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## POLYMERIZATION OF ACRYLAMIDE IN AQUEOUS MEDIUM INITIATED BY REDOX SYSTEM OF 4-CARBOXYBENZOPHENONE AND SULFUR-CONTAINING COMPOUNDS

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### ABSTRACT

A series of sulfur-containing compounds was investigated as electron donors in photoinduced free-radical polymerization, in conjunction with 4-carboxybenzophenone (CB) as sensitizer. These compounds included (phenylthio)acetic acid, ethionine, methionine, Gly-Met, Met-Gly and methionine methyl ester. The results were compared with the nonsulfur-containing compounds, alanine and triethanolamine. The best initiation yields is observed for the system CB-(phenylthio)acetic acid.

*Key Words:* Redox initiators; Aqueous polymerization.

### INTRODUCTION

Redox polymerization, initiated by free radicals formed via oxidation-reduction reactions are characterized by very short induction periods, high polymer yield in a short time, and the possibility of performing polymerization at room temperature or below (1,2). Several authors reported a redox system in polymerization of aqueous and nonaqueous medium (3–8). These include benzophenone, thioxanthone, camphorquinone, and dye structures as the absorbing species and

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amines as electron donors. The great disadvantage of all amines is their high toxicity (9–11) and mutagenicity (12,13). Therefore, it is not a convenient system in the polymerization of materials used in medicine, especially in dental materials, where allergic or mutagenic reactions may be caused by photoinitiators and products of their photolysis. In our earlier work (14,15), it is shown that the benzophenone/sulfur-containing amino and carboxylic acids systems can be effectively used for photoinitiation of free radical polymerization in aqueous media. The main goal of the present study is the comparison of activity of sulfur-containing amino acids, carboxylic acids, and peptides as the electron donors in the polymerization in aqueous medium. Also, a comparison of these systems with other redox ones in the polymerization of aqueous monomer solutions is made.

## EXPERIMENTAL

### Materials

Methionine, ethionine, (phenylthio)acetic acid, alanine, triethanolamine, acrylamide AA (electrophoresis grade), 4-carboxybenzophenone were purchased from Aldrich. Methionine methyl ester and the dipeptides methionyl-glycine (Met-Gly) and glycyl-methionine (Gly-Met) were purchased from Bachem. All these compounds were used as received. Triethanolamine was distilled before using. Water was double distilled.

### Photopolymerization

The light source used was a Innova 90-4 argon-ion laser, Coherent. The wavelengths 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 63 mW/cm<sup>2</sup>. Photopolymerization efficiencies were measured gravimetrically by the irradiation of a quartz cell containing 2.5 cm<sup>3</sup> of an aqueous solution of the monomer, 4-carboxybenzophenone, and the coinitiator. All the solutions were deoxygenated by bubbling high-purity helium through them and were buffered in the presence of phosphate buffer (pH = 6.8) and borax-potassium hydroxide one (pH = 9.5). After irradiation, the contents of the cell were poured into acidified methanol for precipitation, then filtered, and dried to constant weight. The concentrations of 4-carboxybenzophenone, coinitiators, and acrylamide were constant in all experiments being 0.002 M, 0.02 M, and 1 M, respectively.

## RESULTS AND DISCUSSION

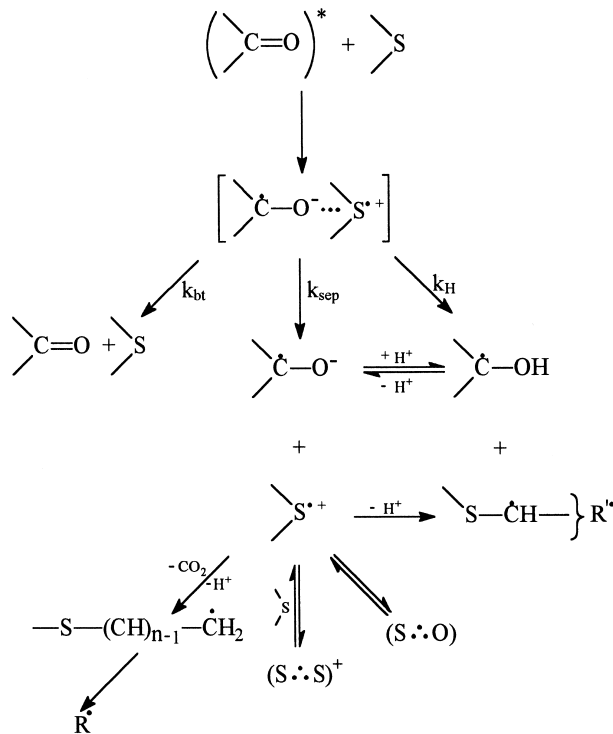
More recently, Marciniak, Bobrowski, and Hug examined the quenching of triplet states of benzophenone by sulfur-containing compounds in aqueous solu-

tion (16–19). According to these authors, the mechanism of photoinduced electron transfer between sulfur-containing compounds involves an electron transfer from the sulfur atom to the triplet state of benzophenone to form a radical-ion pair. Subsequently, 1) the radical ions can diffuse apart ( $k_{\text{sep}}$ ); 2) there can be intramolecular proton transfer within the radical-ion pair ( $k_{\text{H}}$ ); or, 3) back electron transfer ( $k_{\text{bt}}$ ) can occur to regenerate the reactants in their ground state (Sch. 1).

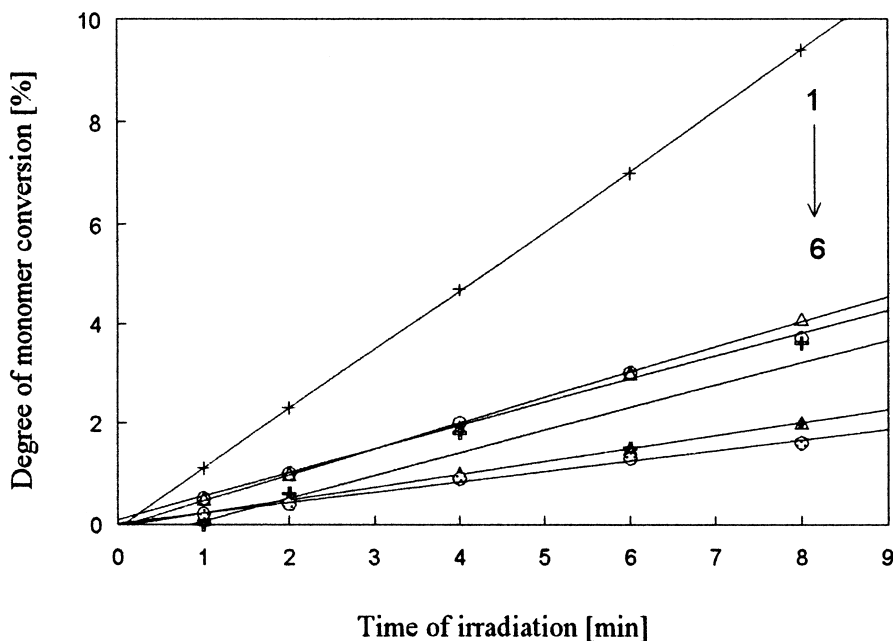
The first process led to the formation of sulfur-centered radical cations that can undergo decarboxylation reactions to give thioalkyl radicals. In the second process, kethyl and  $\alpha$ -(alkylthio)alkyl radicals are obtained.

### Polymerization Results

Photopolymerization experiments were carried out to compare the efficiency of the photoinitiated polymerization as a function of the sulfur-containing and nonsulfur-containing compounds structures. Figure 1 shows the kinetic curves obtained for the polymerization in the presence of carboxybenzophenone (CB) and various compounds as the electron donors. The rates of polymerization determined from the efficiencies of the photopolymerization after 8 min of irradiation



Scheme 1.



**Figure 1.** Photopolymerization of acrylamide at pH=6.8 initiated by 4-carboxybenzophenone and various sulfur-containing compounds: **1**) (phenylthio)acetic acid, **2**) ethionine, **3**) methionine methyl ester, **4**) methionine, **5**) Met-Gly, and **6**) Gly-Met.

are also presented in Table 1. A reference sample containing CB and other components, but without any coinitiator, did not indicate any polymerization.

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 processes, e.g., the rate of the photochemical electron transfer (PET) process and consequences related to this phenomenon (20) and direct PET effect on the photoinitiated polymerization (21,22). However, considering the rate of the CB triplet-state quenching (Tab. 1), one can conclude that, for CB/sulfur-containing compounds and for alanine and triethanolamine nonsulfur-containing systems, the rates of quenching are very similar and vary only slightly in the range  $(1.0-3.0) \times 10^9 \text{M}^{-1}\text{s}^{-1}$ . This leads to the conclusion that, under the experimental conditions used, more than 95% of the CB triplets are quenched by coinitiators. The results in Table 1 show that only for the CB-(phenylthio)acetic acid system almost 100% of radical-ion pairs undergo diffusion apart, leading to the formation of  $\text{CB}^{\cdot-}$  and  $>\text{S}^{\cdot+}$  radical ions. This finding strongly suggests that only for this system the primary process should not limit the observed rate of the photoinitiated polymerization. Therefore, the differences in the measured rates of the polymerization 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. For other coinitiators back electron transfer process must be considered.

**Table 1.** Rate Constants for Quenching of the CB Triplet by Coinitiators, Quantum Yields for the Formation of Carbon Dioxide, the CB Radical Anion, and the CB Ketyl Radical After CB Triplet Quenching, and Rates of Polymerization pH = 6.8

No	Coinitiator	Coinitiator structure	$k_q \times 10^{-9}$ ( $M^{-1}s^{-1}$ )	$\Phi_{CO_2}$	$\Phi_{CB^{\bullet-}}$	$\Phi_{CBH^{\bullet}}$	$R_p$ % min.
1.	(Phenylthio)acetic acid		1.9 <sup>d</sup>	0.92 <sup>d</sup>	0.97 <sup>a</sup>	0	9.3
2.	Ethionine		2.9 <sup>b</sup>	0.16 <sup>b</sup>	$\Phi_{CB^{\bullet-}}$ + $\Phi_{CBH^{\bullet}}$		4.1
3.	Methionine		2.5 <sup>b</sup>	0.28 <sup>b</sup>	0.33 <sup>d</sup>		3.6
4.	Gly-Met		2.0 <sup>b</sup>	0.02 <sup>b</sup>	0.22 <sup>b</sup> pH = 6	0.15 <sup>b</sup> pH = 6	2.0
5.	Alanine		<0.0005 <sup>b</sup>	---	---	---	---
6.	Methionine methyl ester		3.0 <sup>c</sup>	no decarboxyl ation	0.04 <sup>c</sup> pH = 6.4	0.39 <sup>c</sup> pH = 6.4	3.9
7.	Met-Gly		2.1 <sup>b</sup>	0.01 <sup>b</sup>	0.01 <sup>c</sup> pH = 6	0.39 <sup>c</sup> pH = 6	1.6
8.	Triethanolamine	$N-(C_2H_4OH)_3$	---	---	---	---	---

<sup>a</sup> From reference 15.

<sup>b</sup> From reference 17.

<sup>c</sup> From reference 18.

<sup>d</sup> From reference 16.

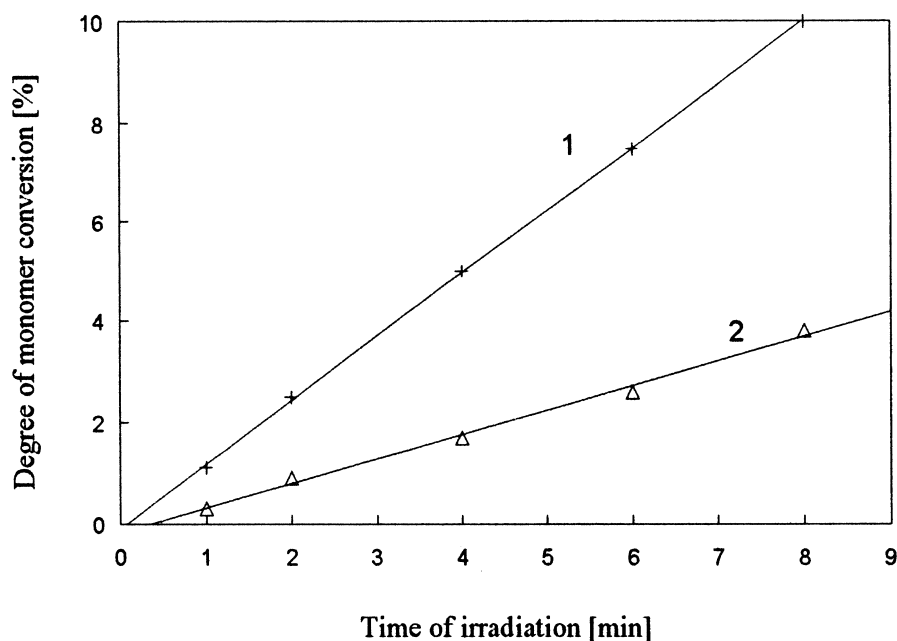
### Radicals Responsible for Initiation

From Figure 1, it is evident that (phenylthio)acetic acid **1** has the highest rate of polymerization. Because of this coinitiator there is no in cage proton-transfer, and  $\Phi_{\text{CO}_2}$  is equal 0.92, there is only one radical  $\text{R}^\bullet$ , capable of initiating polymerization when **1** is used as the coinitiator with CB. The second group of coinitiators (ethionine, methionine methyl ester, and methionine) only partially diffuse out of the complex. The value of  $\text{CBH}^\bullet$  and  $\text{CB}^{\bullet-}$  for these coinitiators is  $< 0.4$  (see Tab. 1), that means that about 60% of molecules return to regenerate the reactants. In the case of methionine and ethionine there are two types of radicals,  $\text{R}^\bullet$  and  $\text{R}^{\bullet-}$ . Previous investigation (15) indicated that radicals that retain the carboxylate moiety are inefficient initiators.

Therefore, radicals  $\text{R}^\bullet$  are responsible for polymerization. For methionine methyl ester there is no decarboxylation, so only radicals  $\text{R}^{\bullet-}$  polymerize AA. Also, the last two sulfur-containing compounds, Gly-Met and Met-Gly, virtually do not undergo decarboxylation. Because radicals  $\text{R}^\bullet$  contain carboxylate moiety, Gly-Met and Met-Gly are very poor initiators of polymerization of acrylamide.

**Table 2.** Anticipated Structures of Free Radicals Formed in Secondary Reactions After Photoinduced Electron Transfer for the Electron Donors Studied at pH = 6.8

No	Electron donor	Radicals formed after decarboxylation $\text{R}^\bullet$	Radicals formed after proton transfer $\text{R}^{\bullet-}$
1.			no proton transfer
2.	$\text{CH}_3\text{-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-COOH}$	$\text{CH}_3\text{-CH}_2\text{-S-CH}_2\text{-CH}_2\text{-}\dot{\text{C}}\text{H-NH}_2$	$\text{CH}_3\text{-CH}_2\text{-S-}\dot{\text{C}}\text{H-CH}_2\text{-CH(NH}_2\text{)-COO}^-$
3.	$\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-COOH}$	$\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-}\dot{\text{C}}\text{H-NH}_2$	$\text{CH}_3\text{-S-}\dot{\text{C}}\text{H-CH}_2\text{-CH(NH}_2\text{)-COO}^-$
4.	$\text{H}_2\text{N-CH}_2\text{-C(=O)-NH-CH}_2\text{-COOH}$   (CH <sub>2</sub> ) <sub>2</sub>   S   CH <sub>3</sub>	$\text{H}_2\text{N-CH}_2\text{-C(=O)-NH-}\dot{\text{C}}\text{H}$   (CH <sub>2</sub> ) <sub>2</sub>   S   CH <sub>3</sub>	$\text{H}_2\text{N-CH}_2\text{-C(=O)-NH-CH}_2\text{-COO}^-$   CH <sub>2</sub>   •CH   S   CH <sub>3</sub>
5.	$\text{CH}_3\text{-CH(NH}_2\text{)-COOH}$	-----	-----
6.	$\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-CH(NH}_2\text{)-COOCH}_3$	-----	$\text{CH}_3\text{-S-}\dot{\text{C}}\text{H-CH}_2\text{-CH(NH}_2\text{)-COOCH}_3$
7.	$\text{H}_2\text{N-CH}_2\text{-C(=O)-NH-CH}_2\text{-COOH}$   (CH <sub>2</sub> ) <sub>2</sub>   S   CH <sub>3</sub>	$\text{H}_2\text{N-CH}_2\text{-C(=O)-NH-}\dot{\text{C}}\text{H}_2$   (CH <sub>2</sub> ) <sub>2</sub>   S   CH <sub>3</sub>	$\text{H}_2\text{N-CH}_2\text{-C(=O)-NH-CH}_2\text{-COO}^-$   CH <sub>2</sub>   •CH   S   CH <sub>3</sub>
8.	$\text{N}^+\text{-C}_2\text{H}_4\text{OH}^{\ominus}_3$	-----	-----



**Figure 2.** Photopolymerization of acrylamide at pH=9.5 initiated by 4-carboxybenzophenone and: 1) (phenylthio)acetic acid, and 2) alanine.

Nonsulfur-containing compounds, alanine and triethanolamine, do not polymerize AA. For alanine, the rate constant of quenching CB triplet state is very low, this is due to the protonation of amine group (23). Triethanolamine is known as one of the best coinitiators of polymerization by water-soluble benzophenones (3). The rates quenching of the triplet state of (*p*-(methyl sodium sulfonate)-benzophenone and (*p*-methyltrimethylammonium chloride)-benzophenone are  $1.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  and  $1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , respectively (24). In spite of that, triethanolamine does not act as a coinitiator of the polymerization of CB in the same conditions as there are ones for the sulfur-containing compounds (the same concentration and time of irradiation).

In pH 9.5, alanine acts as a coinitiator of polymerization but, still this one is worse than (phenylthio)acetic acid is. Triethanolamine in turn does not polymerize the monomer.

## CONCLUSION

Sulfur-containing compounds are efficient coinitiators of the polymerization. The highest initiation yield is observed for the system where there is efficient diffusion apart of the radical-ions pairs. Nonsulfur-containing compounds, alanine and triethanolamine, are worse coinitiators than the sulfur-containing ones. (Phenylthio)acetic acid is the best coinitiator of the polymerization.



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