

Block Copolymers of Cyclohexene Oxide and Ketonic Resins via Condensation and Promoted Cationic Polymerization

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Received 24 November 2006; accepted 14 August 2006

DOI 10.1002/app.26148

Published online 9 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Block copolymers of cyclohexene oxide (CHO) and ketonic resin were prepared by using ketonic resins as free radical photoinitiators via two-step procedure. In the first step, cyclohexanone–formaldehyde and acetophenone–formaldehyde resins were modified during their preparation with benzoin and benzoin isobutyl ether. Then, AB or ABA type block copolymers depending on the resin employed were obtained by irradiation of these resins in the presence of pyridinium salt

and CHO as a cationically polymerizable monomer. By this way, block copolymers of CHO with ketonic resin were prepared and characterized by GPC, DCS, FTIR, and ^1H NMR spectral measurements. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1012–1017, 2007

Key words: resins; photopolymerization; irradiation; block copolymers; cationic polymerization

INTRODUCTION

Copolymers of ketonic resins have been the subject of recent research as the ketonic resin segments improves adhesive, solubility, gloss, and light stability of parent polymers. These copolymers have been synthesized via condensation polymerization, free radical polymerization, and redox polymerization routes.^{1–8}

Benzoin and its derivatives are extensively used as photoinitiators of free radical polymerization in the surface coating industry.^{9–11} Recently, much interest has been shown in the polymeric photoinitiators.¹² Polymeric photoinitiator systems may offer advantages over the monomeric counterparts, such as greater reactivity, storage stability, and compatibility.¹³ Photoactive benzoin bounded ketonic resin can be obtained with a one-step method of *in situ* modification of ketonic resin.⁸ Benzoin and benzoin isobutyl ether bounded ketonic resin (BIBE) were prepared and used for the copolymerization of styrene. Initiating efficiency of benzoin bounded ketonic resin is much higher than benzoin derivatives.

Azo-benzoin type initiators were used as a free radical source to produce benzoin-terminated polymers.^{14,15} Irradiation of these polymers in conjunction with onium salts (On^+), (Scheme 1), in the presence of cyclohexene oxide (CHO) made it possible to synthesize block copolymers of monomers of different chemical nature.¹⁶

In this study, application of condensation and promoted cationic polymerization routes to obtain block copolymers was studied. AB or ABA type block copolymers of benzoin bounded ketonic resin and CHO were prepared in the presence of *N*-ethoxy-2-methyl pyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$). In the first step, cyclohexanone–formaldehyde and acetophenone–formaldehyde resins were modified *in situ* during their preparation with benzoin and benzoin isobutyl ether. In the second step, these photoactive ketonic resins were utilized as an initiator for the polymerization of CHO in the presence of $\text{EMP}^+\text{PF}_6^-$ to obtain block copolymers.

EXPERIMENTAL

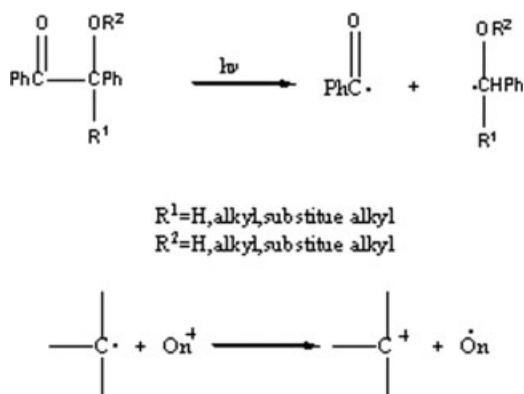
Materials

Benzoin, benzoin isobutyl ether (Fluka Chemical, Bucks, Switzerland), *N*-ethoxy-2-methyl Pyridinium hexafluorophosphate ($\text{EMP}^+\text{PF}_6^-$) (Fluka Chemical, Bucks, Switzerland), cyclohexanone (Merck, Darmstadt, Germany), Acetophenone (Merck, Darmstadt, Germany), and Formaldehyde (Fluka, Chemical, Bucks, Switzerland 37% solution) were used as received. Cyclohexene Oxide (CHO) (Fluka Chemical, Bucks, Switzerland) was purified by distillation.

Analysis

Infrared (IR) spectra were recorded in solid state with KBr (potassium bromide) pellets on a JASCO FTIR

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Scheme 1 Irradiation of benzoin derivatives in presence of onium salt.

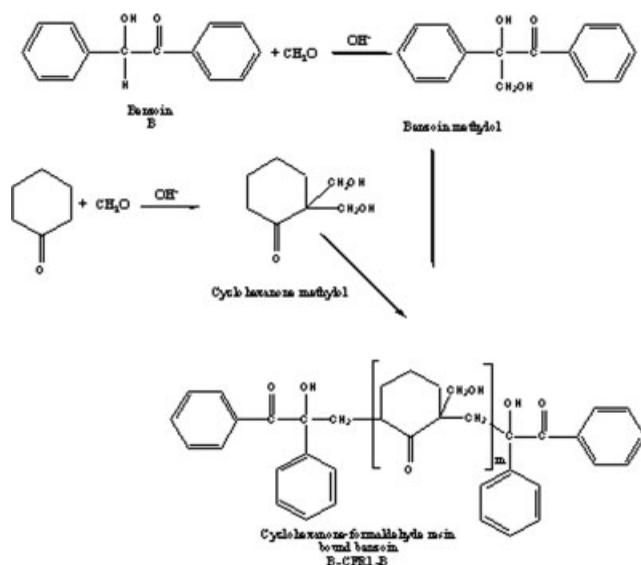
5300 Fourier transform infrared spectrometer (Jasco, Tokyo, Japan).

DSC thermograms were obtained by using Perkin-Elmer DSC-6 instrument; the heating rate was 10°C/min under a nitrogen atmosphere.

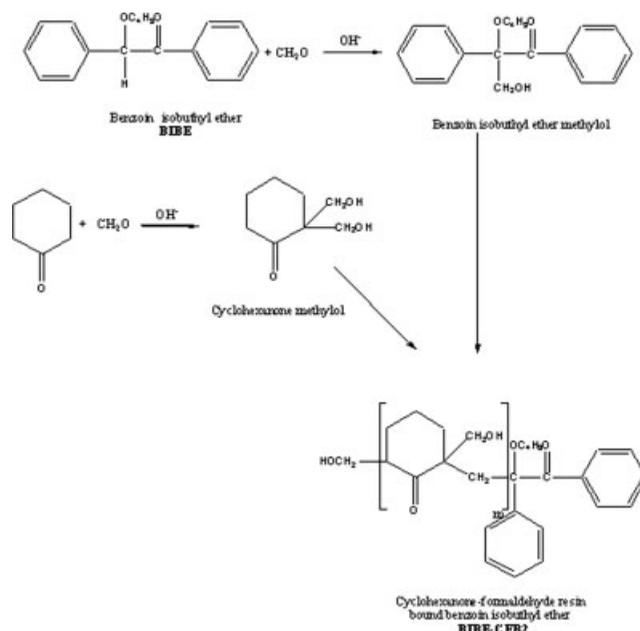
¹H NMR spectra were measured on a Bruker AC (250 MHz, Darmstadt, Germany) spectrometer by using DMSO-d₆ or CDCl₃ as a solvent and tetramethylsilane as the internal standard.

Gel permeation chromatography (GPC) analyses were carried out with a set up consisting of the Agilent pump and refractive-index detector (Model 1100) and 3 Waters styragel columns (HR3, HR4, HR4E). THF was used as the eluent at a flow rate of 0.3 mL/min at 30°C. The molecular weights of the polymers were calculated with the aid of polystyrene standards. UV-Vis spectra were recorded on a Shimadzu UV-1700 spectrophotometer.

Thin layer chromatography (TLC) plates, Silicagel 60 (0.20 mm) with fluorescent indicator 254 nm were used.



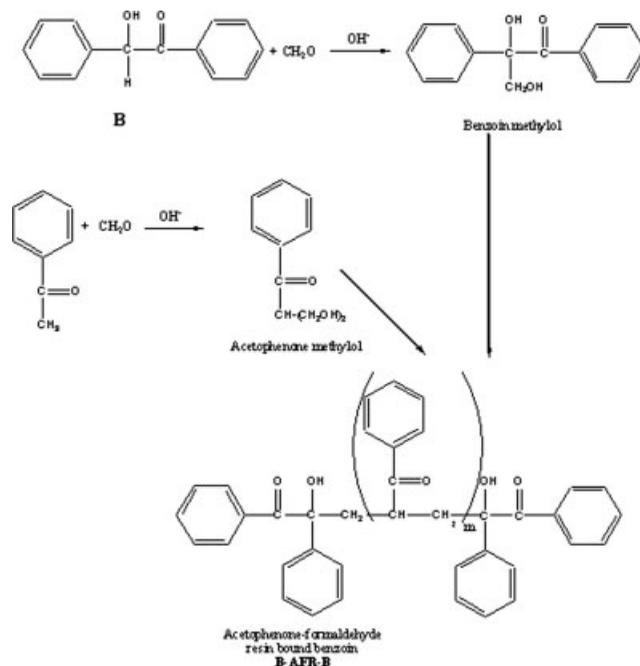
Scheme 2 Formation of benzoin bounded cyclohexanone formaldehyde resin (B-CFR1-B).



Scheme 3 Formation of benzoin isobutyl ether bounded cyclohexanone-formaldehyde resin (BIBE-CFR2).

Preparation of benzoin bounded cyclohexanone formaldehyde resin and benzoin isobutyl ether bounded cyclohexanone-formaldehyde resin

Benzoin bounded cyclohexanone formaldehyde resin (B-CFR1-B) and benzoin isobutyl ether bounded cyclohexanone-formaldehyde resin (BIBE-CFR2) were produced as described previously.⁶ Into a three-necked flask, 1 mol of cyclohexanone, 25 mL of cyclo-



Scheme 4 Formation of benzoin bounded acetophenone formaldehyde resin (B-AFR-B).

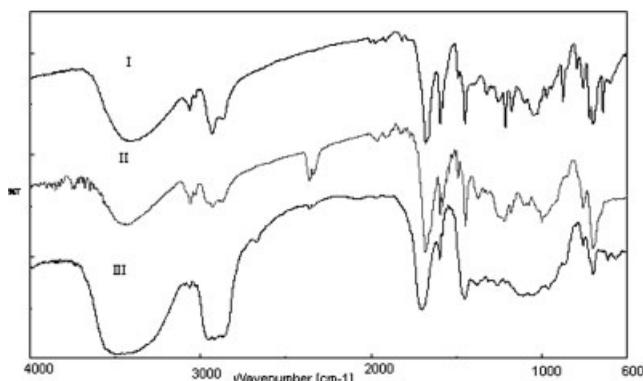


Figure 1 FTIR spectra of (I) B-CFR1-B, (II) B-AFR-B, (III) BIBE-CFR2 resins.

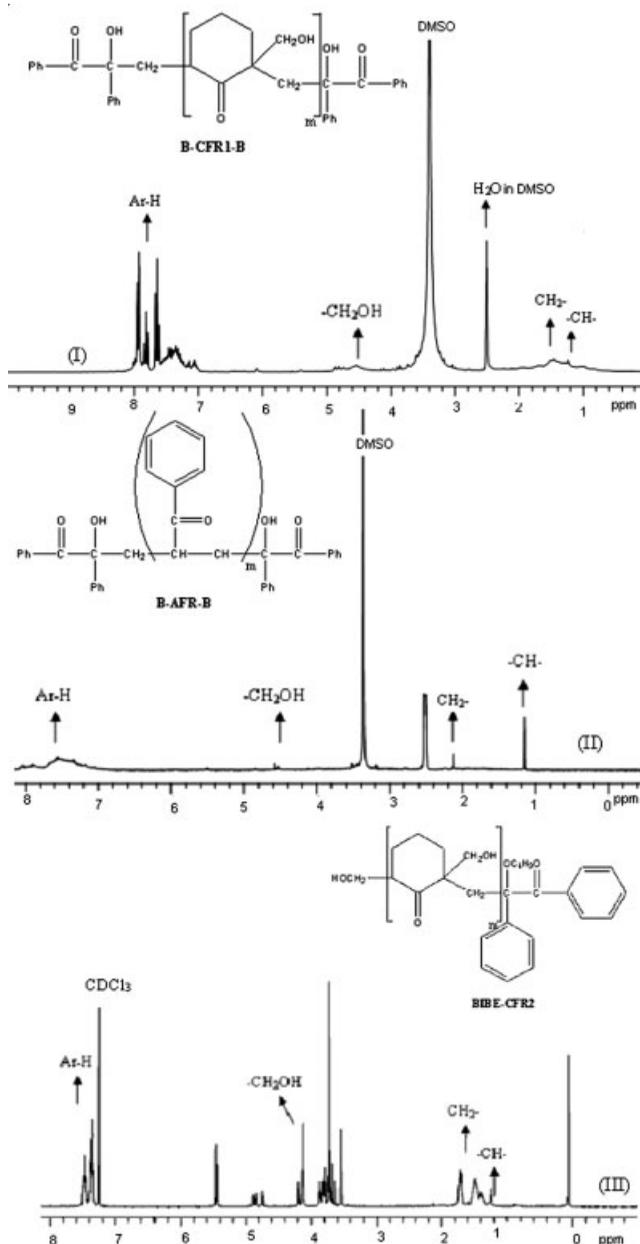


Figure 2 ^1H NMR spectrum of (I) B-CFR1-B, (II) B-AFR-B, (III) BIBE-CFR2 resins.

hexane, 0.2 mol of benzoin or 0.1 mol of BIBE, and 30 g formalin were added and heated to 60°C while stirring. Then 0.36 mL of 20% NaOH was added in equal portions and heated to $75\text{--}80^\circ\text{C}$. Then, 100 g of formalin and 3.64 mL of 20% NaOH were mixed and added continuously at 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 benzoin bounded acetophenone formaldehyde resin (B-AFR-B)

Into a three-necked flask, 1 mol of acetophenone and 30 g of formalin were added and heated to 90°C while stirring. After ~ 6 h, 0.2 mol of benzoin mixture were added into the reaction mixture and continued stirring for a further 10 h, and 6 mL of 40% KOH solution was added drop wise and stirred (pH 11). Modified resin was purified decanting the water layer and washing several times with hot water. It was then dried at 110°C under vacuum.

Promoted cationic polymerization

Appropriate solutions of photoactive resins and monomer (CHO) containing onium salt were placed in pyrex tubes. The mixtures were degassed with nitrogen in the usual manner prior to irradiation with a merry-go-round type photoreactor equipped with 16 Philips 8W/06 lamps emitting light nominally at 350 nm at 30°C . At the end of a given reaction time polymers were obtained from the reaction mixture by precipitation into *n*-hexane or petroleum ether, filtered and dried in vacuum.

Blank experiment

Appropriate solutions of photoactive resins and monomer (CHO) without onium salt were placed in pyrex tubes. The mixtures were degassed with nitro-

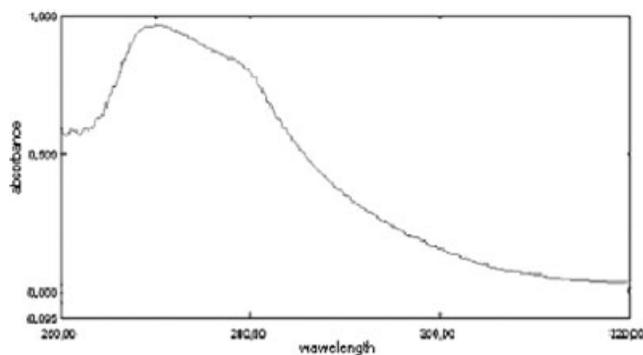
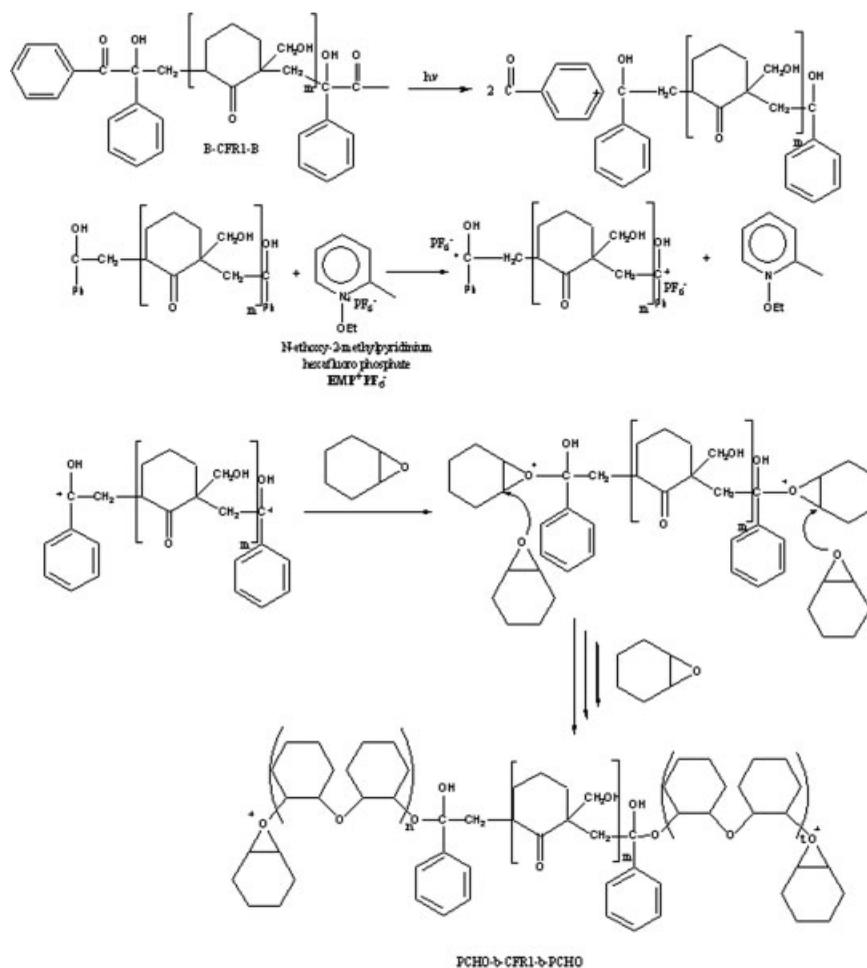


Figure 3 UV spectrum of CH_2Cl_2 solutions of benzoin bounded cyclohexanone formaldehyde resin (B-CFR1-B).



Scheme 5 Promoted cationic polymerization of cyclohexene oxide in conjunction with benzoin bounded ketonic resin in the presence of EMP^+ .

gen in the usual manner prior to irradiation with a merry go round type photoreactor equipped with 16 Philips 8W/06 lamps emitting light nominally at 350 nm at 30°C. After 3 h, the mixture was poured into

n-hexane and the reaction mixture was precipitated. Ketonic resin was recovered. Homo polycyclohexene oxide and copolymer were not obtained.

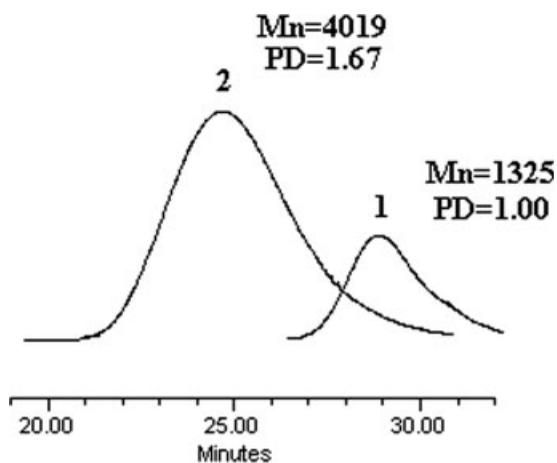


Figure 4 GPC of (I) BIBE-CFR2 resin and (II) CHO-*b*-CFR2 copolymer.

RESULTS AND DISCUSSION

Photoactive benzoin and benzoin isobutyl ether bounded ketonic resins (B-CFR1-B, BIBE-CFR2, B-AFR-B) were prepared by adding benzoin or benzoin isobutyl ether into the reaction mixture during the preparation of ketonic resins, such as cyclohexanone

TABLE I
Physical Properties of the Photoactive Ketonic Resins

Resin	M_n^a	M_w^a	T_m^b (°C)
B-CFR1-B	3,000	3,100	143
B-AFR-B	2,800	2,900	90
BIBE-CFR2	1,325	1,350	80

^a Determined by GPC.

^b Determined by DSC.

TABLE II
Copolymerization of the Cyclohexene Oxide with Ketonic Resin^a

Copolymer	Type of photoactive resin	Conv. (%)	M_n^b	M_w^b	T_m^c (°C)
CHO- <i>b</i> -CFR1- <i>b</i> -CHO	B-CFR1-B	45	11,700	12,100	205
CHO- <i>b</i> -AFR- <i>b</i> -CHO	B-AFR-B	24	8,822	10,995	117
CHO- <i>b</i> -CFR2	BIBE-CFR2	67	4,019	6,640	96

^a [EMP⁺] = 5×10^{-3} mol/L; [Resin] = 0.1 mol/L.

^b Determined by GPC.

^c Determined by DSC.

formaldehyde and acetophenone formaldehyde resins.⁸ Benzoin and benzoin isobutyl ether bounded ketonic resins contain benzoin moieties at chain ends as a photoactive group. The initial reaction is cross aldol condensation of formaldehyde with ketone (cyclohexanone or acetophenone) and benzoin to give ketone methylols and benzoin methylol. The condensation of these methylol compounds results benzoin bounded ketonic resins with the structure shown in the Schemes 2, 3, and 4. The functionality of these photoactive resins depends on the molar ratio of ketone and benzoin. If the ratio of ketone/benzoin was about 6 : 1, the photoactive ketonic resin contains benzoin groups at only one chain end. When the ratio of ketone/benzoin was about 6 : 2 the photoactive ketonic resin contains benzoin groups at both chain ends.

Spectroscopic identification of benzoin bounded ketonic resins was studied by using FTIR and ¹H NMR. FTIR spectra of benzoin and benzoin isobutyl ether bounded ketonic resin are shown in Figure 1. Peaks at 3400 and 1700 cm⁻¹ were due to methylol and carbonyl groups of benzoin bounded resins [Fig. 1 (line I, II, III)]. Peaks at 3050 cm⁻¹ aromatic C[bond]H, 1680 cm⁻¹ aromatic carbonyl, 1600 cm⁻¹ aromatic C—C stretching and 700 cm⁻¹ aromatic C—H bending vibrations were due to aromatic rings of benzoin, benzoin ether, and acetophenone.

The structure of B-CFR1-B and BIBE-CFR2 resins were identified ¹H NMR spectra. The ratio of peak intensities at 1–3 ppm for aliphatic protons of cyclohexanone(—CH, CH₂) and 7.0–8.2 ppm due to aromatic protons of benzoin groups [Fig. 2 (line I and III)] proves the expected structures of the resins having two benzoin groups at each end of the resin for B-CFR1-B and one benzoin group for BIBE-CFR2. ¹H NMR spectrum of B-AFR-B resin showed signals between 1.7 and 2.6 ppm due to —CH that is nearby to carbonyl groups and signals between 3.0 and 3.5 ppm due to —CH₂ of methylene bridges and signals between 3.7 and 4.9 ppm due to methylol and signals between 7.0 and 8.2 ppm due to aromatic protons of benzoin and aromatic protons of acetophenone ring [Fig. 2 (line II)].

The incorporation of benzoin group into the resin was also evidenced by UV spectroscopy in the case of B-CFR1-B. As shown in Figure 3 the absorption spectra of B-CFR1-B contains an absorption band characteristic of the precursor benzoin group. At the irradiation wavelength $\lambda \geq 350$ nm UV irradiation of the benzoin bounded ketonic resins caused α -scission and yielded benzyl radicals and resin-bound radicals. If the photolysis is carried out in the presence of CHO and EMP⁺PF₆⁻ the ketonic resin bounded radicals are converted to the initiating cations to produce block copolymers (Scheme 5).

Benzoin bounded ketonic resin and their copolymers were examined with thin layer chromatography (TLC) and were found to have a cocondensation type structure. Benzoin, cyclohexanone–formaldehyde resin, benzoin bounded ketonic resins and the copolymers were applied to the TLC plate and then eluted with chloroform/benzene, 3/1 mixture. Benzoin bounded ketonic resins showed their own R_f values and did not contain any benzoin or ketonic resin. Similarly, TLC of the copolymers showed that they did not contain any residual components.

GPC analyses of benzoin isobutylether bounded ketonic resin and its copolymer with CHO are shown in the Figure 4. The increase in M_n value from 1325 to 4019 clearly showed the block copolymer formation.

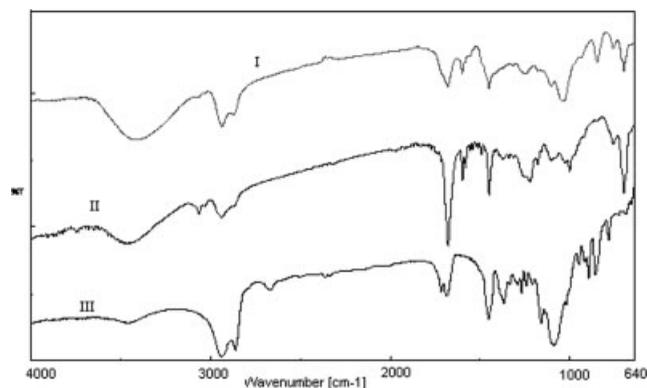


Figure 5 FTIR spectra of (I) CHO-*b*-CFR1-*b*-CHO, (II) CHO-*b*-AFR-*b*-CHO, (III) CHO-*b*-CFR2 copolymers.

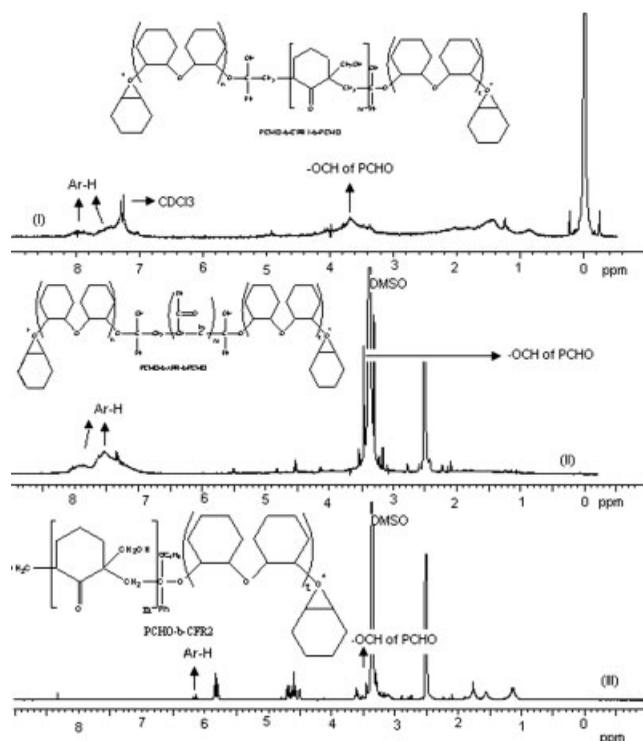


Figure 6 ^1H NMR spectrum of (I) CHO-*b*-FR1-*b*-CHO, (II) CHO-*b*-AFR-*b*-CHO, (III) CHO-*b*-CFR2 copolymer.

TLC and GPC results indicate that all of the benzoin bounded ketonic resin was converted to block copolymer after the photopolymerization process.

Physical properties of benzoin bounded ketonic resins and copolymers are shown in Tables I and II, respectively.

The FTIR spectra the block copolymers show the characteristic ether band of the poly(cyclohexene oxide) (PCHO) segment at 1090 cm^{-1} in addition to the usual resin bands (Fig. 5).

^1H NMR spectra of block copolymers displays signals at 3–3.6 ppm due to —OCH of PCHO and 0.8–2.2 ppm due to CH_2 and CH of PCHO (Fig. 6).

CONCLUSIONS

Block copolymerization via condensation and promoted cationic polymerization routes provides a versatile two-step method applicable to different type of monomers. This procedure can be used to prepare AB- and ABA-type block copolymers according to the type of photoactive resin employed. These block copolymers may exhibit different properties due to incorporation of ketonic resins into the block copolymer structure.

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