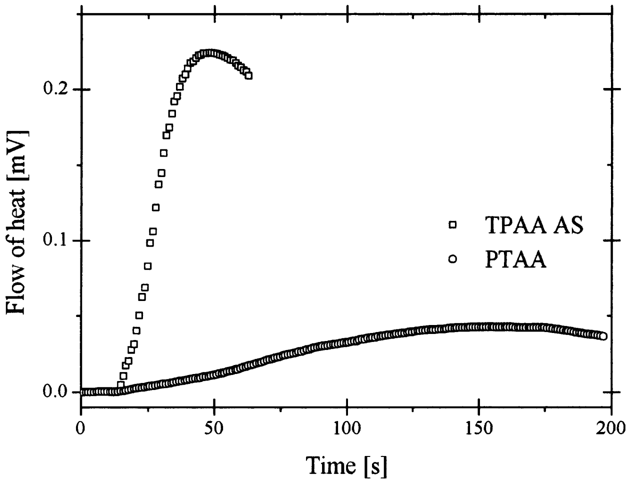


Figure 2. Kinetic curves of TMPTA polymerization initiated by DIPF (1×10^{-3} M) in the presence of (phenylthio)acetic acid (circle) and (phenylthio)acetic acid tetrabutylammonium salts (squares). The concentration of electron donors is equal to 0.1 M. Light intensity equals 70 mW/0.78 cm^2.

a close similarity of photochemical behavior of both benzophenone and DIPF. It should be noted that evidence from independent experiments[17] indicates that the quantum yield of benzophenone ketyl radical formation (equal to the quantum yield of α-(alkylthio)carboxylic radical formation) for benzophenone–TPAA quenching experiments was established to be equal to 0.86. By analogy, one can predict that the quantum yield of α-(alkylthio)carboxylic radical ($R-S-CH^{\bullet}-COOH$) formation for DIPF–PTAA photoredox pair can oscillate in the range 0.8–0.9; e.g., it is greater than the quantum yield of α-alkylthio radical ($R-S-CH_2^{\bullet}$) formation.

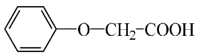
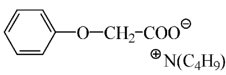
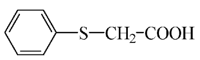
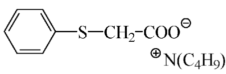
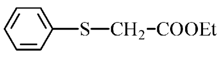
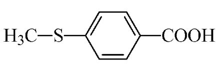
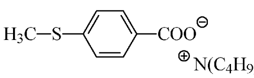
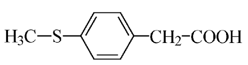
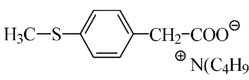
Figure 2 presents the kinetic traces recorded during an argon ion laser photoinitiated polymerization of TMPTA in the presence of 5,7-diiodo-3-pentoxy-6-fluorone (DIPF) as the light absorber and PTAA and its tetrabutylammonium salt (PTAA AS) functioning as the electron-donating molecules.

It is apparent from the inspection of the data shown in Figure 2 that the transformation of PTAA into its tetrabutylammonium salt dramatically increases the sensitivity of the photoinitiating system (more than 1 order of magnitude).

Even more distinct differences are observed in the rates of polymerization when one compares the rate of polymerization photoinitiated by dye-PTAA AS and dye–ethyl (phenylthio)acetate (PTAA EE). The results of polymerization kinetics measurements obtained for all the tested photoinitiating pairs are listed in Table 1.

Inspection of the data collected in Table 1 reveals that there is no correlation between the rates of the electron transfer process and the rates of photoinitiated polymerization. It is easy to see that the change of PTAA into its tetrabutylammonium salt causes an increase of the rate constant of the electron transfer of about 2–3 times, while the rate of photoinitiated polymerization increases at least 1 order of magnitude. There is also no correlation between the quantum yield of the free radical formation and the rates of polymerization. These observations permit to conclude that there is an additional factor affecting the rate of photoinitiated polymerization. We believe that the observed lack of correlation is caused by different reactivity of the free radicals formed after the electron transfer between the dye and the tested electron donors.

Table 1. Rate Constants of Electron Transfer and Relative Rates of Photoinitiated Polymerization of TMPTA for Tested Photoredox Pairs

Electron donor	DIPF	
	R_p [au]	k_{el} [$M^{-1}s^{-1}$]
	1.07	0.88×10^6
	1.75	7.48×10^6
	7.50	1.29×10^7
	183	3.93×10^7
	2.59	3.86×10^6
	0.95	---
	2.90	---
	1.74	---
	36.7	---

In this study several other electron donors, being aromatic carboxylic acids, were tested. The results of the photoinitiation efficiency measured for all the dye–electron donor combinations are also summarized in Table 1. The first important feature shown in Table 1 is associated with the properties of phenoxyacetic acid (PAA) and its tetrabutylammonium salt. It is obvious that these compounds are rather poor co-initiators. The reason for the very low photoinitiation efficiency observed for PPA as the electron donor might come from its low rate of the dye triplet state quenching.

Finally, to clarify all the mechanistic problems of photoinitiation, we tested an influence of the light intensity on the observed rate of polymerization. This relationship is shown in Figure 3.

The results presented in Figure 3 are not surprising. A low photoinitiation ability α-(alkylthio)carboxylic radical ($R-S-CH^{\bullet}-COOH$) is also demonstrated in behavior presented in Figure 3. The increase of its concentration caused by an increase of light intensity only slightly affects the final rate of polymerization. For PTAA AS the situation is quite different. An increase of light intensity causes dramatic extension of polymerization rate.

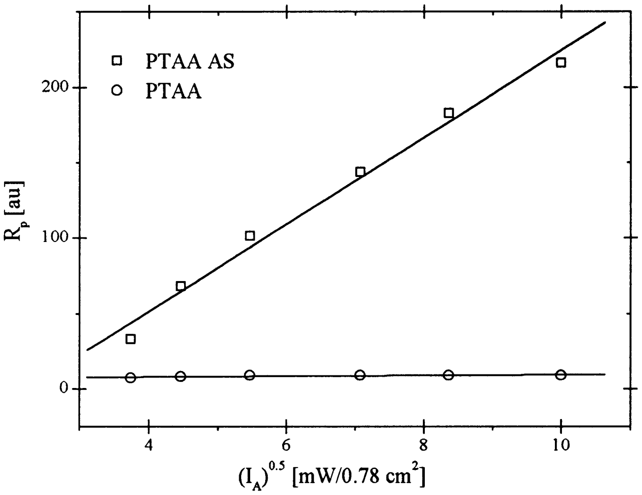


Figure 3. Observed initial rate of photoinitiated by DIBF polymerization of TMPTA as a function of absorbed light intensity.

Acknowledgment. This research was sponsored by the State Committee for Scientific Research (KBN), Grant 4 T09A 051 22. We are also very grateful to Professors M. A. J. Rodgers and D. C. Neckers from Center for Photochemical Sciences, Bowling Green State University, for putting the nanosecond laser flash photolysis apparatus at our disposal.

References and Notes

(1) Oster, G. *Nature (London)* **1954**, *173*, 300.
(2) (a) Shi, J.; Zhang, X.; Neckers, D. C. *J. Org. Chem.* **1992**, *57*, 4418. (b) Shi, J.; Zhang, X.; Neckers, D. C. *J. Org. Chem.* **1993**, *58*, 2614. (c) Polykarpov, A. Y.; Hassoon, S.; Neckers, D. C. *Macromolecules* **1996**, *29*, 8274. (d) Hassoon, S.; Neckers, D. C. *J. Phys. Chem.* **1995**, *99*, 9416.
(3) (a) Chatterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326. (b) Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329. (c) Kabatc, J.; Pietrzak, M.; Pączkowski, J. *Macromolecules* **1998**, *31*, 4651.
(4) (a) Encinas, M. V.; Majmund, C.; Lissi, E. A.; Scaiano, J. C. *Macromolecules* **1991**, *24*, 2111. (b) Encinas, M. V.; Lissi, E. A.; Majmund, C.; Cosa, J. J. *Macromolecules* **1993**, *26*, 6284.
(5) Previtali, C. M.; Bertolotti, S. G.; Neumann, M. G.; Pastre, I. A.; Rufs, A. M.; Encinas, M. V. *Macromolecules* **1994**, *27*, 7454.
(6) (a) Kucybała, Z.; Pietrzak, M.; Pączkowski, J. *Chem. Mater.* **1998**, *10*, 2555. (b) Kucybała, Z.; Pączkowski, J. *J. Photochem. Photobiol., A: Chem.* **1999**, *128*, 135.
(7) For exclusive reviews see: Pączkowski, J.; Neckers, D. C. Photoinduced Electron-Transfer Initiating Systems for Free-Radical Polymerization. In *Electron Transfer in Chemistry*; Gould, I. R., Ed.; Wiley-VCH: New York, 2001; Vol. 5, p 516. Pączkowski, J.; Kucybała, Z.; Ścigalski, F.; Wrzyszczyñski, A. Dyeing Photoinitiators. Electron-Transfer Processes in Photoinitiating Systems. *Res. Trends* **1999**, *No. 5*, 79−93.
(8) (a) Pączkowski, J.; Pietrzak, M.; Kucybała, Z. *Macromolecules* **1996**, *29*, 5057. (b) Kabatc, J.; Kucybała, Z.; Pietrzak, M.; Ścigalski, F.; Pączkowski, J. *Polymer* **1999**, *40*, 735. (c) Wrzyszczyñski, A.; Filipiak, P.; Hug, G. L.; Marciniak, B.; Pączkowski, J. *Macromolecules* **2000**, *33*, 1577. (d) Andrzejewska, E.; Hug, G. L.; Andrzejewski, M.; Marciniak, B. *Macromolecules* **1999**, *32*, 2173.
(9) Peters, K. S.; Cashin, A.; Timbers, P. *J. Am. Chem. Soc.* **2000**, *122*, 107.
(10) (a) Bobrowski, K.; Marciniak, B.; Hug, G. L. *J. Am. Chem. Soc.* **1992**, *114*, 102279. (b) Marciniak, B.; Bobrowski, K.; Hug, G. L.; Rozwadowski, J. *J. Phys. Chem.* **1994**, *98*, 4854.
(11) (a) Bobrowski, K.; Pogocki, D.; Schöneich, C. *J. Phys. Chem.* **1998**, *102*, 10512. (b) Bobrowski, K.; Pogocki, D.; Schöneich, C. *J. Phys. Chem.* **1993**, *97*, 13677.
(12) (a) Hug, G. L.; Bonifačič, M.; Asmus, K.-D.; Armstrong, D. A. *J. Chem. Phys. B* **2000**, *104*, 6674. (b) Korzeniowska-Sobczuk, A.; Hug, G. L.; Carmichel, I.; Bobrowski, K. *J. Phys. Chem. A* **2002**, *106*, 9251−9260.
(13) (a) Davidson, R. S.; Steiner, P. R. *J. Chem. Soc. C* **1971**, 1682. (b) Davidson, R. S.; Harrison, P. R.; Steiner, P. R. *J. Chem. Soc., Chem. Commun.* **1971**, 3480. (c) Barthomolew, D. R.; Brimage, D. R. G.; Davidson, R. S. *J. Chem. Soc., Chem. Commun.* **1971**, 3482.
(14) Su, Z.; Mariano, P. S.; Falvey, D. E.; Yoon, U. C.; Oh, S. W. *J. Am. Chem. Soc.* **1998**, *120*, 10676.
(15) Wrzyszczyński, A.; Pietrzak, M.; Bartoszewicz, J.; Kozubek, H.; Hug, G. L.; Marciniak, B.; Pączkowski, J. *J. Am. Chem. Soc.* **2003**, *125*, 11182.
(16) Klimtchuk, M.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem.* **1992**, *96*, 9817.
(17) Bartoszewicz, J.; Kozubek, H.; Hug, G. L.; Marciniak, B.; Pączkowski, J., to be published.

MA021679P