Photoinduced Electron Transfer Polymerization. 4.[||] 4-Carboxybenzophenone−Sulfur-Containing Carboxylic Acids Photoredox Pairs as a Photoinitiating System for Free-Radical Polymerization

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ABSTRACT: A series of sulfur-containing carboxylic acids (SCCA) was investigated as electron donors in photoinduced free-radical polymerizations, in conjunction with 4-carboxybenzophenone (CB) as sensitizer. These carboxylic acids included (phenylthio)acetic acid, *S*-benzylthioglycolic acid, 4-(methylthio)-phenylacetic acid, 2-(methylthio)ethanoic acid, 4-(methylthio)benzoic acid, 2,2′-thiodiethanoic acid, and 3,3′-thiodipropionic acid. The results were compared to the simplest thioether, dimethyl sulfide. The mechanism of the radicals' formation was established using nanosecond laser flash photolysis and photochemical steady-state measurements of carbon dioxide formation. Photopolymerizations were carried out in aqueous solutions of acrylamide. Several conclusions follow from the experimental data: (1) The rates of polymerization of the CB/SCCA/acrylamide systems are affected by the yields of secondary processes that follow photoinduced electron transfer, e.g. decarboxylation or deprotonation. This is in addition to the reactivity of the free radicals themselves. (2) The highest initiation yield is observed for the system where there is efficient diffusion apart of the radical−ion pairs, followed by efficient decarboxylation. The resulting radicals are localized on carbons adjacent to the sulfur atom. (3) Free radicals with aromatic moieties are better initiators than are the analogous aliphatic radicals. (4) Radicals that retain the carboxylate moiety are inefficient initiators. (5) Photopolymerization of these systems appears to proceed by the conventional mechanism where termination is bimolecular.

Introduction

Using visible or ultraviolet light to initiate polymerization is an area of intense interest in organic photochemistry. The traditional way to initiate polymerization through photochemistry has been by direct photolysis of a precursor that provides free radicals by direct bond scission. Panchromatic sensitization of vinyl polymerization has also been extensively used as a more flexible alternative, but it has its own limitations because it requires the presence of suitable dyes to serve as the primary absorber. In particular, it is necessary to choose the sensitizer (absorber) and co-initiator so that energy transfer occurs to the co-initiator. Photoinduced intermolecular electron-transfer represents an alternative to such a restriction. This process involves the use of light to initiate electron transfer from a donor to an acceptor molecule.[1]

Davidson and co-workers[2] developed a picture of the benzophenone photosensitized decarboxylation of acids of the type $RXCH_2COOH$, where X = O, S, and NH. The mechanism that emerged from this work was that benzophenone reduction occurs initially by electron transfer from the acid to give a carboxylate radical. This radical then undergoes decarboxylation, yielding an alkyl radical that is able to abstract a hydrogen atom from the reaction medium. However, at that time, there was no time-resolution information available on these systems, and a definite conclusion describing the mechanism of the reactions was not possible.

More recently, Marciniak, Bobrowski, and Hug[3] examined quenching of triplet states of benzophenones by sulfur-containing amino acids and sulfur-containing carboxylic acids in water and water/acetonitrile solutions. According to these authors, the mechanism of photoinduced electron transfer between sulfur-containing amino acids or carboxylic acids (examined using steady-state and laser photolysis techniques) involves an electron transfer from the sulfur atom to the triplet state of benzophenone to form a radical−ion pair. Subsequently (i) the radical ions can diffuse apart, (ii) there can be intramolecular proton transfer within the radical−ion pair, or (iii) back electron transfer can occur to regenerate the reactants in their ground states. The first process led to the formation of sulfur-centered radical cations, which sometimes undergo fast protonation depending on the medium. In this work, a secondary process of forming additional ketyl radicals was discovered; they were formed from the one-electron reduction of benzophenone by α-aminoalkyl-type radicals. The source of the strongly reducing α-aminoalkyl radicals was the free-radical cation of the amino acids after an intramolecular electron transfer from the carboxyl group to the sulfur-centered radical cation, followed by decarboxylation.

In our earlier paper,[4] it is shown that the benzophenone/sulfur-containing amino acid systems can be effectively used for photoinitiation of free-radical polymerization in aqueous media. Also recent nanosecond

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flash photolysis investigations of the mechanism of the photoreduction of benzophenones by alkyl sulfides[5] and by 2,4,6-trimethyl-1,3,5-trithiane[6] have shown that photoreduction occurs by an electron transfer from the sulfur atom to the benzophenone triplet, followed by proton transfer. However, it is necessary to point out that under conditions typical for the polymerization of acrylates, linear aliphatic sulfides reduce benzophenone with low efficiency because of the facile back electron-transfer process within the radical−ion pair. This is not observed for trithianes, where it was found that these compounds are active co-initiators in benzophenone-induced photopolymerization.[7]

Little concrete detail is known of the advantages and disadvantages of using benzophenone/sulfur-containing carboxylic acid systems for photopolymerization and their potential applications. This is especially true in aqueous solutions, where separation of radical ions can be a significant reaction channel following electron transfer. The radical cations of the sulfur-containing carboxylic acids often decarboxylate (pseudo Kolbe reaction)[8] yielding only one type of free radical capable of initiating free-radical polymerization. In the current work, we revisit the benzophenone/sulfur-containing carboxylic acid systems using laser photolysis to check whether some representative systems can be effective in photoinitiating free-radical polymerization and to characterize the relationship between the structure of the free radicals and their photoinitiation ability.

Experimental Section

Materials. All sulfur-containing carboxylic acids, dimethyl sulfide, 4-carboxybenzophenone (CB), and acrylamide (AA, electrophoresis grade) were purchased from Aldrich as the best available grades and were used without further purification.

Laser Flash Photolysis Experiments. The nanosecond laser flash photolysis apparatus has been described in detail elsewhere.[9,10] A nitrogen laser (337 nm) from a Laser Photonics PRA/model UV-24 was operated at 4−6 mJ/ pulse (pulse width about 8 ns). Laser excitation was at a right angle with respect to the monitoring light beam. Transient absorbances at preselected wavelengths were monitored by a detection system containing of a monochromator (Spex 270 M), a photomultiplier tube (Hamamatsu R955), and a pulsed xenon lamp (1 kW) as the monitoring light source. The signal from the photomultiplier was processed by a LeCroy 7200 digital storage oscilloscope and a PC-AT compatible computer.[9] Rectangular quartz cells (0.5 × 1 cm) with a path length of 0.5 cm for the monitoring beam were used. Typically 3−10 laser shots were averaged for each kinetic trace.

The concentrations of CB were 2×10^{-3} M in all laser experiments. The concentrations of quenchers were in the range 10^{-5}−10^{-3} M in the quenching experiments and 0.02 M for the quantum yield determinations (to quench >95% of CB triplets). The pH of the solutions was adjusted by adding sodium hydroxide or perchloric acid. All solutions were deoxygenated by bubbling high-purity argon through them.

Steady-State Photolysis Experiments. The steady-state photolysis was carried out in 1 × 1 cm rectangular cells on an optical bench irradiation system. The photolytic source was a high-pressure mercury lamp, HBO 200. The radiation from this lamp was passed through a combination of glass and interference filters to isolate radiation of wavelength 313 nm. A solution of 2-hexanone in cyclohexane was used as an actinometer,[11] and the intensity of the incident light was determined to be $I_0 = 6.6 \times 10^{-6}$ einstein dm^{-3} s^{-1}. Solutions containing CB (2×10^{-3} M) and quencher (0.02 or 0.01 M) were buffered in the presence of $Na_2H_2PO_4$/ Na_2HPO_2 (0.025 M), purged with high-purity argon, and then irradiated. Irradiation times were chosen to limit conversion of CB to the range 5−40%. Changes in the CB concentration during irradiation were determined spectroscopically using a Hewlett-Packard 8452 diode array spectrophotometer and using high-pressure liquid chromatography (HPLC) performed on a Waters 600E instrument with photodiode array detection (reversed phase C18 Waters Nova Pak; eluent 1:4 (v/v) acetonitrile/water mixture containing 0.1 M CH_3COONH_4). The concentration of CO_2, produced in the irradiations was measured by gas chromatography in the following fashion. After irradiation, the solutions were acidified with concentrated HCl, and the vapor phase in the reaction cell was analyzed for the presence of CO_2 using a Hewlett-Packard 5890 series II chromatograph. The detection system involved a thermal conductivity detector at the end of a Para Plot Q column. The CO_2 quantum yields obtained for at least five different irradiation times were then extrapolated to zero irradiation time.

Photopolymerization. The light source used was an Innova 90-4 argon-ion laser, Coherent. The wavelengths used were a 1:1 mixture of 351.1 and 363.3 nm. The incident light intensity at the sample position was measured with a Coherent power meter type 543−500 mA and was determined to be 66 mW/cm^2. Photopolymerization efficiencies were measured gravimetrically by irradiation of a quartz cell containing 2.5 cm^3 of an aqueous solution of the monomer, 4-carboxybenzophenone, and the co-initiator. All solutions were deoxygenated by bubbling high-purity helium through them and were buffered in the presence of phosphate buffer (pH = 6.8). After irradiation, the contents of the cell were poured into acidified methanol for precipitation and then filtered and dried to constant weight. The concentrations of 4-carboxybenzophenone, co-initiators, and acrylamide were constant in all experiments being 0.02, 0.02, and 1.4 M, respectively.

Results and Discussion

Photopolymerization measurements were performed for acrylamide in aqueous solutions. The laser flash photolysis and steady-state photolysis experiments were performed in water for the sulfur-containing carboxylic acids (SCCA) tested.

The absorption spectra of mixtures of CB and the phenyl-substituted carboxylic acids used in this work were examined spectroscopically for any evidence of ground-state complex formation. Like for aliphatic derivatives,[3c] the absorption spectra of the mixtures of CB and phenyl-containing carboxylic acids were shown to be equal to those expected by adding the spectra of separate solutions of CB and the various acids. No evidence for ground-state complex formation was found under the experimental conditions used. Flash excitation of solutions of CB (2×10^{-3} M) and the various acids (0.02 M) at neutral pH resulted in the appearance of the absorption corresponding to various transients depending on the time delay and the type of acid used. The concentration of each acid was chosen to be high enough so that it would quench more than 95% of the CB triplets.

Spectral Resolutions and Quantum Yields. The time-resolved spectra were generated from the sets of individual kinetic traces collected at 10 nm intervals, choosing appropriate time delays and time windows. The spectra were resolved into component species by a linear regression technique using known spectra of appropriate components. Further details of this method together with the reference spectra of CB transients (ketyl radical anion, $CB^{\bullet-}$ and ketyl radical, $CBH^{\bullet}$) have been described elsewhere.[3e]

Typical spectral resolutions of the transient absorption spectra obtained in this work are presented in

Table 1. Rate Constants for Quenching of the CB Triplet by Co-Initiators, Quantum Yields for the Formation of Carbon Dioxide, the CB Radical Anion, and the CB Ketyl Radical Following CB Triplet Quenching, and Rates of Polymerization

no.	co-initiator	co-initiator structure	$k_q \times 10^{-9}$ (M^{-1} s^{-1})	Φ_{CO_2}[a]	$\Phi_{CB^{-\bullet}}$[b]	$\Phi_{CBH^\bullet}$[b]	R_p (%/min)
1	phenyl(thioacetic) acid	$C_6H_5-S-CH_2COOH$	1.9	0.92	0.97	0	11.7
2	*S*-benzylthioglycolic acid	$C_6H_5--CH_2-S-CH_2COOH$	1.5	0.57	0.84	0.16	8.0
3	4-(methylthio) phenylacetic acid	$CH_3-S-C_6H_4-CH_2COOH$	1.9	0.29	*e*	*e*	7.2
4	2-(methylthio)ethanoic acid[c])	CH_3-S-CH_2-COOH	2.1	0.86	0.87	0.12	7.0
5	4-(methylthio)benzoic acid	$CH_3-S-C_6H_4-COOH$	1.9	<0.05	*e*	*e*	1.0
6	2,2′-thiodiethanoic acid[c])	$HOOC-CH_2-S-CH_2-COOH$	1.0	0.80	0.84	0.16	1.2
7	3,3′-thiodipropionic acid[c])	$HOOC-(CH_2)_2-S-(CH_2)_2-COOH$	1.0	<0.03	0.90	0.09	0
8	dimethyl sulfide[d])	CH_3-S-CH_3	1.5		0.16	0.10	1.4

[a] From steady-state measurements, extrapolated to zero percent of CB conversion, with estimated errors ±10%. [b] From the laser flash photolysis, extrapolated to the end of the flash, with estimated errors ±10% except **1** and **2** (±5%). [c] From ref 3c. [d] From ref 5. [e] Could not be estimated (see text).

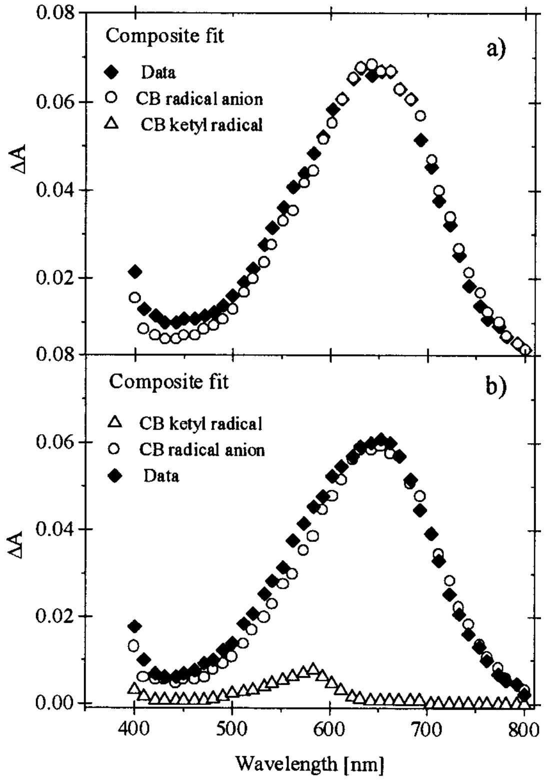


Figure 1. Resolution of the spectral components in the transient absorption spectra following the quenching of CB-triplet by $C_6H_5-S-CH_2-COOH$ (Figure 1a) and $C_6H_5-CH_2-S-CH_2-COOH$ (Figure 1b) taken at 1.5 μs after the flash (pH = 7.2, [CB] = 2 × 10^{-3} M, [Q] = 0.02 M).

Figure 1. In the case of (phenylthio)acetic acid (**1**) (Figure 1a), the transient spectrum indicates that the ketyl radical anion ($CB^{\bullet -}$) is a main absorbing species. The difference between the observed spectrum and the composite fit in the short-wavelength spectral region < 400 nm may be due to the absorption of transients derived from sulfur-containing acids, e.g. $C_6H_5-S-CH_2^\bullet$ radical.[12] As shown in Figure 1b for compound **2** ($C_6H_5-CH_2-S-CH_2-COOH$), the transient spectrum is reminiscent of those of the ketyl radical anion ($CB^{\bullet -}$) and the ketyl radical ($CBH^\bullet$). These two species are the only transients observed in the spectral region 400−800 nm. In the case of compound **3** ($CH_3-S-C_6H_4-CH_2-COOH$) and compound **5** ($CH_3-S-C_6H_4-COOH$), strong absorptions from new transients (sulfur-containing intermediates) were observed in the region of 400−800 nm, in addition to the absorptions by $CB^{\bullet -}$ and $CBH^\bullet$ radicals. Without accurate reference spectra for these new transients, it was not possible to resolve the spectra quantitatively.[13]

The concentrations of transients obtained from the procedure described above, together with the additional actinometry measurements, allowed us to determine the quantum yields of the appropriate transients (eq 1) . A

$$\Phi = \frac{[\text{transient}]\epsilon_T l}{\Delta A_T} \qquad (1)$$

solution of CB (2 × 10^{-3} M at neutral pH) was used as the actinometer where the CB triplet absorbance was monitored at 535 nm immediately after the flash, where [transient] is a molar concentration of the transient taken from the resolved absorption spectrum at a particular delay time; ΔA_T is the CB triplet absorbance change at 535 nm immediately after the flash (for actinometry); ϵ_T is the molar absorption coefficient of the CB triplet in water taken as 6250 M^{-1} cm^{-1},[14] and l is the optical path length in cm. A detailed procedure for determining the quantum yields has been described elsewhere.[3d] The Φ values obtained for various delay times were then extrapolated to the end of the laser flash. The extrapolated values were used in the following discussion. Results from the flash photolysis experiments and the quantum yields of SCCA radical cation decarboxylation from steady-state measurements are summarized in Table 1, along with the SCCA structures.

From the data obtained in the laser flash photolysis and steady-state measurements, it is possible to follow some of the main species directly or to make inferences about the processes occurring in the tested systems after the absorption of light. The data are consistent with Scheme 1.

Polymerization Results. Photopolymerization experiments were carried out to compare the efficiency of the photoinitiated polymerization as a function of the SCCA structures. Figure 2 shows the kinetic curves obtained for the laser-initiated polymerization in the presence of CB and various SCCA's. The rates of polymerization determined from the efficiencies of the photopolymerization after 6 min of irradiation are also presented in Table 1. A reference sample containing CB and other components, but without any co-initiator, did not indicate any polymerization even for the time of irradiation several times longer than one used for photopolymerization initiated in the precence of co-initiator.

The rate of photoinitiated polymerization can be controlled by any of the processes that limit the formation of free radicals. These processes could include the rate of the primary process, e.g. the rate of the photochemical electron transfer (PET) process and consequences related to this phenomenon,[15] and a direct PET

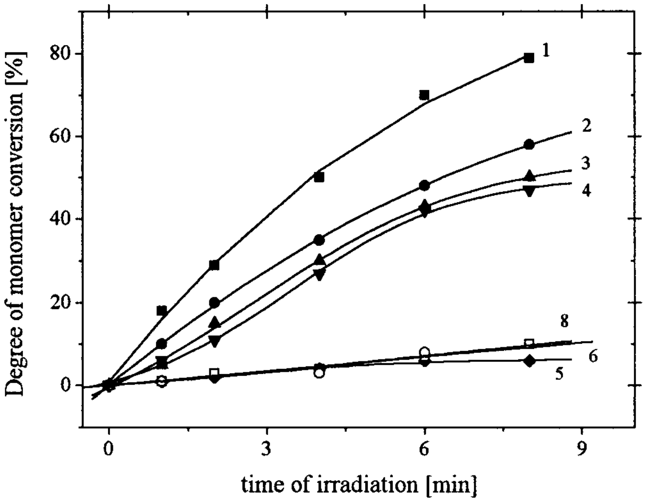
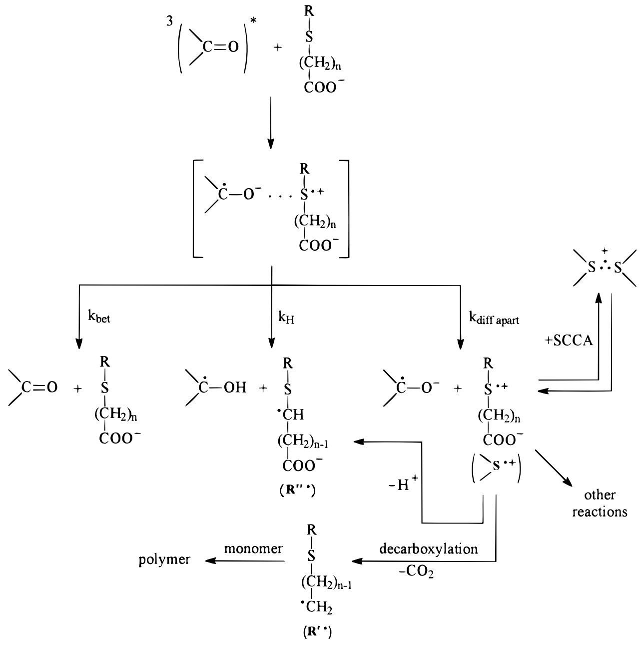


Figure 2. Photopolimeryzation of acrylamide at pH = 6.8 initiated by 4-carboxybenzophenone and various sulfur-containing carboxylic acids: (**1**) phenyl(thioacetic)acid, (**2**) *S*-benzylthioglycolic acid, (**3**) 4-(methylthio)phenylacetic acid, (**4**) 2-(methylthio)ethanoic acid, (**5**) 4-(methylthio)benzoic acid, (**6**) 2,2′-thiodiethanoic acid, and (**8**) dimethyl sulfide.

Scheme 1



effect on the photoinitiated polymerization.[16] However, considering the rate of the CB triplet-state quenching (see Table 1), one can conclude that, for these CB/SCCA systems, the rates of quenching are very similar and vary only slightly in the range (1.0−2.0) × 10^9 M^{-1} s^{-1}. This leads to the conclusion that, under the experimental conditions used, more than 95% of the CB triplets are quenched by the co-initiators. The results in Table 1 show that the main photochemical channel is the diffusion apart of the radical−ion pairs, leading to the formation of $CB^{\bullet -}$ and $>S^{+\bullet}$ radical ions. This finding strongly suggests that the primary process should not limit the observed rate of the photoinitiated polymerization. Therefore, the differences in the measured rates of the polymerizations are likely affected by the yield of secondary processes that follow PET, e.g. decarboxylation or deprotonation, and/or by the reactivity of the free radicals.

Polymerization Kinetics. From the kinetic point of view, a mechanism describing photoinitiated polymerization via a PET process can be presented as follows:

$$\mathrm{CB} \xrightarrow{h\nu,\mathrm{ED}} \mathrm{CB}^{\bullet} + \mathrm{R}^{\bullet} \quad I_{\mathrm{A}}\Phi_{\mathrm{R}^{\bullet}} \tag{2}$$

$$\mathrm{R}^{\bullet} \xrightarrow{k_{\mathrm{d}}} \text{products} \quad k_{\mathrm{d}}[\mathrm{R}^{\bullet}] \tag{3}$$

$$\mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_{\mathrm{i}}} \mathrm{RM}^{\bullet} \quad k_{\mathrm{i}}[\mathrm{M}][\mathrm{R}^{\bullet}] \tag{4}$$

$$\mathrm{R}^{\bullet} + \mathrm{R}^{\bullet} \xrightarrow{k_{\mathrm{r}}} \mathrm{R{-}R} \quad k_{\mathrm{r}}[\mathrm{R}^{\bullet}]^2 \tag{5}$$

$$\mathrm{RM}_n^{\bullet} + \mathrm{M} \xrightarrow{k_{\mathrm{p}}} \mathrm{RM}_{n+1}^{\bullet} \quad k_{\mathrm{p}}[\mathrm{RM}_n^{\bullet}][\mathrm{M}] \tag{6}$$

$$\mathrm{RM}_{n+1}^{\bullet} + \mathrm{RM}_{m+1}^{\bullet} \xrightarrow{k_{\mathrm{t}}} \mathrm{RM}_{n+m+2} \quad k_{\mathrm{t}}[\mathrm{RM}_{n+1}^{\bullet}][\mathrm{RM}_{m+1}^{\bullet}] \tag{7}$$

$$\mathrm{RM}_{n+1}^{\bullet} + \mathrm{R}^{\bullet} \xrightarrow{k_{\mathrm{t}}'} \mathrm{RM}_{n+1}{-}\mathrm{R} \quad k_{\mathrm{t}}'[\mathrm{RM}_{n+1}^{\bullet}][\mathrm{R}^{\bullet}] \tag{8}$$

where ED is the electron donor (co-initiator), M is the monomer, I_A is the intensity of absorbed light, and $\Phi_{R^\bullet}$ is the quantum yield of free-radical formation.

Assuming the rate of reaction 2 is slow relative to reactions 3 and 4, making the steady-state assumption for the total radical concentration, and taking $k_r = k_t = k_t'$, one can obtain the following equation describing the rate of polymerization:[17]

$$R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}]\sqrt{\frac{\Phi_{\mathrm{R}^\bullet}\phi_{\mathrm{RM}^\bullet}I_{\mathrm{A}}}{k_{\mathrm{t}}}} \tag{9}$$

where $\phi_{RM^\bullet}$ is a branching ratio defined by

$$\phi_{\mathrm{RM}^\bullet} = \frac{k_{\mathrm{i}}[\mathrm{M}]}{k_{\mathrm{i}}[\mathrm{M}] + k_{\mathrm{d}}} \tag{10}$$

Analyzing eqs 9 and 10, one can consider two specific conditions:

1. For $k_d \ll k_i[M]$, one obtains for the rate of polymerization

$$R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}]\sqrt{\frac{\Phi_{\mathrm{R}^\bullet}I_{\mathrm{A}}}{k_{\mathrm{t}}}} \tag{11}$$

2. for $k_d \gg k_i[M]$, the rate of polymerization is described as follows:

$$R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}]^{1.5}\sqrt{\frac{k_{\mathrm{i}}\Phi_{\mathrm{R}^\bullet}I_{\mathrm{A}}}{k_{\mathrm{t}}k_{\mathrm{d}}}} \tag{12}$$

Equations 11 and 12 clearly show that the rate of polymerization depends on the monomer concentration, the quantum yield of free-radical formation, and the reactivity of free radicals produced after the photoinduced electron-transfer process.

Kinetic studies of photoinitiated polymerization of CB/SCCA systems show that the tested photoredox pairs exhibit classical properties for this type of polymerization. The photopolymerization of the system appears to proceed by the conventional mechanism in which termination is bimolecular. This conclusion is supported by the experimental results indicating that the rate of polymerization (R_p) is a linear function of square root of the light intensity (I_A). This observation indicates that bimolecular termination is the main process terminating

Table 2. Anticipated Structures of Free Radicals Formed in Secondary Reactions Following PET for the Electron Donors Studied

no.	electron donor	radicals formed	
		after decarboxylation ($R'^{\bullet}$)	after proton transfer ($R''^{\bullet}$)
1	$C_6H_5{-}S{-}CH_2{-}COOH$	$C_6H_5{-}S\text{-}{}^{\bullet}CH_2$	no proton transfer
2	$C_6H_5{-}CH_2{-}S{-}CH_2{-}COOH$	$C_6H_5{-}CH_2{-}S\text{-}{}^{\bullet}CH_2$	$C_6H_5{-}CH_2{-}S\text{-}{}^{\bullet}CH{-}COO^{-}$ $C_6H_5\text{-}{}^{\bullet}CH{-}S{-}CH_2{-}COO^{-}$
3	$CH_3{-}S{-}\ C_6H_4{-}CH_2{-}COOH$	$CH_3{-}S{-}\ C_6H_4\text{-}{}^{\bullet}CH_2$	${}^{\bullet}CH_2{-}S{-}\ C_6H_4{-}CH_2{-}COO^{-}$
4	$CH_3{-}S{-}CH_2{-}COOH$	$CH_3{-}S\text{-}{}^{\bullet}CH_2$	$CH_3{-}S\text{-}{}^{\bullet}CH{-}COO^{-}$ ${}^{\bullet}CH_2{-}S{-}CH_2{-}COO^{-}$
5	$CH_3{-}S{-}\ C_6H_4{-}COOH$	no decarboxylation	${}^{\bullet}CH_2{-}S{-}\ C_6H_4{-}COO^{-}$
6	$HOOC{-}CH_2{-}S{-}CH_2{-}COOH$	${}^{\bullet}CH_2{-}S{-}CH_2{-}COO^{-}$	${}^{-}OOC\text{-}{}^{\bullet}CH{-}S{-}CH_2{-}COO^{-}$
7	$HOOC{-}(CH_2)_2{-}S{-}(CH_2)_2{-}COOH$	no decarboxylation	${}^{-}OOC{-}CH_2\text{-}{}^{\bullet}CH{-}S{-}(CH_2)_2{-}COO^{-}$
8	$CH_3{-}S{-}CH_3$		$CH_3{-}S\text{-}{}^{\bullet}CH_2$

polymerization. Furthermore, there is a linear relationship (see eq 11) between the rate of polymerization and the monomer concentration for the CB/(phenylthio)acetic acid photoinitiating system. This relationship held over the monomer concentration range tested (0.7–4.0 M).

There is another interesting feature of eqs 11 and 12. They show that the rate of photoinitiated polymerization is proportional to the square root of the quantum yield of free-radical formation ($\Phi_{R^{\bullet}}$). It is evident from Scheme 1 that there are two types of radicals ($R'^{\bullet}$ and $R''^{\bullet}$) that could initiate polymerization. The quantum yield of $R'^{\bullet}$ production can be taken to be equal to the quantum yield of CO_2. The quantum yield of $R''^{\bullet}$ could be estimated by

$$\Phi_{R''^{\bullet}} = \Phi_{CBH^{\bullet}} + (\Phi_{CB^{\bullet -}} - \Phi_{CO_2}) \qquad (13)$$

Radical Structures. It is possible to anticipate the structures of the free radicals that are formed after PET by analyzing the quantum yields of the processes presented in Scheme 1 and from a study of the data in Table 1. For example, from Table 1 it is seen that co-initiator **1** has its quantum yields of CO_2 formation and $CB^{\bullet -}$ formation almost equal. If Scheme 1 is followed for co-initiator **1**, then only the α-thioalkyl radical, $Ph{-}S{-}{}^{\bullet}CH_2$, shown in the third column of Table 2 can be formed. The procedure for writing down the expected radicals from co-initiator **2** is somewhat more complicated. There is a significant quantum yield of CO_2 indicating that the radical $Ph{-}CH_2{-}S{-}{}^{\bullet}CH_2$, in column 3 (Table 2) is formed. However, there is a significantly lower quantum yield of CO_2 than for $CB^{\bullet -}$, which indicates that a large amount of the $>S^{\bullet +}$ from the diffusion apart of the radical–ion pair is not decarboxylating into the $R'^{\bullet}$. In addition, since the yield of $CBH^{\bullet}$ is nonzero, $R''^{\bullet}$ radicals are forming from the in-cage protonation within the radical–ion pair (Scheme 1). One final example is co-initiator **7** that shows no measurable CO_2 following quenching events. Thus, only the nondecarboxylated $R''^{\bullet}$ radicals from the in-cage protonation and/or from deprotonation of the $>S^{\bullet +}$ radicals are expected and listed in Table 2. Using analogous considerations, the other free-radical structures were enumerated and presented in Table 2.

Radicals Responsible for Initiation. The co-initiators in Table 1 appear to fall neatly into two separate groups with respect to their polymerization rates; the first four have significantly larger R_p values than do the last four. In addition, the first four also have quite large quantum yields of decarboxylation compared to three of the last four co-initiators. When these observations are considered in conjunction with eqs 11 and 12, a tentative hypothesis is that $\Phi_{R^{\bullet}}$ can be replaced in eqs 11 and 12 by Φ_{CO_2}. This is equivalent to assuming that the $R'^{\bullet}$ radicals (Scheme 1) are primarily responsible for initiating the polymerization. As a first approximation, we also assume the other parameters associated with the polymerization remain the same for the different co-initiators. With these assumptions, there should be a linear relationship between R_p and $\sqrt{\Phi_{CO_2}}$. A plot of R_p vs $\sqrt{\Phi_{CO_2}}$ is shown in Figure 3 for all co-initiators used.

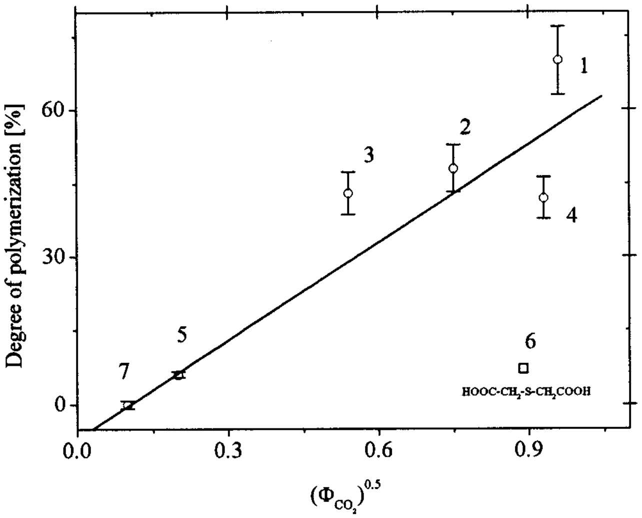


Figure 3. Degree of monomer conversion vs square root of the quantum yield of decarboxylation for the electron donors studied: (**1**) Phenyl(thioacetic)acid, (**2**) *S*-benzylthioglycolic acid, (**3**) 4-(methylthio)phenylacetic acid, (**4**) 2-(methylthio)-ethanoic acid, (**5**) 4-(methylthio)benzoic acid, (**6**) 2,2′-thiodiethanoic acid, and (**7**) 3,3′-thiodipropionic acid.

From Figure 3, it is evident that (phenylthio)acetic acid (**1**) has the highest rate of polymerization and the largest CO_2 yields, which is consistent with eqs 11 and 12 and the assumption that $\Phi_{R^{\bullet}} = \Phi_{CO_2}$. On the basis of the analysis above, there is only one radical, $R'^{\bullet}$, capable of initiating polymerization when **1** is used as the co-initiator with CB. Thus, the highest initiating ability is observed for the system in which there is no in-cage proton-transfer process; e.g., there is no formation of radicals localized on carbons adjacent to the carboxylate ion.

The trend in R_p vs $\sqrt{\Phi_{CO_2}}$ extends to *S*-benzylthioglycolic acid (**2**) and 4-(methylthio)phenylacetic acid (**3**), where one observes sharp decreases in their quantum yields of decarboxylation, accompanied by corresponding decreases in their rates of photopolymerization. This is not due merely to decreases in overall radical formation because there are actually quite large yields of radicals, particularly for **2**, as can be seen by the accompanying quantum yields of $CB^{\bullet -}$ and $CBH^{\bullet}$ formation. Thus, it is not the overall radical formation that appears to influence the rate of polymerization with

2 and **3** as co-initiators; it is specifically the radicals, R′•, from decarboxylation that appear to be critical for efficient initiation. For these three compounds, the assumptions motivating the making of Figure 3 appear to be justified.

The qualitative trend continues for 2-(methylthio)-ethanoic acid (**4**), but its high quantum yield of decarboxylation is not accompanied by as large a rate of polymerization as would be expected from the linear relationship based on the data from **1**, **2**, and **3**. Co-initiators **5** and **7** are also consistent with the linear relationship under consideration. However, the co-initiator 2,2′-thiodiethanoic acid (**6**) clearly does not follow the same pattern as the other co-initiators. For this co-initiator there is a high yield of decarboxylation but a very low free-radical polymerization efficiency.

On the basis of these observations, it is apparent that the better initiators are the free radicals possessing aromatic moieties compared to similar aliphatic radicals (compare co-initiators **1**, **2**, and **3** with co-initiator **4**). Another conclusion is that radicals that retain the carboxylate ion appear to be very poor co-initiatiors (for the aromatic co-initiators compare **1** and **2** with **5** and for the aliphatic co-initiators compare **4** with **6** or **7**). The observation is a justification for the R_p vs $\sqrt{\Phi_{CO_2}}$ plot in Figure 3, which implies that the nondecarboxylated radicals are ineffective co-initiators.

It is not clear why the radicals containing the carboxylate moiety are not effective co-initiators, but that it is true can be seen by looking more closely at the results. Co-initiators **6** and **7** are particularly of note with respect to the reactivity of nondecarboxylated radicals. 3,3′-Thiopropionic acid (**7**) in the presence of CB does not initiate free-radical polymerization, despite a relatively high total quantum yield of $CB^{\bullet -}$ formation (see Table 1). Only the α-thioalkyl radical with two carboxylate moieties is possible. For co-initiator **6**, all radicals formed should be carboxylate-substituted α-thioalkyl radicals, and its rate of polymerization is also quite low. For **6**, even its partially decarboxylated radical should still have one carboxylate site. The low efficiency of polymerization initiation for the nondecarboxylated α-thioalkyl radicals could be attributed to several processes. These processes might include a low efficiency for the formation of free radicals centered on carbons adjacent to the sulfur (R″•), a high rate for the chain termination processes, and/or a low value for $\phi_{RM^\bullet}$.

An additional argument supporting the fact that the radicals R′• obtained from decarboxylation are mainly responsible for the initiation of polymerization is based on the results obtained for co-initiator **8**. The sensitized CB photooxidation of dimethyl sulfide leads to the formation of $^\bullet CH_2{-}S{-}CH_3$ radicals with a quantum yield estimated to be in the range of 0.10−0.26 (Table 1, eq 13). The same initiating radicals were obtained via the decarboxylation of **4**, but with a much higher quantum yield. However, the polymerization rate for co-initiator **8** is 5 times lower than for **4**, and this ratio is in agreement with the ratio of square root of radical quantum yields for these compounds (estimated as about 3). A correlation of the results obtained for co-initiator **8** with those for the sulfur-containing carboxylic acids **1**−**7** is also shown in Figure 3. Note that in this case the *x*-axis value represents a lower limit of $(\Phi_{^\bullet CH_2SCH_3})^{0.5}$.

Conclusions

(1) The rates of polymerization of the CB/SCCA/acrylamide systems are affected by the yields of secondary processes that follow photoinduced electron transfer, e.g. decarboxylation or deprotonation. This is in addition to the reactivity of the free radicals themselves. (2) The highest initiation yield is observed for the system where there is efficient diffusion apart of the radical−ion pairs, followed by efficient decarboxylation. The resulting radicals are localized on carbons adjacent to the sulfur atom. (3) Free radicals with aromatic moieties are better initiators than are the analogous aliphatic radicals. (4) Radicals that retain the carboxylate moiety are inefficient initiators. (5) Photopolymerization of these systems appears to proceed by the conventional mechanism where termination is bimolecular.

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