

Novel Sulfur—Containing Benzophenone Derivative as Radical Photoinitiator for Photopolymerization

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ABSTRACT: A novel, highly efficient, polymerizable sulfur-containing photoinitiator for free radical polymerization, benzophenone thio-acetic acid (BP-S-CH₂-COOH) was synthesized, characterized, and compared to photoinitiator parameters of the benzophenone (BP) and benzophenone/(phenylthio)acetic acid couple. The photoinitiator possesses a greatly redshifted UV maximal absorption in comparison to BP. Laser flash photolysis studies suggest that photoinitiator radicals are generated by photocleavage

of C—S bond. Photopolymerization of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) demonstrated that one-component system BP—S—CH₂—COOH is more efficient for polymerization than two-component system. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2604–2608, 2011

Key words: photoinitiators; benzophenone; photopolymerization

INTRODUCTION

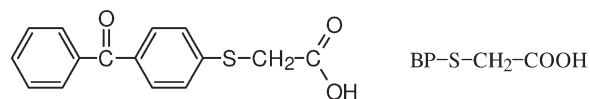
The process of the photoinitiated polymerization may be started by a direct photolysis of precursor providing free radicals by bond dissociation (Type I photoinitiators). The radicals may also be formed in bimolecular processes,^{1,2} which include bimolecular reactions between an excited chromophore and electron donor (Type II photoinitiators). The sulfur-carbon bond is relatively low bond (257–293 kJ mol⁻¹).^{3,4} Consequently, if incorporated into molecule possessing a suitable chromophore, this bond undergoes an easy cleavage upon irradiation producing both a carbon and a sulfur radical. Besides, the introduction of the thio atom may red shift their absorption maxima. This feature has been used in the design of various sulfur-containing initiators.^{5–11}

Benzophenone is very attractive chromophore owing to its photochemical properties.

Because the nucleophilic sulfur atom is very susceptible to oxidation, ketones and the dyes are reduced by sulfur-containing compounds, and as a result sulfur-centered and carbon-centered radicals are formed.^{12–15} For this reason sulfur-containing carboxylic acids¹⁶ and thioamino acids¹⁷ (as electron

donors) and 4 carboxybenzophenone,¹⁸ thioxanthone,^{19,20} and xanthene dyes^{14,21} (as electron acceptors) were used in Type II of initiators for radical photopolymerization of the acrylates.

In this article, we report the synthesis and the use of benzophenone thio-acetic acid as one-component photoinitiator of the structure shown below, as a photoinitiator for free radical polymerization of acrylate. We also compared photochemical, spectroscopic, and photoinitiating properties of the compound with those of the commercial initiator, benzophenone and benzophenone/(phenylthio)acetic acid couple.



EXPERIMENTAL

Materials

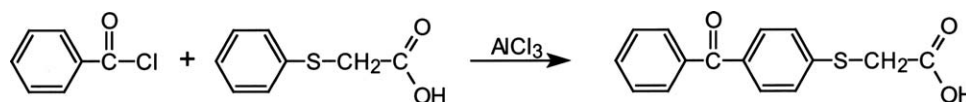
All reagents (the best available grade) were obtained from Aldrich except acetonitrile (Merck), and were used without further purification.

Synthesis

BP—S—CH₂—COOH was synthesized according to the modified method described in early literature.²² A mixture of carbon disulfide (100 g, 1.3 mol) and aluminum chloride (10.36 g, 0.08 mol) was placed in

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Scheme 1 Synthesis route for BP-S-CH₂-COOH.

round-bottomed flask equipped with thermometer and stirrer. The temperature was held between 10 and 15°C and then benzoyl chloride (3.09 g, 0.02 mol) was added over 15 min. Next (phenylthio)acetic acid (3.36 g, 0.02 mol) and nitrobenzene (2.46 g, 0.02 mol) were added periodically in over 20 min and were stirred 20 min in 15°C and 3 h in room temperature (~ 22°C). After that time the mixture was poured into 700 cm³ of diluted hydrochloric acid containing ice. The precipitate was separated and washed with diluted hydrochloric acid. The crude product was partially purified by dissolving it in 150 cm³ of aqueous NaHCO₃, filtering, acidifying, and drying. Further purification was affected by crystallization from carbon tetrachloride containing small amount of petroleum ether. Yield 76%, mp 134–135°C.

¹H NMR (DMSO-*d*₆) δ (ppm): 12.96 (br, s, 1H, (COOH)), 7.72–7.42 (m, 9H), 3.97 (s, 2H (CH₂)).

¹³C NMR (DMSO-*d*₆) δ (ppm): 194.61 (CO), 170.06 (COOH), 142.70 (C), 137.06 (C), 133.46 (C), 132.35 (CH), 130.19 (CH), 129.32 (CH), 128.41 (CH), 125.73 (CH), 33.71 (CH₂).

IR (KBr) ν (cm⁻¹): 1718 (C=O, carboxyl group), 1638 (C=O, ketone).

Analysis

¹H NMR (200 MHz) and ¹³C NMR (50 MHz) spectra were recorded on a Varian Gemini 200 MHz spec-

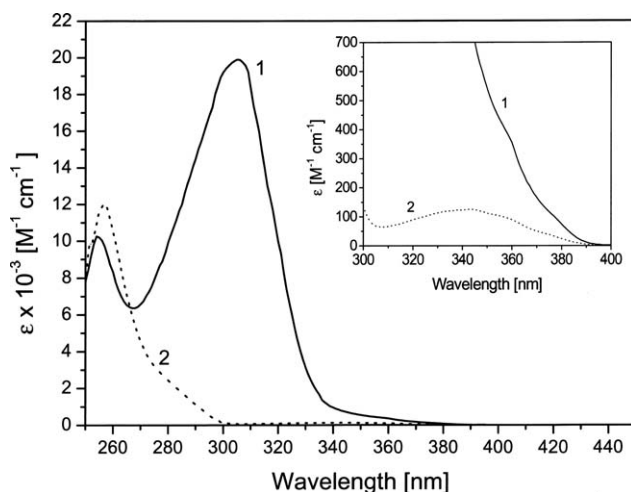


Figure 1 Absorption spectra of (BP-S-CH₂-COOH)(1) and benzophenone(2) in ethyl acetate.

trometer with tetramethylsilane as the internal standard.

FTIR spectra were recorded using Bruker Vector 22 spectrophotometer in the range of 400–4500 cm⁻¹ by KBr pellet technique.

The electronic absorption spectra were recorded with UV-vis Shimadzu MultiSpec-1501 photodiode array absorption spectrophotometer and nanosecond laser flash photolysis experiments were performed 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⁻¹ (pulse width about 4–5 ns).

The initiator concentration in the study of the rate of BP-SCH₂COOH triplet decay and the transient spectra was adjusted so that the optical density was about 0.3.

Photopolymerization

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 homemade microcalorimeter.^{23,24} The irradiation of the polymerization mixture was carried out using a Innova 90-4

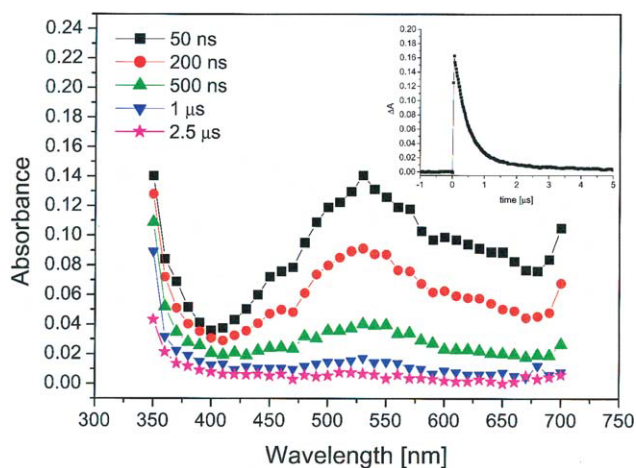
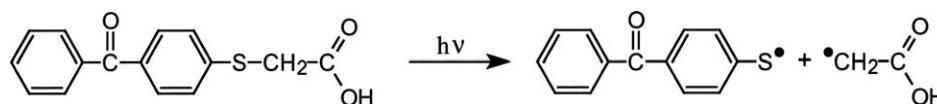


Figure 2 Transient absorption spectrum following 355-nm laser flash photolysis of BP-S-CH₂-COOH in deaerated acetonitrile recorded at four different delays times. Inset shows kinetic trace at 530 nm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



Scheme 2 Photolysis of BP-S-CH₂-COOH in acetonitrile.

argon-ion laser, Coherent. The wavelengths were 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.

RESULTS AND DISCUSSION

Polymerizable photoinitiator comprising a structure of benzophenone and thio-acetic acid, was synthesized according to Scheme 1, and its structure was confirmed by spectroscopic analysis.

The UV absorption spectrum of BP-S-CH₂-COOH in ethyl acetate is shown in Figure 1 using benzophenone as the reference. Compared with benzophenone, photoinitiator possesses significantly red-shifted maximum absorption. Transition of benzophenone in the region 250–300 nm are well known to belong to π - π^* type transition. The introduction of thioatom shifts the main absorption maximum toward red, which may be caused by increased electron donation via the sulfur atom.

Figure 2 shows the transient absorption spectrum of a deoxygenated acetonitrile solution containing BP-S-CH₂-COOH. This spectrum was generated after a few different times (between 50 ns and 2.5 μ s) following the laser pulse. Inset in Figure 2 shows the decay kinetic of the transient absorption at 530

nm. We assigned this transient as the triplet state of BP-S-CH₂-COOH. Its spectral position and shape are reminiscent of benzophenone's triplet-triplet absorption.^{7,15} Its decay is monoexponential in argon-saturated solution and it is quenched by oxygen, both of which are consistent with the transient being a triplet-state absorption. Laser flash excitation of benzophenone in the presence of (phenylthio)acetic acid resulted in the appearance of an absorption corresponding to the presence of the benzophenone ketyl radical (λ_{max} 550 nm).²⁵ It is caused by electron transfer from sulfur atom to benzophenone triplet state followed by hydrogen abstraction and decarboxylation producing α -thioalkyl type radicals which are very active radicals for the polymerization. We could not find benzophenone ketyl radical in the transition spectrum of BP-S-CH₂-COOH which suggests that there is no intra or intermolecular electron transfer from sulfur atom to benzophenone triplet state. So, benzophenone thio-acetic acid behaves quite different than one-component Type II photoinitiators.^{19,26} Therefore we suggest that on light irradiation C-S bond cleavage is the main primary process, resulting in S-centered and C-centered radicals. Direct photolysis of (phenylthio)acetic acid leads to C₆H₅-S• and •CH₂COOH radicals.²⁷ Therefore we suggest that C-S bond cleavage in BP-S-CH₂-COOH leads to *p*-benzoylphenylthiyl and alkyl radicals, shown in Scheme 2.

We were not able to detect any transient absorption from the *p*-benzoylphenylthiyl radical because

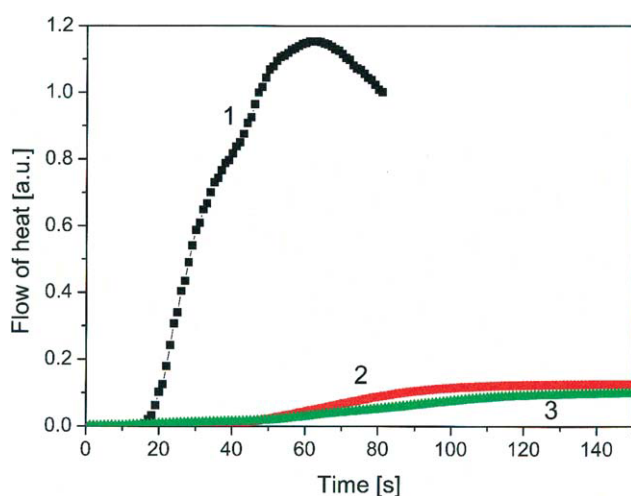


Figure 3 Kinetic curves of TMPTA polymerization initiated by BP-S-CH₂-COOH, (1) BP (phenylthio)acetic acid couple (2) and benzophenone (3) for comparison. Concentration of the initiators was that the absorbance at 355 nm was identical for both Compounds (0.8), concentration of the acid $c_0 = 0.05M$, incident light intensity $I_0 = 25 \text{ mW cm}^{-2}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

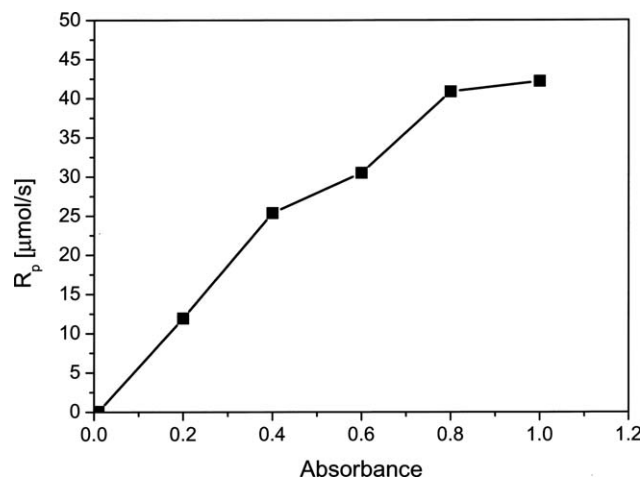


Figure 4 Rate of polymerization of TMPTA versus optical density (initiator BP-S-CH₂-COOH, incident light intensity $I_0 = 25 \text{ mW cm}^{-2}$).

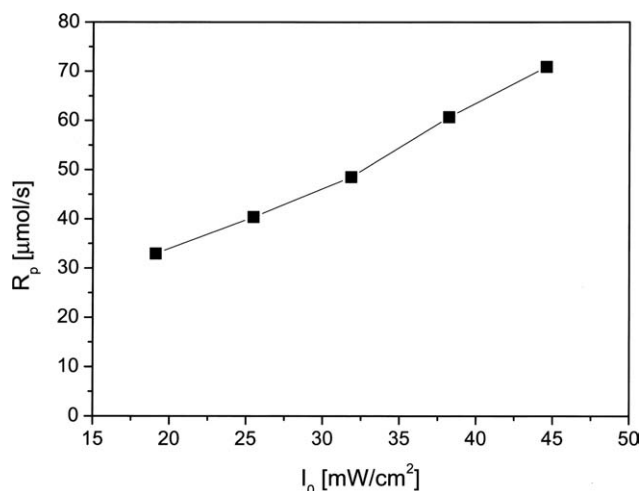


Figure 5 Rate of polymerization of TMPTA versus incident light intensity. Initiator BP-S-CH₂-COOH. OD = 0.8.

its lifetime is too short²⁸ to be detected on the nano-second time scale.

In our earlier work,^{16,21,25} it is shown that 4-carboxybenzophenone, benzophenone, and xanthene dyes are photoreduced by sulfur-containing carboxylic acids. As a result α -thioalkyl radicals are generated. These radicals initiate polymerization of acrylamide and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA). In this work we synthesized benzophenone thio-acetic acid as one-component photoinitiator. Figure 3 shows the kinetic curves obtained for the polymerization of TMPTA initiated by BP-S-CH₂-COOH and also benzophenone itself and benzophenone/thio-acetic acid couple for comparison. The absorbance of the incident light intensity in all experiments was the same. From Figure 3, it is evident that BP-S-CH₂-COOH photoinitiator initiates the polymerization of TMPTA most efficiently. Especially it is worth nothing that incorporation of thio-acetic acid into benzophenone dramatically increases the sensitivity of the photoinitiating system in comparison to BP/(phenylthio)acetic acid couple. Hydrogen abstracting benzophenone generates radical by hydrogen abstraction from the monomer and formed in this way radicals leads to polymer formation. The reaction of benzophenone with (phenylthio)acetic acid generate ketyl radical and α -thioalkyl radicals (Ph-S-CH₂•). The latter are very sufficient toward the polymerization of vinyl monomers. The higher rate of the polymerization of TMPTA by BP-S-CH₂-COOH in comparison to BP/(phenylthio)acetic acid couple indicates that formation of the radicals in bimolecular reactions (Type II initiator) is less effective than in unimolecular (Type I initiator).

The dependence of the rate of the polymerization (R_p) of TMPTA, on the optical density OD, is shown

in Figure 4. Initially the rate is proportional to the OD and consequently the amount of initiator. At a higher initiator concentration (higher OD) there is plateau. The observed reduction of R_p at high initiator concentration may result from the light absorption effects, where the light is absorbed completely within a small layer of the sample. This leads to a high local concentration of the radicals, and self-quenching processes may dominate.

The rate of the polymerization is also proportional to the incident light intensity I_0 (Fig. 5).

It is therefore easy to control R_p through simple change of incident light intensity.

CONCLUSIONS

The photoinitiator BP-S-CH₂-COOH initiates free radical polymerization of TMPTA efficiently. Laser flash photolysis studies suggest that initiator radicals are formed by photocleavage of S-C bond in the molecule. BP-S-CH₂-COOH is more effective initiator than benzophenone and benzophenone/(phenylthio)acetic acid couple. The rate of the polymerization is proportional to optical density OD and of incident light intensity.

References

- Rabek, J. F. *Mechanism of Photophysical Processes and Photochemical Reactions in Polymers*; Wiley: New York, 1987.
- Dietliker, K. K. *Photoinitiators for Free Radical and Cationic Polymerization*; Gardiner House: London, 1991.
- Luo, Y. R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press LC: Boca Raton, 2003.
- Bernardi, F.; Csizmadia, I. G.; Mangani, A. *Studies in Organic Chemistry, Organic Sulfur Chemistry*; Elsevier: Amsterdam, 1985.
- Fouassier, J. P.; Loughnot, D. J. *Polym Commun* 1990, 31, 418.
- Wrzyszczyński, A.; Janota, H. *Polimery (Warsaw)* 1996, 41, 560.
- Wrzyszczyński, A.; Bartoszewicz, J.; Hug, G. L.; Marciniak, B.; Pączkowski, J. *J Photochem Photobiol A Chem* 2003, 155, 253.
- Tomioka, H.; Takimoto, Y.; Fouassier, J. P.; Ruhlmann, D. *J Photochem Photobiol A Chem* 1990, 53, 359.
- Allen, N. S.; Corrales, T.; Edge, M.; Catalina, F.; Bianco, M.; Green, M. A. *Polymer* 1998, 39, 903.
- Allen, N. S.; Edge, M.; Catalina, F.; Corrales, T.; Bianco-Pina, M.; Green, A. *J Photochem Photobiol A Chem* 1997, 110, 183.
- Wang, H.; Wei, J.; Jiang, X. *J Polym Sci A Polym Chem* 2006, 44, 3738.
- Bobrowski, K.; Marciniak, B.; Hug, G. L. *J Am Chem Soc* 1992, 114, 10279.
- Marciniak, B.; Bobrowski, K.; Hug, G. L. *J Phys Chem* 1994, 98, 4854.
- Wrzyszczyński, A.; Pietrzak, M.; Pączkowski, J. *Macromolecules* 2004, 37, 41.
- Filipiak, P.; Bartoszewicz, J.; Hug, G. L.; Kozubek, H.; Pączkowski, J.; Marciniak, B. *J Photochem Photobiol A Chem* 2007, 191, 167.
- Wrzyszczyński, A.; Filipiak, P.; Hug, G. L.; Marciniak, B.; Pączkowski, J. *Macromolecules* 2000, 33, 1577.

17. Wrzyszczyński, A. *Polym Commun* 1999, 40, 3247.
18. Wrzyszczyński, A. *J Macromol Sci A* 2001, 38, 281.
19. Aydin, M.; Arsu, N.; Yagci, N.; Jockusch, S.; Turro, N. *J Macromolecules* 2005, 38, 4133.
20. Ścigalski, F.; Pączkowski, J. *Macromol Chem Phys* 2008, 209, 1872.
21. Wrzyszczyński, A.; Pączkowski, J. *Polimery (Warsaw)* 2004, 9, 49.
22. Walker, D.; Leib, J. *J Org Chem* 1963, 28, 3077.
23. Pączkowski, J.; Pietrzak, M.; Kucybała, Z. *Macromolecules* 1996, 29, 5057.
24. Kabatc, J.; Kucybała, Z.; Pietrzak, M.; Ścigalski, F.; Pączkowski, J. *Polymer* 1999, 40, 735.
25. Wrzyszczyński, A.; Pietrzak, M.; Bartoszewicz, J.; Kozubek, H.; Hug, G. L.; Marciniak, B.; Pączkowski, J. *J Am Chem Soc* 2003, 125, 11182.
26. Allen, N. S.; Lam, E.; Howells, M. *Eur Polym Mater* 1990, 26, 1345.
27. Filipiak, P.; Hug, G. L.; Marciniak, B. *J Photochem Photobiol A Chem* 2006, 177, 295.
28. Autrey, T.; Devadoss, C.; Sauerv, B.; Franz, J. A.; Schuster, G. B. *J Phys Chem* 1995, 99, 869.