# **Ketonic Resins as Free Radical Photoinitiators**

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ABSTRACT: Photoreactive cyclohexanone-formaldehyde and acetophenone-formaldehyde resin-bound benzoin and benzoin isobutyl ether resins were successfully prepared by the method of in situ modification of ketonic resins. These photoinitiators were used to polymerize styrene using UV lamp with wavelength of 350 nm. Initiating efficiencies of ketonic resin-bound benzoin and benzoin ether were much higher than benzoin and benzoin ether. The products were ketonic-resin-polystyrene block copolymers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 927–934, 1999

Key words: ketonic resin; photoinitiators; benzoin; benzoin isobutyl ether

# INTRODUCTION

Recently, much interest has been shown in polymeric photoinitiators.<sup>1</sup> A fundamental reason for investigating polymeric photoinitiator systems is that they may offer advantages over the monomeric counterparts, such as greater reactivity. Another reason is that the chemistry of macromolecular radicals may be eludicated. There will be a clear distinction between the chemistry of terminal and pendant free radicals, because the former are likely to be far less sterically encumbered. The terminal macromolecular radicals may lead to the formation of a block copolymer or may participate in radical-radical combination or radical-radical disproportionation reactions. A number of polymeric photoinitiators-such as polymer-bound benzoin, methylol benzoin ethers,  $\alpha$ -hydroxyacetophenone, oxime ester, trichloroacetophenone, benzophenone, and thioxanthene-have been described.<sup>1-3</sup> Polymer-bound photoinitiators were prepared by either copolymerization of a vinyl monomer containing the photoinitiator moiety or by linking photoinitiator to a polymer backbone containing appropriate functional groups.

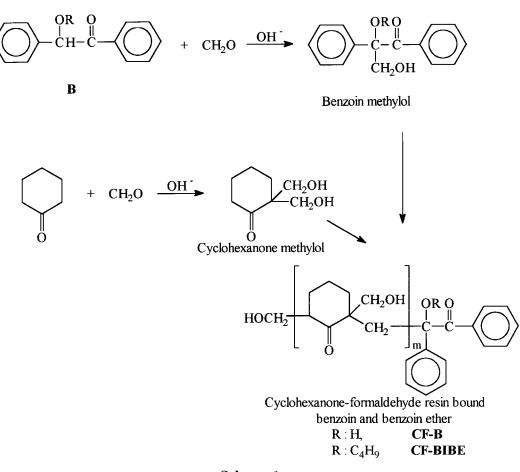
Benzoin and its derivatives are well known. They are extensively used as photoinitiators of free radical polymerization in the surface coating industry.  $^{\rm 3-5}$ 

The main cleavage reaction for polymeric benzoin type photoinitiators is  $\alpha$ -cleavage with very little secondary cleavage taking place. It well documented that, in systems where secondary cleavage occurs, the whole of the photoinitiator molecule is freed from the polymer backbone and initiation occurs by truly free radicals (benzoyl and benzoylmethyl). Thus, the greater reactivity of the polymeric initiators must be in their role as chain terminators.

However, the polymer-bound immobilized benzyl radical was shown to take part in the initiation process.<sup>6</sup> This is contrast with the results for monomolecular benzoin ethers where most evidence points toward termination and recombination processes as the main reaction pathways for the substituted benzyl radical. The polymerization rate of styrene was found to be four times larger with the polymeric benzoin methyl ether systems, compared with benzoin methyl ether. It was suggested that the enhancement of photoinitiation activity by poly(methyl benzoin acrylate) is a gel effect and the higher reactivity of free radicals anchored to the polymeric matrix.<sup>3</sup>

In this work, ketonic resin-bound benzoin and benzoin isobutyl ether (BIBE) were prepared and used for the polymerization of styrene.

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#### Scheme 1

# **EXPERIMENTAL**

#### **Analysis and Materials**

Fourier transform infrared (FTIR) spectra were recorded on a Jasco 5300 FTIR.

<sup>1</sup>H-NMR spectra were taken on Bruker AC (200 MHz) and Bruker (250 MHz) spectrophotometers in  $\text{CDCl}_3$  and dimethylsulfoxide solution with tetramethylsilane as the internal standard. Gel permeation chromatograms were obtained with a differential refractometer and a UV (254 nm) detector by using tetrahydrofuran as the eluent at a flow rate of 1 mL min<sup>-1</sup>. Molecular weights were calculated by using a polystyrene standard.

Benzoin (Fluka) and benzoin isobutyl ether (Fluka) were used as received. Cyclohexanone-formaldehyde resin was produced as previously described.<sup>7</sup>

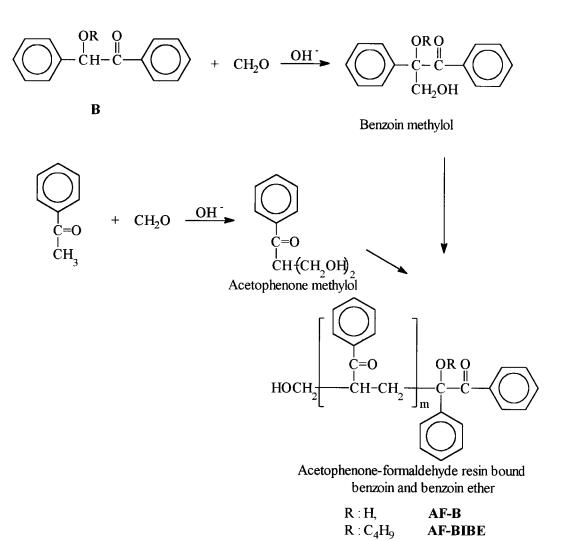
## Preparation of Cyclohexanone-Formaldehyde Resin-Bound Benzoin (CF-B) and CF-BIBE

Into a three-necked flask, 1 mol of cyclohexanone, 20 g of cyclohexane, 0.1 mol of benzoin or BIBE,

and 30 g of formalin were added and heated to 60°C while stirring. Then, 0.36 mL of 20% NaOH was added in equal portions. When the temperature of the mixture rose to 75°–80°C, refluxing began. Then, 100 g of formalin and 3.64 mL of 20% NaOH were mixed and added continuously at a gradually increasing rate sufficient to maintain vigorous refluxing. After 4 h, the reaction was completed. The upper phase was decanted. It was then washed several times in hot water and dried at 120°C under vacuum.

#### Preparation of Acetophenone-Formaldehyde Resin-Bound Benzoin (AF-B) and AF-BIBE

Into a three-necked flask, 1 mol of acetophenone and 30 g of formalin were added and heated to 90°C while stirring. After  $\sim$  6 h, 0.1 mol of benzoin or BIBE/formalin mixture were added into the reaction mixture and stirring continued for a further 10 h, and 6 mL of 40% KOH solution was added dropwise and stirred (pH 11). Modified resin was purified by decanting the water layer and washing several times with hot water. It was then dried at 110°C under vacuum.





#### Photopolymerization

Ketonic resin-bound benzoin or BIBE (0.5 g), 2 mL of chloroform, and 2 mL of styrene were placed in a pyrex tube. The mixture was degassed in the usual manner before irradiation with annular type photoreactor equipped with lamps emitting light with a wavelength of 350 nm at 25°C. After 3 h, the polymer was precipitated by pouring the mixture into methanol. The copolymers were dissolved in ethyl methyl ketone and precipitated with methanol, then filtered, washed several times with petroleum ether, and dried at 20°C in vacuum for 4 h.

#### Surface Coating with UV Curing

Films of photoreactive resin were prepared by casting from dichloromethane solution on the metal plate. Then, the films were illuminated with lamps emitting light with a wavelength of 350 nm at 25°C. After 5 min, hard brittle films were obtained.

#### **Blank Experiments**

Cyclohexanone-formaldehyde or acetophenoneformaldehyde resin (1 g), 0.1 g of benzoin, and 2 mL of styrene were dissolved in chloroform and placed in a Pyrex tube. The mixture was degassed in the usual manner before irradiation with an annular-type photoreactor equipped with lamps emitting light with a wavelength of 350 nm at 25°C. After 3 h, the reaction mixture was precipitated by pouring the mixture into methanol. The products were dissolved in ethyl methyl ketone and precipitated with methanol. Ketonic resin was recovered. Homopolystyrene and copolymer were not obtained.

		Melting					Ŵ	Solubilities	S		
	Photoreactive Ketonic Resins	Point (°C)	$M_n$	$M_w$	DMF	CHCl <sub>3</sub>	CHCl <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> CO CCl <sub>4</sub> MeOH	$CCI_4$	MeOH	$C_6H_5CH_3$	THF
CF-B	Cyclohexanone-formaldehyde resin-bound benzoin	125	3300	3400	ß	Ø	ß	ß	hs	ß	ß
CF-BIBE	Cyclohexanone-formaldehyde resin-bound benzoin isobutyl	80	570	920	ß	ß	S	hs	hs	ß	ß
AF-B	Acetophenone-formaldehyde resin- bound benzoin	80			ß	ß	ω	$\mathbf{sl}$	hs	ß	$\mathbf{sl}$
AF-BIBE	Acetophenone-formaldehyde resin- bound benzoin isobutyl ether	Soft			ß	ß	ß	$\mathbf{sl}$	sl	ß	ß



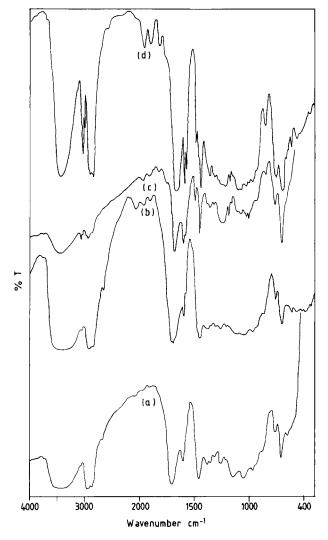


Figure 1 FTIR spectrum of ketonic resin-bound photoinitiators. (a) CF-B. (b) CF-BIBE. (c) AF-B. (d) AF-BIBE.

Benzoin (0.2 g) and 2 mL of styrene were dissolved in chloroform and placed in a Pyrex tube. The mixture was degassed in the usual manner before irradiation with an annular-type photoreactor equipped with lamps emitting light with a wavelength of 350 nm at 25°C. After 3 h, the reaction mixture was precipitated by pouring the mixture into methanol. Homopolystyrene (0.2 g)was then obtained.

# **RESULTS AND DISCUSSION**

In this work, ketonic resin-bound benzoin and benzoin ether photoinitiators were synthesized and used for polymerization of styrene.

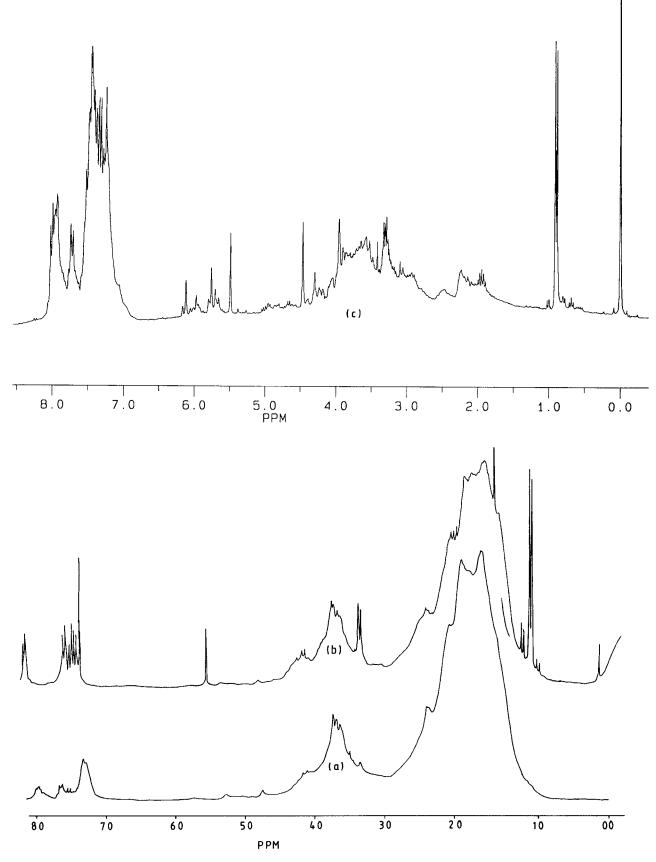
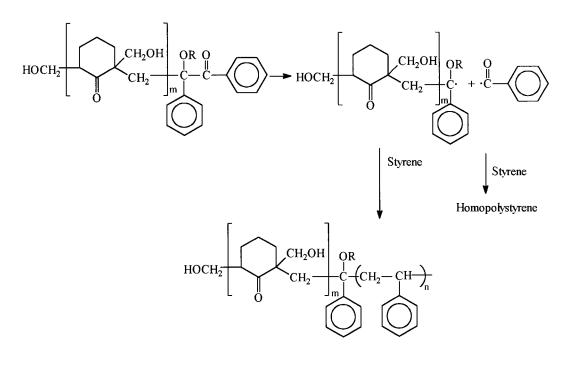


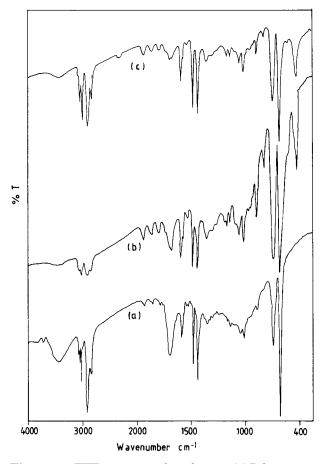
Figure 2  $\,^{1}$ H-NMR spectrum of ketonic resin-bound photoinitiators. (a) CF-B. (b) CF-BIBE. (c) AF-BIBE.



Scheme 3

Ketonic resin-bound benzoin (CF-B) and CF-BIBE were prepared by adding benzoin or benzoin ether to the mixture during cyclohexanoneformaldehyde and acetophone-formaldehyde resin preparation.<sup>7,8</sup> The reaction probably occurred via cross aldol condensation of formaldehyde with cyclohexanone and benzoin to give cyclohexanone methylol and benzoin methylol, which condensed to give CF-B or CF-BIBE (Scheme 1). The similar reactions between acetophenone, formaldehyde, and benzoin may also occur to give AF-B and AF-BIBE. The purposed structure of the AF-B and AF-BIBE is shown in Scheme 2. Some chain branching in both cyclohexanone-formaldehyde resin, acetophenoneformaldehyde resin, and their benzoin-modified cyclohexanone-formaldehyde and acetophoneformaldehyde resins may be present.

The physical properties of photoreactive ketonic resin is shown in Table I. Ketonic resinbound benzoin was examined with thin-layer chromatography, and spectroscopic identification was conducted using FTIR and nuclear magnetic resonance (NMR). FTIR spectra of ketonic resinbound benzoin and benzoin butyl ether (CF-B, CF-BIBE, AF-B, and AF-BIBE) are shown in Figure 1. Both peaks due to benzoin, benzoin ether, and ketonic resin were observed. Peaks at 3400 cm<sup>-1</sup> and 1700 cm<sup>-1</sup> were due to methylol and



**Figure 3** FTIR spectrum of copolymers. (a) Polystyrene-CF-B. (b) Polystyrene-CF-BIBE. (c) Polystyrene-AF-BIBE.

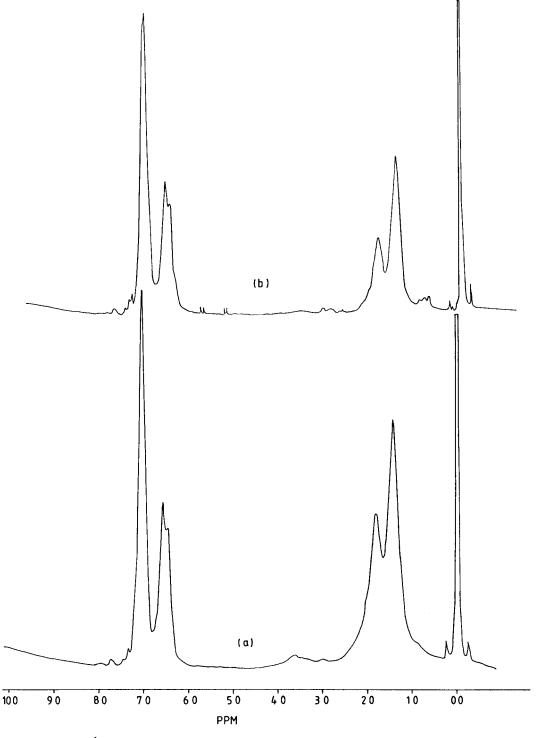


Figure 4  $\,$   $^1\text{H-NMR}$  spectrum of copolymers. (a) Polystyrene-CF-B. (b) Polystyrene-CF-BIBE.

carbonyl groups of ketonic resin. Peaks at 3060 and 3030  $\rm cm^{-1}$  were due to aromatic rings of benzoin and benzoin ether, and acetophenone groups.

<sup>1</sup>H-NMR spectrum of CF-B resin showed signals between 7–8 ppm due to aromatic protons of benzoin and signals between 3–4.5 ppm due to methylene protons of methylols and 1–3 ppm due

				Polymeric Product			
Photoinitiating System	Polymer/ Copolymer	Amount (g)	B or BIBE Moiety (wt %)	Conversion (%)	g mmol <sup>-1</sup> of Benzoin Unit	$M_n$	$M_w$
В	PS	0.2	100	14	0.3	_	
BIBE	$\mathbf{PS}$	0.2	100	14	0.3	_	
В	$\mathbf{PS}$	0.5	100	60	0.5		_
B + CF resin	_	0.1 + 0.4	25	0	0.0		
CF-B	PS-CF-B	0.5	3	60	9.5	_	
CF-BIBE	PS-CF-BIBE	0.5	37	70	2.0	4,400	12,720
AF-B	PS-AF-B	0.5	20	71	3.0		
AF-BIBE	PS-AF-BIBE	0.5	25	73	3.2	17,300	130,000

Table II Polymerization of Styrene with Ketonic Resin-Bound Benzoin and BIBE

 $t = 25^{\circ}C$ ;  $\lambda = 350$  nm; h = 3; solvent =  $CHCl_3$  (2 mL); styrene = 2 mL; B = benzoin; PS = polystyrene.

to aliphatic hydrogens [Figure 2(a)]. Molecular weights of the CF-B was calculated using NMR spectrum by assuming one benzoin molecule joined to each ketonic resin molecule. The integration ratio of signals between 7–8 ppm and 1–4.5 ppm gave an  $M_n$  value of ~ 3280 (Table I). Acetophone-formaldehyde resin-bound benzoin and BIBE showed that characteristic aromatic hydrogen signals appeared between 7–8 ppm. Protons of two methyl groups appeared as a doublet at ~ 1 ppm [Figure 2(c)].

Ketonic resin-bound benzoin and benzoin ether were used for photopolymerization of styrene in chloroform and the copolymers of polystyrene-ketonic resin were obtained. UV irradiation of the photoreactive ketonic resins caused  $\alpha$ -scission and yielded benzoyl radicals and polymer-bound radicals according to Scheme 3. Both of these radicals may then initiate the polymerization of styrene. It was demonstrated that both radicals are equally effective as initiators in the polymerization for successful block copolymerization.<sup>6</sup> In all cases, the amount of homopolystyrene formed by benzoyl radicals was reduced, because termination of polystyrene radicals may also occur via combination of polystyrene radical chains produced by ketonic resin-bound alkoxy radicals.

The block copolymers obtained from the polymerization of styrene with resin-bound benzoin and BIBE showed peaks due to both photoreactive ketonic resin and polystyrene. Peaks at 3500 cm<sup>-1</sup> and 1730 cm<sup>-1</sup> due to hydroxyl and carbonyl groups of photoreactive ketonic resin were clearly seen in Figure 3. <sup>1</sup>H-NMR spectrum of polysty-

rene-ketonic resin block copolymers are shown in Figure 4. NMR and FTIR spectrum of these block copolymers were similar to polystyrene-ketonic resin block copolymers prepared previously.<sup>9,10</sup> As seen in Table II, ketonic resin-bound benzoin and benzoin ethers were much more active than benzoin and BIBE, with the polymerization rate of styrene being 5–15 times larger with polymeric systems. Besides, the product block copolymers obviously have some improvement in their adhesive properties due to their ketonic resin blocks.

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