Polymer 40 (1999) 3247–3249

polymer

Polymer Communication

Polymerization of acrylamide in aqueous medium initiated by a redox system of 4-carboxybenzophenone and sulfur-containing amino acids

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Received 5 June 1998; revised 24 August 1998; accepted 24 August 1998

Abstract

The photopolymerization of acrylamide in aqueous medium initiated by redox system consisting of 4-carboxybenzophenone and sulfur-containing amino acids was studied. The rate of polymerization depends on the quenching rate of the 4-carboxybenzophenone triplet by the sulfur-containing amino acid and on the kind of radicals obtained. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Redox initiators; Aqueous polymerization

1. Introduction

Benzophenone is photoreduced by aliphatic and aromatic amines [1–7]. The photopolymerization of monomers initiated by the benzophenone–amine redox system has been known for many years [8–12]. Recently, water-soluble benzophenone derivatives possessing ionic hydrophilic groups have been used in the polymerization of water-soluble monomers [13–16]. In all cases α-aminoalkyl radicals were responsible for the polymerization. The ketyl radical is insufficiently reactive to initiate polymerization. The work of Bobrowski et al. indicates that 4-carboxybenzophenone sensitizes the photooxidation of sulfur-containing amino acids [17,18]. The products of the reaction are the ketyl radical, α-aminoalkyl radicals and α-(alkylthio)alkyl radicals. Amines are known as carcinogenic compounds and, as such, are not recommended as co-initiators in the formulations used in medicine (especially in photocuring dental materials). Sulfur-containing amino acids are biologically less toxic, non-allergic and probably non-mutagenic, so they can replace harmful amines as co-initiators. To the best of the author’s knowledge, the polymerization of aqueous systems by water-soluble benzophenones and sulfur-containing amino acids has not been reported previously.

2. Experimental

4-Carboxybenzophenone (CB), the sulfur-containing amino acids and acrylamide (AA; electrophoresis grade) from Aldrich, alanine and proline from Roanal (best available grades) were used without further purification. The light source used was an Osram high-pressure xenon lamp (150 W). The incident light intensity at the sample position was measured with an IL 1400 A radiometer (Int. Light Inc., USA) and was 45 mW/cm^2. A glass filter was used to cut off the radiation below 320 nm. Photopolymerization efficiencies were determined gravimetrically by irradiating a quartz cell apparatus containing 3 cm^3 of aqueous solution containing monomer, carboxybenzophenone and co-initiator. All solutions were deoxygenated by bubbling high-purity helium through them. They were buffered in the presence of phosphate buffer (pH $=$ 6.8) or concentrated sodium hydroxide (pH $\approx$ 11.5). After irradiation, the contents of the cell were poured into acidic methanol for precipitation, then filtered and dried to constant weight. The concentration of carboxybenzophenone, co-initiators and acrylamide was constant in all experiments, being 0.002 M, 0.1 M and 0.7 M, respectively.

3. Results and discussion

The excited triplet state of 4-carboxybenzophenone is quenched by sulfur-containing amino acids and by alanine, an amino acid that does not contain sulfur (Scheme 1). The nature of quenching processes is electron transfer in character. In neutral aqueous solution the quenching occurs via electron transfer from the sulfur atom to the triplet state of CB [17].

The values of quenching rate constants depend on the structure of the amino acids (Table 1). The results of

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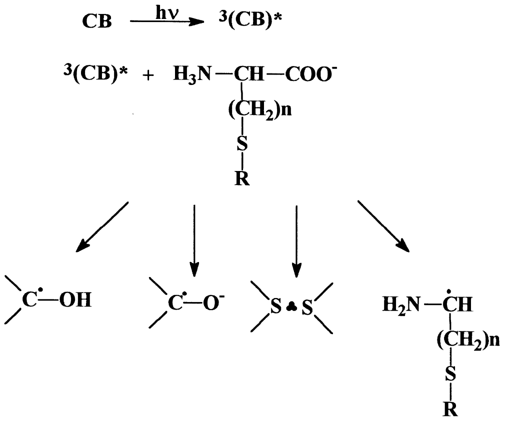
PII: S0032-3861(98)00603-X



Scheme 1 [17].

quenching the 4-carboxybenzophenone triplet state are the ketyl radical of carboxybenzophenone ($CB^{\cdot}$), the radical anion of carboxybenzophenone ($CB^{\cdot -}$), the ($S^{\cdot +}$) radical cation and the α-aminoalkyl radical (α-N). Fig. 1 shows the results of the polymerization of AA in aqueous solution at pH = 6.8. The results presented indicate that ethionine is the best co-initiator of polymerization in the 4-carboxybenzophenone/sulfur-containing amino acid redox system. Under these conditions alanine and proline (an analogue of thiaproline) do not initiate the polymerization of monomer. The lack of polymerization initiation is due to the difference in quenching rate of the CB triplet state by alanine and proline, compared with the sulfur-containing amino acids. The quenching constant for alanine at pH = 6.8 is several orders of magnitude lower than *kq* obtained for the sulfur-containing amino acids (Table 1). The investigations of Pączkowski et al. show that free-radical dye-initiated photopolymerization depends on the rate of photoinduced electron transfer, which is determined by ΔG° of this process as described by the Rehm–Weller equation [19,20]. Because the rate of electron transfer is a function of the rate of quenching *kq*, the polymerization efficiences are also dependent on this value. The rate of quenching of the 4-carboxybenzophenone triplet by sulfur-containing amino acids is not affected by changing the state of protonation of the amine group in the acids. The values of *kq* measured at pH ≈ 11.5 are high and are similar to those obtained at pH = 6.8 (Table 1). On the other hand, for alanine, the value of *kq* measured at pH ≈ 11.5 is at last three orders of magnitude higher than the analogous one at pH = 6.8, but is still an order of magnitude lower than the *kq* values obtained for the sulfur-containing amino acids (Fig. 2). Therefore alanine initiates photopolymerization of AA at pH ≈ 11.5. Not only the quenching rate of the 4-carboxybenzophenone triplet by the sulfur-containing amino acids is responsible for the photopolymerization, but also the kind of radical obtained plays a very important role. For methionine, for instance, a lack of $SN^{\cdot}$ radicals at pH ≈ 11.5 is observed compared with the situation at pH = 6.8. In all polymerization experiments the curves do not originate from zero and show an induction period as observed by other authors for the polymerization of acrylamide in water solution [21,22].

Table 1
Quenching of the 4-carboxybenzophenone triplet by sulfur-containing amino acids and alanine [17,18]

Amino acid	$kq \times 10^{-9}$ ($M^{-1}\,s^{-1}$)	
	pH = 11.5	pH = 6.8
Thiaproline	2.6	2.1
Ethionine		2.9
Methionine	2.7	2.6
4-Carboxymethylcysteine	0.75	0.81
Alanine	0.18	$\leq 6 \times 10^{-4}$

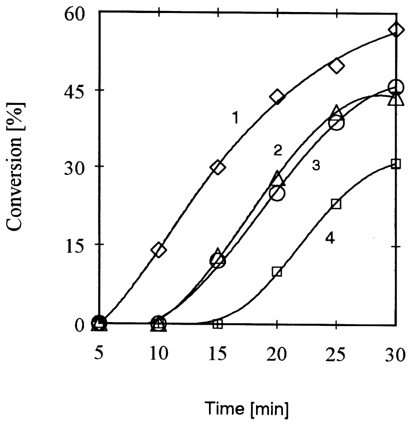


Fig. 1. Photopolymerization of acrylamide at pH = 6.8 initiated by 4-carboxybenzophenone and various sulfur-containing amino acids: 1 — ethionine; 2 — methionine; 3 — thiaproline; 4 — carboxymethylcysteine.

In conclusion, it should be pointed out that sulfur-containing amino acids are very efficient co-initiators of the polymerization of aqueous acrylamide solution. The rate of polymerization is not affected by pH, as is in the case of non sulfur-containing amino acids. The advantage of this new system is that sulfur-containing amino acids

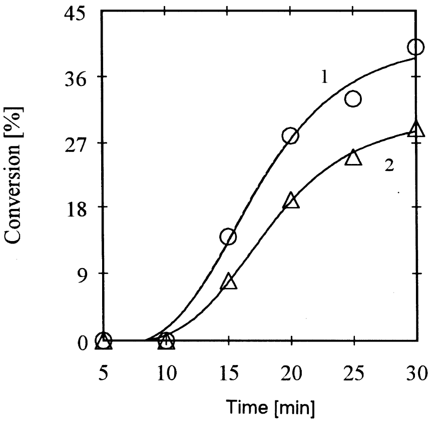


Fig. 2. Photopolymerization of acrylamide at pH = 11.5 initiated by: 1 — methionine and 2 — alanine.

should be biologically less harmful than the amines traditionally applied as co-initiators of the polymerization.

Acknowledgements

This project was sponsored by the State Commitee for Scientific Research (KBN), Poland, grant no. 3 TO9B 087 15. The author is most grateful for this support.

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