

Synthesis of Di (4-Hydroxyl Benzophenone) Sebacate and Its Usage as Initiator in the Photocrosslinking of Polyethylene

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ABSTRACT: A new benzophenone (BP) derivative with a long carbon chain and two chromophoric groups—di (4-hydroxyl benzophenone) sebacate (BP-S) used as a photoinitiator in the photocrosslinking of polyethylene (PE) has been synthesized and characterized by ultraviolet (UV) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. The kinetic characteristics of BP-S photoinitiated crosslinking of PE in the melt and its compatibility with PE resin have been examined by gel content measurement and thermal migration experiment. The results show that BP-S is an excellent photoinitiator, which has better compatibility, less volatility, higher photoinitiating efficiency, and longer storage time than BP itself. It is promising for industrial applications of the photocrosslinking of polyolefins. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1581–1586, 2002

Key words: initiators; compatibility; polyethylene (PE); photochemistry; crosslinking

INTRODUCTION

In recent years, the photoinitiated crosslinking of bulk polyethylene has been studied systematically.^{1–5} The alkyl radical intermediates and the microstructure of crosslinks produced in the photocrosslinking of low-density polyethylene (LDPE) and its model compounds have been identified by spin-trap electron spin resonance (ESR)^{6,7} and ¹³C nuclear magnetic resonance (NMR).⁸ The photolytic products of benzophenone as a photoinitiator in the photocrosslinking of polyethylene (PE) have also been characterized by means of fluorescence, ESR, and NMR.⁹ At the same time, a photocrosslinking process for PE and its indus-

trial irradiation apparatus have been developed and applied successfully to the manufacture of thin wall crosslinked PE (XLPE) high voltage television wires^{4,10} and power cables.^{11,12}

Benzophenone (BP) as a photoinitiator used extensively in the photocrosslinking of PE has some advantages, such as its cheap price, high photoinitiating efficiency, etc. However, BP has two main shortcomings in practical applications. The first is its high volatility, which results in a decrease of BP concentration during process. The second shortcoming is its poor compatibility with PE resin. BP is easy to migrate to the surface of PE blend and thus remarkably decreases the photoinitiating efficiency because of its concentration loss. Therefore, there is a pressing demand for developing new photoinitiators with low volatility, good compatibility with PE, high photoinitiating efficiency, and long storage time to satisfy for the industrial applications.

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Table I Parameters of LDPE Resin Used in This Work

	Density (g/cm)	Melt Index	$M_n^* \times 10^{-4}$	$M_w^a \times 10^{-4}$	M_w/M_n
1I2A-1	0.921	2.0	2.9	103.6	36

^a Measured by GPC analysis.

It has been found that only some kinds of additives having C₈–C₁₆ alkyl groups have good compatibility with PE resin and can be retained in PE.^{13,14} In our previous work, we have prepared two BP derivatives with a long carbochain—dodecyl-benzophenone (BP-D) and hexadecyl-benzophenone (BP-H).¹⁵ All of them have excellent compatibility with PE, while their photoinitiating efficiencies are only a little higher than BP. More tries have been made to search for new photoinitiators with much higher photoinitiating efficiencies and better compatibility.

In this work, another new kind of BP derivative di (4-hydroxyl benzophenone) sebacate (BP-S) with a long carbochain and two chromophores were synthesized and characterized by ultraviolet (UV) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. Then the photoinitiating efficiency of BP-S as a new photoinitiator in the photocrosslinking of PE and its compatibility with PE resin were examined and discussed in comparison with BP and BP-H.

EXPERIMENTAL

Materials

Phenol (analytical reagent) from Shanghai Reagent Plant No.1, benzoyl chloride (analytical reagent) from Qunli Chemical Engineering Co. Ltd., Shanghai, and sebacic acid (chemical pure) from Shanghai Reagent Plant No.3 were used in this work. Thionyl chloride (chemical pure) and anhydrous aluminum chloride (analytical reagent) were obtained from Xingta Chemical Plant, Shanghai. 4-Hydroxyl benzophenone and benzoyl chloride were synthesized in our laboratory according to the literature (refs. 16 and 17, respectively).

The LDPE resin used in this work was obtained from Yanshan Petrochemical Co. Ltd., Beijing. The symbol of the LDPE resin and some physical properties are listed in Table I. Photoinitiator BP from Shanghai Reagent Plant No.1

(chemical pure), and crosslinker triallyl isocyanurate (TAIC) from Anhui Institute of Chemical Engineering were used in the present work. Photoinitiator BP-H was obtained from our previous work.¹⁵

Sample Preparation

LDPE resin with the desired amount of additives was mixed at 150°C for 10 min using a XSS-300 torsion rheometer (made in Shanghai, China). After mixing, the mixtures were hot pressed to sheets with a thickness of 1 mm or films with a thickness of 0.05 mm at 150°C using a hot press.

Samples were irradiated at 140°C under N₂ atmosphere in a UV-CURE device constructed in our laboratory.¹ The UV lamp used was a high-pressure mercury lamp (Philips HPM 15), operated at 2 kW, at a distance of 10 cm from the surface of sample.

Thermal Migration Test

To accelerate the migration of photoinitiators in PE blends to the surface, we have designed the following two experiments:

1. The films of PE samples containing different photoinitiator were put into an oven at the temperature of 75 ± 0.1°C. Every hour, one piece of film for each sample was taken out of this oven for immediate measurement of FTIR spectrum.
2. The sheets of PE samples containing different photoinitiator were kept at the same oven temperature. Every 5 h, three sheets for each sample were taken out of the oven, UV-irradiated immediately for 60 s at 140°C, and then their gel contents were determined.

Analysis of Samples

Gel Content

Gel content was measured by extracting the UV irradiated samples for 48 h with boiling xylene.

The solvent was renewed after the first 24 h. Usually, three samples were analyzed to determine the average gel content for a given set of irradiation conditions.

Ultraviolet and Infrared Spectra

UV and FTIR spectra were recorded on a Shimadzu UV-2100 scanning spectrophotometer and a Nicolet MAGNA-IR 750 spectrometer, respectively.

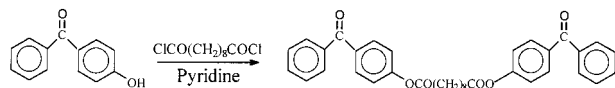
Elemental Analysis

Elemental analysis data were obtained on a PE 240c elemental analyzer.

RESULTS AND DISCUSSION

Synthesis of Di (4-hydroxyl benzophenone) sebacate

The reaction can be presented as the following formula:



4-Hydroxyl benzophenone (21.8 g—0.11 mol) dissolved in 20 mL anhydrous pyridine were placed in a 100-mL conical flask fitted with a calcium chloride drying tube. Sebacoyl chloride (10.7 mL—0.05 mol) was then dropped into this flask in 10 min with vigorous stirring. The temperature of the reaction mixture rose spontaneously, and a yellow deposit appeared. When no further hydrogen chloride was evolved, the flask was cooled in an ice bath. A mixture of ice-water with concentrated hydrochloric acid was dropped in with vigorous stirring.

The product was collected in a buchner funnel and washed twice with water, 5% sodium hydroxide, and water, respectively. Then the product was sucked as dry as possible, and air dried at room temperature. Di (4-hydroxyl benzophenone) sebacate (BP-S) was obtained as a white powder, yield 78–81%, m.p. 101.5–103.2°C.

Characterization of BP-S Product

The UV spectra of BP-S and BP in carbon tetrachloride are shown in Figure 1(A) and (B), respectively. The characteristic absorption peaks of

BP-S [Fig. 1(A)] are very similar to those of BP [Fig. 1(B)]. There are one strong peak at 260 nm and one absorption peak within 310–400 nm, whose center position is near 340 nm. These spectra show that BP-S has the similar chromophore as BP. The data of molar absorption coefficients of absorption peaks of these two photoinitiators are listed in Table II. It can be seen that BP-S has higher absorption coefficient than BP, which means the former absorbs more UV energy and perhaps has higher photoinitiating efficiency in the photocrosslinking of PE.

Figure 2 represents the FTIR spectrum of BP-S. The main absorption peaks appear at 3058, 2925, 2850, 1758, 1653, 1600, and 721 cm^{-1} . The peaks at 2925 and 2850 cm^{-1} are assigned to the stretching vibration absorption of alkyl group $-\text{CH}_2-$, while the peak at 721 cm^{-1} is due to the bending vibration of $-(\text{CH}_2)_n-$ ($n > 4$) groups. The absence of peaks at 2960 and 2870 cm^{-1} indicates the nonexistence of $-\text{CH}_3$ group in BP-S. At the same time, the peaks at 3058 and 1600 cm^{-1} confirm the benzene ring structure in BP-S. The peak at 1758 cm^{-1} is due to the ester group in BP-S. The absorption peak of ketone group in

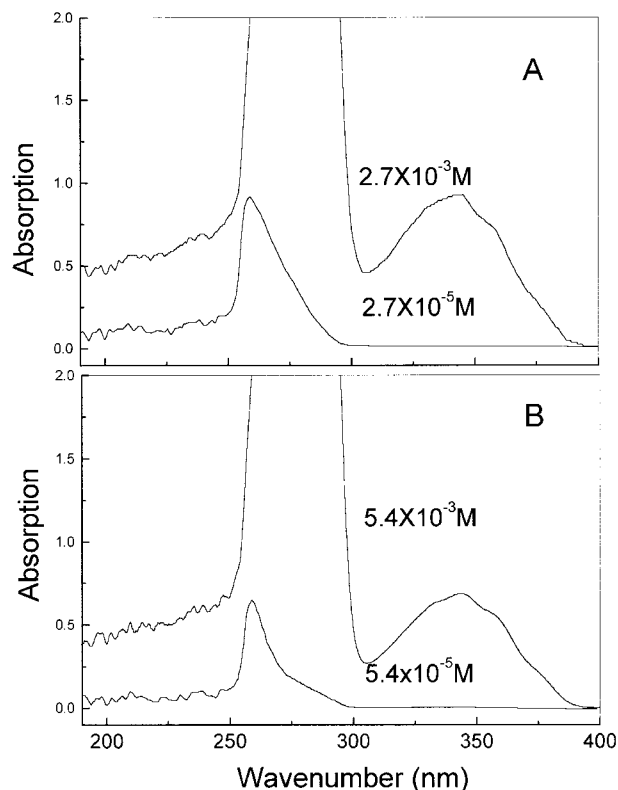


Figure 1 UV absorption spectra of photoinitiators BP-S (A) and BP (B) in CCl_4 .

Table II Data of UV Absorption wavelength and Molar Absorption Coefficient of BP and BP-S

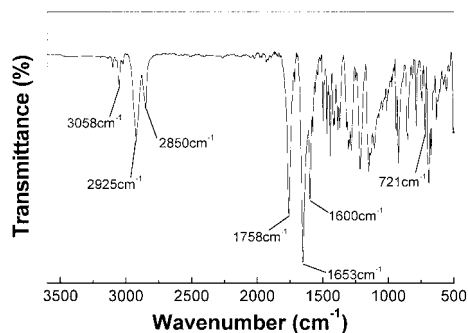
Compound	λ (nm)	ϵ ($L \cdot mol^{-1} \cdot cm^{-1}$)
Benzophenone (BP)	260	1.2×10^4
	340	1.3×10^2
Di (4-Hydroxyl Benzophenone) Sebacate (BP-S)	260	3.4×10^4
	340	3.4×10^2

BP-S appears at 1653 cm^{-1} , which is the same as the absorption of ketone group in 4-hydroxyl benzophenone. Therefore, the above analysis of FTIR spectra further confirms the ph-CO-ph molecular structure with carbochain existing in the BP-S.

The elemental analysis data of BP-S is listed in Table III, together with the theoretical values calculated from the molecular structure of BP-S. Apparently, the experimental data are in good agreement with the theoretical values, which further gives the evidence that the synthesized product is BP-S compound.

Photocrosslinking Kinetic Characteristics and Photoinitiating Efficiency of BP-S

Figure 3 represents the gel formation as a function of irradiation time for the photoinitiated crosslinking of LDPE samples with BP, BP-S, and BP-H as photoinitiators. The concentrations of photoinitiators in 100 g LDPE are 0.0055, 0.0027, and 0.0055 mol for BP, BP-S, and BP-H, respectively. Considering BP-S having two chromophores, its concentration was reduced to one-half. Apparently, the crosslinking kinetic characteristics of three PE samples with different initiators have the same features: (1) the initial rate of

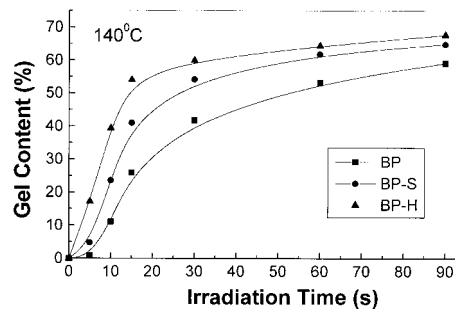
**Figure 2** FTIR spectrum of photoinitiator BP-S.**Table III Elemental Analytical Data of BP-S**

	C%	H%
Theoretical value	76.87	6.05
Experimental value	76.13	6.11

crosslinking during the first 15 s is very fast; (2) after 40 s, the rate decreases to a certain level; and (3) after 60 s, the gel content is almost constant. However, the photoinitiating efficiencies of three photoinitiators are different. Under the same conditions of irradiation, the initial rate of crosslinking and final gel content level of sample containing BP-S are higher than those of BP; but they are slightly lower than those of BP-H when the same concentrations of chromophore in different samples are considered.

Figure 4 compares the initiating efficiencies of BP, BP-S, and BP-H combined with crosslinker TAIC in the enhanced crosslinking of LDPE. The kinetic characteristics of enhanced crosslinking systems are similar to that of Figure 3.

Why does BP-S have higher initiating efficiency than BP in the photocrosslinking of PE? There are two main reasons. One is that the energy absorption of BP-S is more efficient than BP, which can be seen from the molar absorption coefficient of UV absorption (see Table 1). Another is that BP-S has much lower vapor pressure than BP because of its higher molecular weight, which decreases the loss of BP-S during the photocrosslinking processes and thus increases its photoinitiating efficiency. However, the photoinitiating efficiency of BP-S in PE is lower than BP-H from the point view of the single chro-

**Figure 3** Kinetics of gel formation during photocrosslinking of LDPE in the melt (140°C). Concentrations of photoinitiator in 100 g LDPE: (■) 5.5×10^{-3} mol BP; (●) 2.7×10^{-3} mol BP-S; (▲) 5.5×10^{-3} mol BP-H. No crosslinker TAIC.

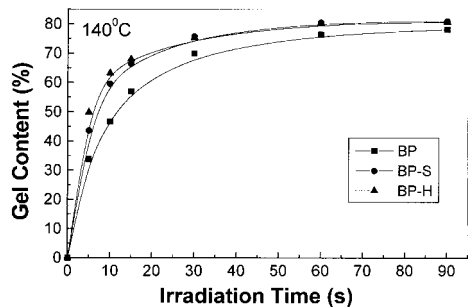


Figure 4 Comparison of initiating efficiencies of photoinitiator combined with the crosslinker in the enhanced crosslinking of LDPE in the melt (140°C). Concentrations of the photoinitiator in 100 g LDPE: (■) 5.5×10^{-3} mol BP; (●) 2.7×10^{-3} mol BP-S; (▲) 5.5×10^{-3} mol BP-H. Concentration of crosslinker TAIC: 1 wt %.

mophore, especially for the PE samples without crosslinker, which is probably due to the two excited chromophores in BP-S being quenched each other.

Compatibility of BP-S with PE

Figure 5(A) and (B) shows the IR spectra of PE films containing photoinitiators BP and BP-S before and after thermal migration experiment, respectively. The absorption peaks at 1667 and 1653 cm^{-1} represent the IR absorption of the carbonyl group in BP and BP-S, respectively. The peak at 1667 cm^{-1} disappears after the PE films kept in the oven at 75°C for only 1 h [Fig. 5(A)], which indicates that most of BP has migrated to the surface of PE and was lost within an hour. On the contrary, the absorption intensity of 1653 cm^{-1} decreases only 3.0% after the sample kept at the same temperature for 5 h [Fig. 5(B)]. These results show that the loss of BP-S from PE blends is much slower than that of BP, which indicates that BP-S has much better compatibility in PE blends than BP.

At the same time, the effects of photoinitiator loss on the photoinitiated crosslinking of PE have also been examined. Figure 6 shows the change of gel content in XLPE sample UV-irradiated for 60 s at 140°C with the thermal migration (TM) time. As can be seen, the gel contents of sample containing BP decrease rapidly with the increase of TM time to 13% after TM 25 h from the original value 49% before TM. This decrease of gel content is caused by the concentration decrease of BP during the thermal migration process. However, the decrease of gel content in the samples with

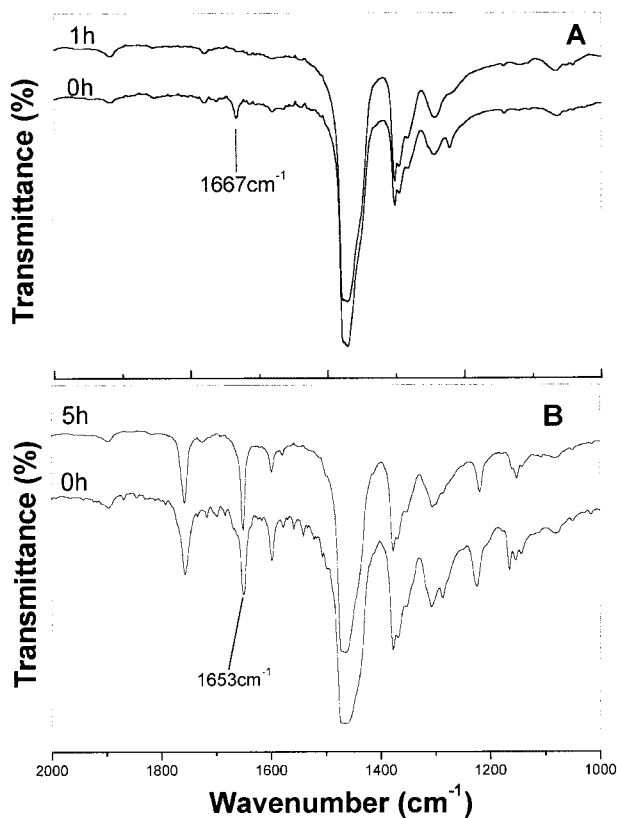


Figure 5 FTIR spectra of PE films with different photoinitiators before and after thermal migration experiment. (A) BP; (B) BP-S.

BP-S is much smaller than that with BP. The gel contents of samples with BP-S keep almost constant before and after the TM time increases to 25 h. This result gives the evidence again that the photoinitiator BP-S has much better compatibility with PE than BP.

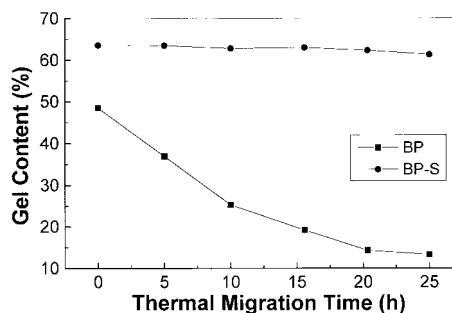


Figure 6 Changes of gel content obtained from the PE samples photocrosslinked in the melt with the thermal migration time. Concentrations of the photoinitiator in 100 g LDPE (■) 5.5×10^{-3} mol BP; (●) 2.7×10^{-3} mol BP-S. No crosslinker TAIC; Irradiation time: 60 s.

CONCLUSION

1. A new photoinitiators Di (4-Hydroxyl Benzophenone) Sebacate (BP-S) used in the photoinitiated crosslinking of polyethylene has been successfully synthesized and characterized by UV spectra, IR spectra, and elemental analysis.
2. The data of gel content show that BP-S is high efficient photoinitiator in the photocrosslinking of PE. The initiating efficiency of single chromophore in BP-S is higher than BP, while it is lower than BP-H because of the possible quenching of two excited chromophores in BP-S molecule.
3. The results obtained from thermal migration experiments show that BP-S with a long chain of hydrocarbon has much better compatibility with PE resin, less volatility, and longer storage time than BP itself.

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