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Novel Photosensitive Polymer: Synthesis, Characterization and Thermal Properties of Polymer having Pendant Photocrosslinkable Group

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New methacrylic monomer having free radical polymerizable methacryloyl group and photocrosslinkable functional group was synthesized by reacting hydroxyl chalcone with methacryloyl chloride. The monomer was homopolymerized in methyl ethyl ketone solvent using benzoyl peroxide as an initiator at 70°C. The prepared homopolymer was characterized by UV, FT-IR, ¹H-NMR and ¹³C-NMR spectra. The molecular weights (M_w and M_n) were estimated by gel permeation chromatography. The thermal stability of the polymer was measured by thermogravimetric analysis. The glass transition temperature of the polymer was determined by differential scanning calorimetry. The photocrosslinking property of the polymer was also studied.

Keywords: 4-(benzyloxycinnamoyl)phenyl methacrylate; photocrosslinking; photoresist; ¹H-NMR spectra; thermal properties

1 Introduction

In recent years, functional polymers have received increasing attention in scientific research. Photocrosslinkable polymers have acquired significant importance in various avenues of industrial applications such as microlithography, printing materials, liquid crystalline materials, nonlinear optical materials, photoconductors, energy exchange materials, etc. (1–5). Polymers containing pendant α,β -unsaturated carbonyl groups are known as chalcone groups, e.g., cinnamoyl groups. The cinnamate groups presented either in the backbone or in the side position of their chains undergo crosslinking reaction upon irradiation with UV light or an electron beam, and such polymers are regarded as negative-type photoresists. Photosensitive polymers possess, with a combination of properties such as high photosensitivity, good solubility, good thermal stability, the ability to form films, resistance towards solvents after crosslinking, as well as resistance towards plasmas and etching agents. These are essential requirements for the practical use of a polymer. The polymers having pendant photo functional groups, such as cinnamoyl esters of poly(vinyl alcohol) (6), poly(2-hydroxyethyl methacrylate) (7), poly(2-vinyloxyethyl cinnamate)

(8), poly(vinyl-4-methoxy cinnamate) (9) and other similar systems (10–13) have been already reported. The photochemistry involved in a number of photoresists and their technological applications have also been reviewed (14–21). Polymers having a benzyloxy group were used in the production of high photo speed, radiation-hardenable and heat developable light sensitivity materials (22, 23).

The synthesis of 4-(benzyloxycinnamoyl) phenyl methacrylate monomer nor its polymers has not been reported by chemical abstracts. In continuation of our efforts, we synthesized this novel polymeric material for industrial applications. The present research article mainly focuses on the work involved in the synthesis, characterization and photocrosslinkable property of novel methacrylate polymer containing the pendant chalcone group as a photocrosslinkable unit. The thermal properties of the polymer were also reported.

2 Experimental

2.1 Materials

4-Benzyloxybenzaldehyde and 4-hydroxyl acetophenone were used as received from Wako Chemical Industries. Benzoyl peroxide (BPO, Aldrich) was recrystallized from a chloroform-methanol (1:1) mixture. Triethylamine, methacrylic acid and benzoyl chloride were used as received from Wako. All solvents were purified by distillation prior to their use.

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2.2 Measurements

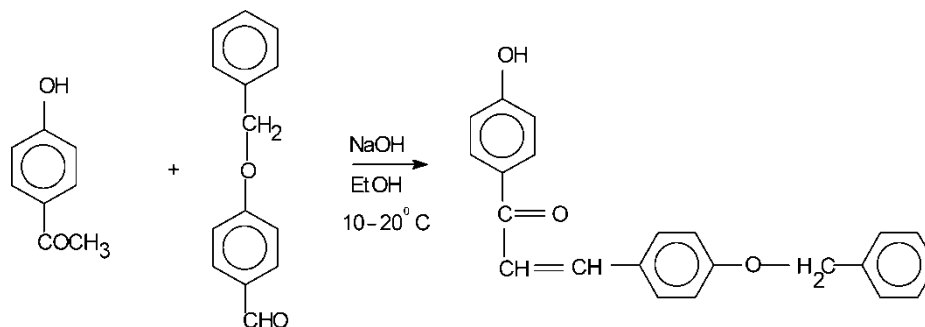
Elemental analysis was performed with a Perkin-Elmer C-H-N analyzer. The UV spectra were recorded in a Shimadzu UV-1700 spectrophotometer. Infrared spectra were recorded with a Jasco 460 FT-IR spectrophotometer as KBr pellets. $^1\text{H-NMR}$ spectra of the monomer and all the polymer samples were run on a JEOL 400 MHz FT-NMR spectrophotometer at room temperature using CDCl_3 solvent and TMS as an internal standard, respectively. The proton decoupled $^{13}\text{C-NMR}$ spectrum was run on the same instrument operating at 100 MHz at room temperature, and the corresponding chemical shifts were recorded under similar conditions. The molecular weights (M_w and M_n) were estimated by using Shimadzu Gel Permeation Chromatography, where tetrahydrofuran was used as an eluent with polystyrene standards for calibration. Thermogravimetric analysis was performed with a Shimadzu thermal analyzer under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The glass transition temperature was determined with a Shimadzu DSC-60 differential scanning calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

2.3 Synthesis of 4-(benzyloxycinnamoyl) Phenol (BCP)

4-Benzyloxybenzaldehyde (11.7 g, 0.055 mol) and 4-hydroxyacetophenone (7.5 g, 0.05 mol) were dissolved in 40 ml of ethanol and cooled at $15\text{--}20^\circ\text{C}$. An aqueous solution of sodium hydroxide (4.4 g in 40 ml of water) was then added dropwise by constant stirring. The temperature was then maintained between $10\text{--}20^\circ\text{C}$. Furthermore, the reaction mixture was stirred for 12 h at room temperature. Then, it was neutralized with dilute HCl in order to isolate the product. The solid product was filtered, washed with ice cold water, dried and recrystallized from absolute ethanol. The yield is 64% (13 g). The reaction scheme for the synthesis of BCP is shown in Scheme 1. The chemical structure of 4-(benzyloxycinnamoyl) phenol was examined by the elemental analysis, FT-IR and $^1\text{H-NMR}$ techniques.

Elemental Analysis: Calculated for $\text{C}_{22}\text{H}_{18}\text{O}_3$; C, 80%; H, 5.45%, Found C, 79.94%; H, 5.40%.

FT-IR cm^{-1} ; 3200 (-OH), 3007 and 2829 (-C-H); 1660 ($>\text{C}=\text{O}$), 1602 ($\text{CH}=\text{CH}$).



Sch. 1. Synthesis of BCP.

The $^1\text{H-NMR}$ spectrum of the BCP monomer is shown in Figure 1. The spectrum shows signals at 9.87 ppm (Ar-OH), 7.86–7.26 (aromatic protons), 7.09–7.02 ppm ($-\text{CH}=\text{CH}$), 6.25 and 5.82 ppm ($\text{CH}_2=\text{C}$), 5.31–5.10 ppm (benzyloxy protons), 2.14 ppm ($\alpha\text{-CH}_3$).

2.4 Synthesis of 4-(benzyloxycinnamoyl) Phenyl Methacrylate (BCPM)

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride utilizing the procedure of Stampel et al. (24). For the synthesis of BCPM, BCP (10 g, 0.030 mol) was reacted with methacryloyl chloride (2.90 ml, 0.030 mol) in the presence of triethylamine (4.2 ml, 0.030 mol) in MEK at $0\text{--}5^\circ\text{C}$. The yield is 72%. The monomer was examined by elemental analysis, FT-IR, $^1\text{H-NMR}$ spectra.

Elemental Analysis: calculated for $\text{C}_{26}\text{H}_{22}\text{O}_4$; C, 78.39%; H, 5.53%, Found C, 78.36%; H, 5.48%

IR cm^{-1} ; 3110 and 3033 ($=\text{C-H}$), 2961 and 2930 (C-H stretching), 1730 (ester, $>\text{C}=\text{O}$), 1655 (ketone, $>\text{C}=\text{O}$), 1600 ($\text{CH}_2=\text{C}$), 1571 and 1456 (aromatic $\text{C}=\text{C}$), 1315 (CH_3 symmetrical bending), 1143 (C-O), 864 (C-H out-of-plane bending).

$^1\text{H-NMR}$, ppm; 7.86–7.26 (aromatic protons), 7.01–6.98 ($-\text{CH}=\text{CH}-$), 6.26 and 5.86 ($\text{CH}_2=\text{C}$), 5.16–5.11 (benzyloxy protons), 2.14 ($\alpha\text{-CH}_3$).

2.5 Polymerization

BCPM was polymerized as a 2 M solution in methyl ethyl ketone using benzoyl peroxide initiator at $70 \pm 1^\circ\text{C}$. Pre-determined quantities of BCPM, MEK and BPO (0.5 wt% of monomer) were placed in a standard polymerization tube and the mixture was flushed with oxygen free nitrogen for 20 min. The tube was then tightly sealed and immersed in an oil bath at $70 \pm 1^\circ\text{C}$. After the required time, the polymer was precipitated in methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from chloroform solution using methanol and finally dried in a vacuum at 50°C for 24 h.

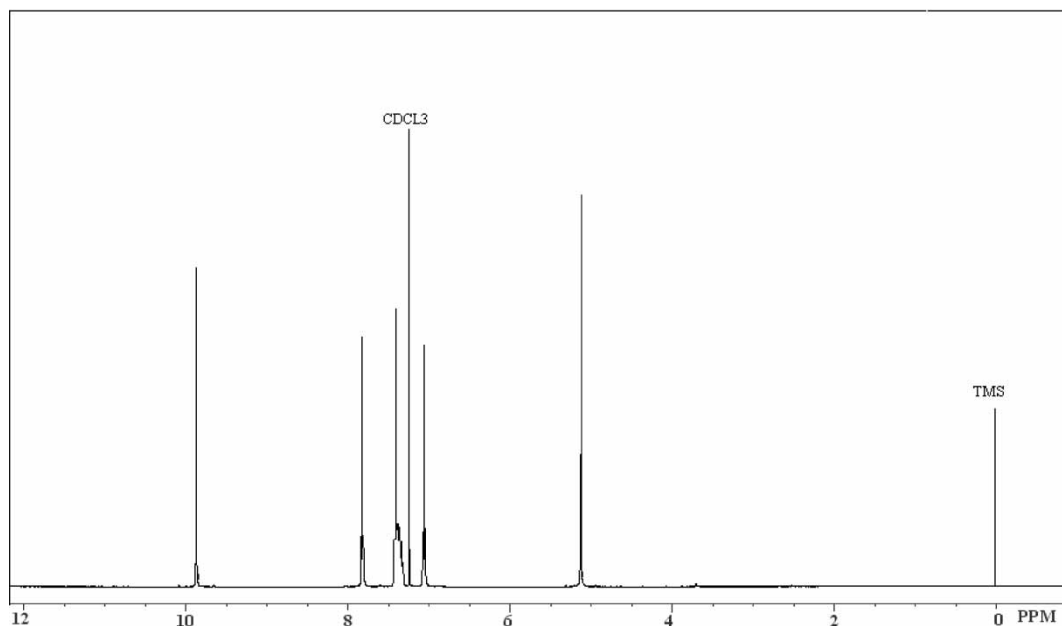


Fig. 1. $^1\text{H-NMR}$ spectrum of BCP.

2.6 Solubility Studies

The solubility nature of the synthesized polymers was checked in various polar and non-polar solvents. About 5–10 mg of the polymer was added to about 2 ml of the solvent in a standard test tube. The tube was then closed tightly and kept overnight. The solubility of the polymers was observed after 24 h.

2.7 Photoreactivity Measurements

An ultraviolet lamp (Funakoshi Corporation, 6 watts) was used for the irradiation of polymers. The quartz cell containing the polymer solution was kept at a distance of 5 cm from the UV lamp for different time intervals of irradiation. The UV spectra of the polymer solution were recorded immediately after each exposure time, and the rate of disappearance of $\text{C}=\text{C}$ double bond of the chalcone moiety in the polymer was monitored by using the following expression:

$$\text{Rate of conversion (\%)} = \frac{A_0 - A_r}{A_r} \times 100$$

where A_0 and A_r are the absorption intensities due to $\text{>C}=\text{C}<$ after irradiation times $t = 0$ and $t = T$, respectively.

3 Results and Discussion

3.1 Synthesis of Polymer

The new methacrylate monomer, BCPM having a photosensitive chalcone unit was synthesized in two steps. Firstly, by Claisen–Schmidt condensation reaction, the hydroxyl chalcone was prepared by reacting 4-benzyloxy benzaldehyde

with 4-hydroxyacetophenone in a water-ethanol mixture in the presence of sodium hydroxide. Then, in the second step, the prepared hydroxyl chalcone was reacted with methacryloyl chloride in the presence of triethylamine in MEK at 0 to -5°C to obtain the monomer, BCPM. The structure of hydroxyl chalcone and the monomer were confirmed by elemental analysis, FT-IR and $^1\text{H-NMR}$ spectra.

The poly(BCPM) having pendant photocrosslinkable chalcone units were obtained by a free-radical solution polymerization of the monomer, BCPM in MEK at $70 \pm 1^\circ\text{C}$. The conversion of monomer to polymer has been restricted to 40–50% in order to avoid any possibility of cross-linking at higher conversions.

3.2 Polymer Characterization

One of the essential requirements for a photosensitive polymer is its solubility in different organic solvents. The solubility of poly(BCPM) obtained after different time intervals of polymerization were tested. It was found that the polymers obtained up to 3 h of reaction time and up to 40% yield were easily soluble in the polar solvents viz. chloroform, methylene chloride, dimethylformamide, N-methyl-2-pyrrolidone and dimethylacetamide, but insoluble in hydrocarbons such as benzene, toluene, xylene and the hydroxyl group containing solvents such as methanol, ethanol and 2-propanol. However, the conversions of above 50%, the solubility of poly(BCPM) gradually decreased with increasing conversions. The polymer which is obtained at about 70% conversion was found to be completely insoluble even at the boiling temperature of the solvents. This might have been due to cross linking.

3.3 UV Spectroscopy

Poly(BCPM) exhibits UV absorption maxima in chloroform solution at 305 nm corresponding to the pendant chalcone group. The bathochromic shift of UV absorption maxima in the polymer occurs on the higher wavelength side (305 nm) and this might be due to the presence of the electron donating benzyloxy group at the para-position of the aromatic ring of the cinnamoyl group.

3.4 Infrared Spectroscopy

The FT-IR spectrum of the copolymer poly(BCPM) is shown in Figure 2. It shows a characteristic peaks at 2997 and 2913 cm^{-1} corresponding to the C-H stretching of the aromatic groups. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2870 and 2835 cm^{-1} . The absorption band at 1726 cm^{-1} corresponds to ester carbonyl stretching. The ketonic carbonyl stretching is observed at 1660 cm^{-1} . A strong absorption band at 1603–1610 cm^{-1} corresponds to the stretching vibrations of the ethylenic double bond of the pendant chalcone unit. The aromatic C=C stretching vibration band appears at 1600, 1509, and 1427 cm^{-1} , respectively. The symmetrical bending vibrations of methyl groups are seen at 1390 cm^{-1} . The C-H out-of-plane bending vibrations of the aromatic nuclei is observed at 832 and 736 cm^{-1} .

3.5 $^1\text{H-NMR}$ Spectroscopy

The $^1\text{H-NMR}$ spectrum of the copolymer of poly(BCPM) is shown in Figure 3. It shows a multiplet signals at 7.86–6.56 ppm corresponding to the aromatic protons overlapped with those of pendant olefinic protons. The benzyloxy protons show a signal at 5.16–5.11 ppm. The broad resonance signals between 2.45–1.25 ppm are due to the existence of tacticity of backbone methylene groups and α -methyl group.

3.6 $^{13}\text{C-NMR}$ Spectroscopy

The proton decoupled of $^{13}\text{C-NMR}$ spectrum of poly(BCPM) is shown in Figure 4. $^{13}\text{C-NMR}$ chemical shift assignments were made from the off-resonance decoupled spectra of the polymers. It shows a resonance signals at 188.65 ppm due to the ester carbonyl carbon. Any functional group that introduces more electron density on the carbonyl carbon tends to cause an upfield shift. The extent of the chemical shift depends on the extent of conjugation with electrons and π system on the substituent. Normally, the ketone carbonyl carbon shows a resonance signal at about 200 ppm. However, due to the presence of long conjugation in this polymer, a small upfield shift of the ketone carbonyl carbon results. The resonance signal at 175.02 ppm corresponds to the ester

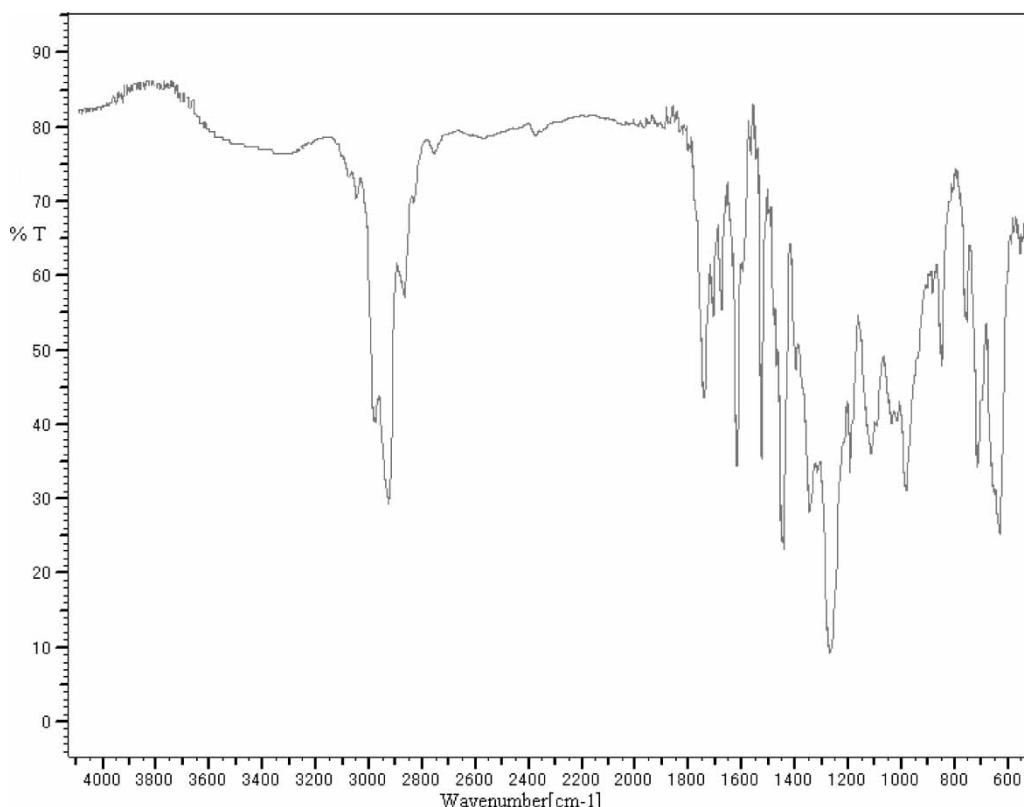


Fig. 2. FT-IR spectrum of poly(BCPM).

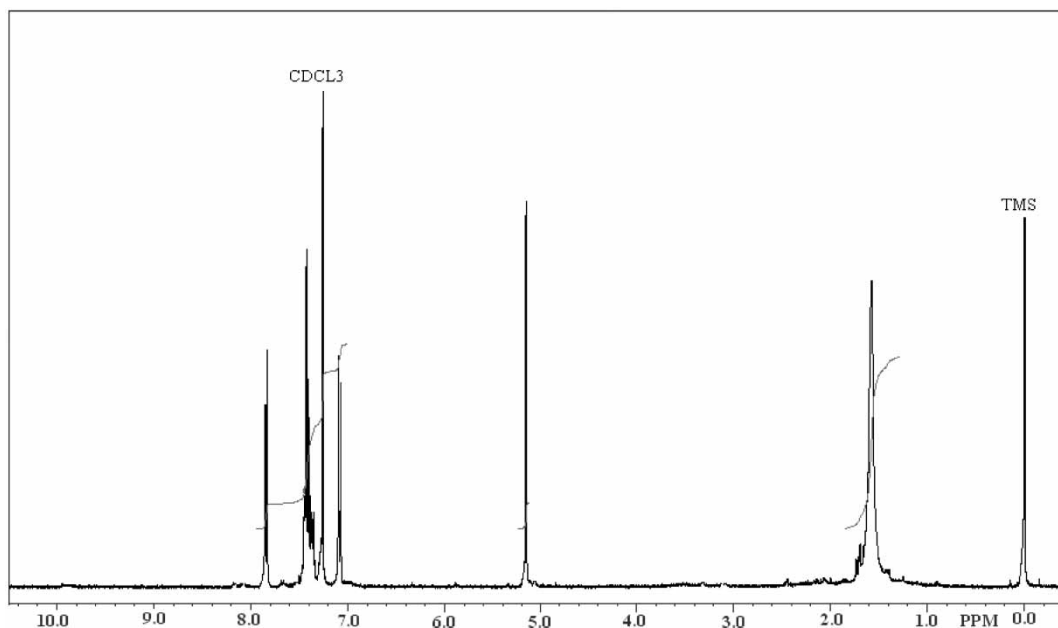


Fig. 3. ^1H -NMR spectrum of poly(BCPM).

carbonyl carbon. The aromatic carbon attached to the oxygen atom shows a signal at 154.53 ppm. The resonances of the other aromatic and ethylenic ($>\text{C}=\text{C}<$) carbons are observed between 143.01 and 121.80 ppm. The strong resonance signal observed at 67.12 ppm corresponds to the benzyloxy carbon. The backbone tertiary carbon and methylene carbon signals are observed at 55.62 and 44.80 ppm. The α -methyl carbon of the polymer appears at 18.94 ppm.

3.7 Molecular Weights

The number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity index of poly(BCPM) were determined by gel permeation chromatography are as follows:

$$M_w \times 10^{-4} = 3.95; M_n \times 10^{-4} = 2.12.$$

$$M_w/M_n = 1.86.$$

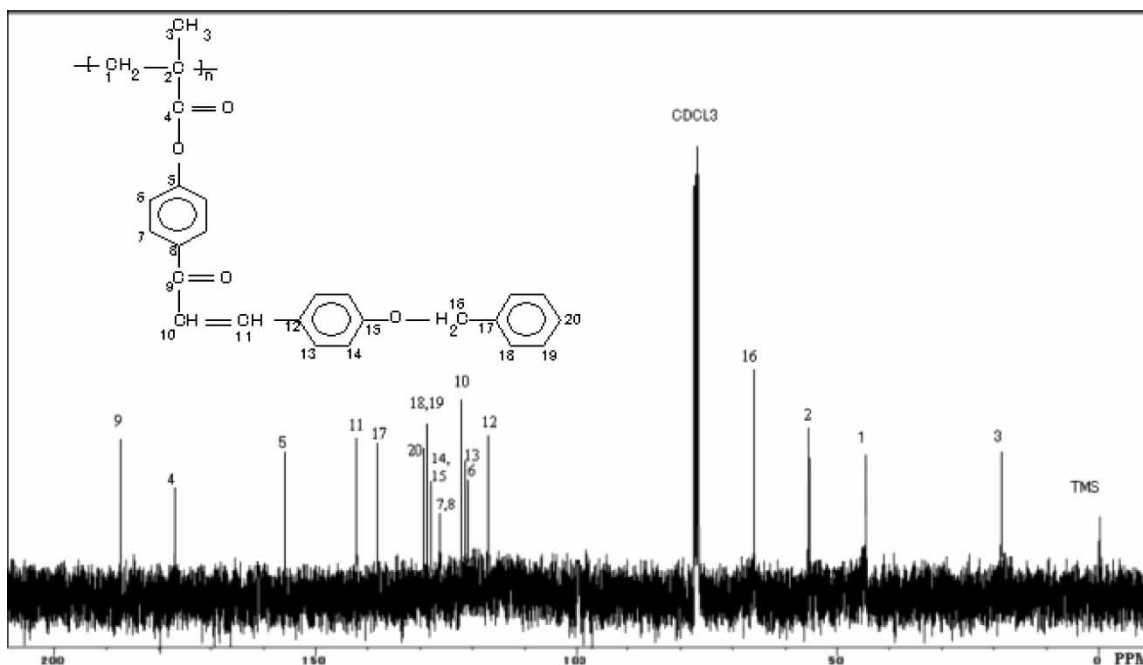


Fig. 4. ^{13}C -NMR spectrum of poly(BCPM).

The theoretical value of M_w and M_n for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively (25, 26). Generally, the poly dispersity index (M_w/M_n) of poly(meth)acrylates (27) prepared by free-radical polymerization of the monomer depends, among other factors, on the chain termination mechanism. Hence, the polydispersity index value of poly(BCPM) suggests that the tendency for chain termination by disproportionation predominates over coupling.

3.8 Glass Transition Temperature (T_g)

The glass transition temperature (T_g) of poly(BCPM) determined by differential scanning calorimetry in nitrogen atmosphere was found to be 152°C. This high T_g value of the polymer is due to the inflexible, bulky pendant chalcone units and also the presence of α -CH₃ group, which facilitates the chain entanglement.

3.9 Thermogravimetric Analysis (TGA)

The thermal stability of the polymers was studied by thermogravimetric analysis in nitrogen atmosphere. The thermogravimetric analysis (TGA) of the polymer is shown in Figure 5. The initial decomposition temperature (IDT) of poly(BCPM) is 223°C and 50% weight loss occurs at about 302°C. The thermogram clearly indicates that poly(BCPM) undergoes two-stage decomposition. This behavior can be explained by assuming the following mechanism for the decomposition. The first step of decomposition is due to the cleavage of weak linkages of the pendant molecule and thereby volatilization of low molecular weight species. This process is subsequently followed by the breakage of benzene ring in the main chains and thereby volatilization of the cleaved products.

Thus, TGA results clearly strongly indicate that the polymer possesses very good thermal stability for negative photoresists.

3.10 Photocrosslinking Properties of the Polymer

The photosensitivity of poly(BCPM) was measured by irradiation with an ultraviolet lamp. The irradiation was carried out in polymer solutions in the presence and absence of sensitizers. Figure 6 show changes in the UV spectral patterns of poly(BCPM), in a chloroform solution (20 mg/l), for different intervals of irradiation, at room temperature, and also in the absence of a sensitizer. The polymer shows the UV absorption band at 305 nm due to the formation of cyclobutane ring by π - π^* transitions associated with $>C=C<$ of the pendant chalcone moiety. The intensity of the band at 305 nm decreases very rapidly with the radiation time due to the formation of cyclobutane ring formation and disappears almost completely within 5 min of irradiation. Upon further irradiation, an isobestic point was observed at about 265–270 nm, which clearly indicates that the double bond present in the polymer undergoes cis-trans isomerization. The polymer on continuous irradiation for about 10 min was rendered insoluble in the solvents, in which it was soluble before irradiation. This may be due to the cross-linking of the polymer chains through 2+2 cycloaddition of $>C=C<$ group of the pendant chalcone unit as shown in Scheme 2. Thus, the decreases in UV absorption intensities with irradiation time clearly indicate that 2+2 cycloaddition destroys conjugation in the entire π -electron system (28, 29).

The photosensitivity of the polymer poly(BCPM) containing a α,β -unsaturated carbonyl group is generally measured in terms of the rate of disappearance of $>C=C<$ with irradiation time and graphical representation is shown in Figure 7. The polymer shows conversions of 40 at 30 s and

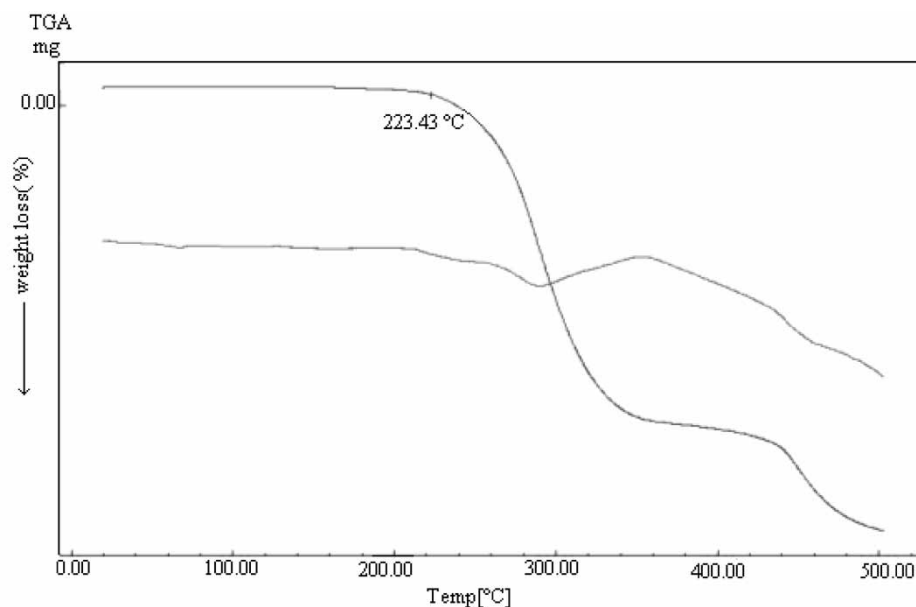


Fig. 5. TGA and DTA curves of poly(BCPM).

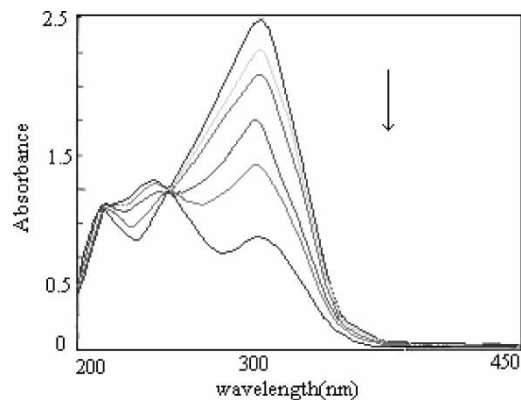
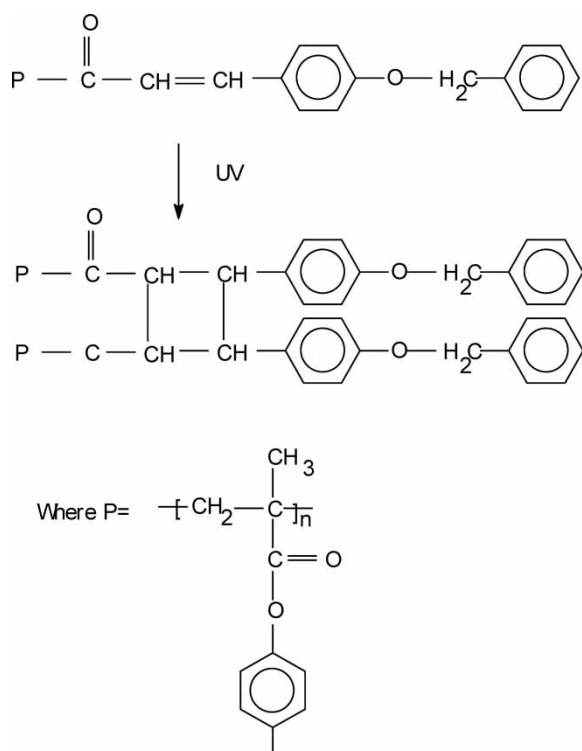


Fig. 6. Effect of UV irradiation (0–300 s) on poly(BCPM).

75% after 60s of irradiation time, respectively. It is observed that within 3 min of irradiation about 80% conversion takes place. In order to understand, these types of polymers are mainly used as negative photoresist materials, the polymer sample was further irradiated under UV light for 1 h. The crosslinked polymer was obtained by evaporating the solvents. The solubility tests of this crosslinked polymer show that it is insoluble in various organic solvents. It also confirms the formation of rigid cyclobutane ring in the polymer.

In order to observe the effect of sensitizers on the rate of photocrosslinking, the polymer samples were irradiated in the presence of triplet sensitizers such as benzoin and benzophenone. The result shows that there is no significant change



Sch. 2. Photocrosslinking reaction of poly(BCPM).

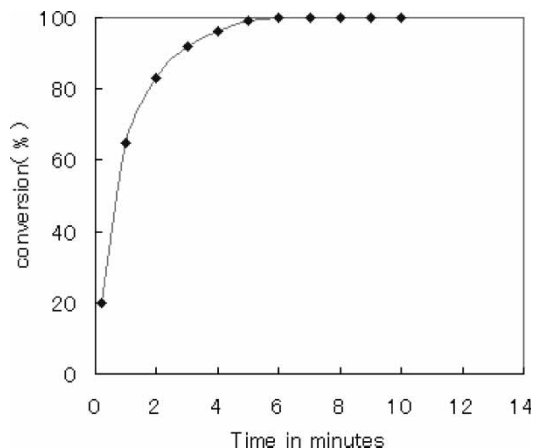


Fig. 7. Rate of disappearance of pendant chalcone double bond on poly(BCPM) with UV radiation.

in the rate of photocrosslinking reaction. This behavior is similar to that reported for photosensitive polymers having such as α -phenylmaleimide (30) and α -cyanocinnamic ester (31), which have a high photosensitivity but cannot be sensitized. This strongly indicates that the photocrosslinking might not be taking place by triplet (T) state, but alternatively through the single state electrons leading to a one-step, concerted (2 + 2) cycloaddition (32).

Poly(BCPM) with pendant chalcone moiety has a higher rate of photocrosslinking, even in the absence of sensitizers, leading to insolubility of the polymer. It might be expected that these polymers can be effectively used as negative photoresist materials.

Thus, poly(BCPM) possesses high photosensitivity, high thermal and high rigidity properties when comparing to other polymer systems (21) due to the presence of electron donating benzyloxy bulky group in their side chain.

4 Conclusions

The novel photosensitive polymer poly(BCPM) was synthesized by free radical solution polymerization using benzoyl peroxide as an initiator. The synthesized polymer was characterized by UV, FT-IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral techniques. The solubility of the polymer was tested in different organic solvents. The polydispersity index value of the polymer indicates that there is a stronger tendency for chain termination by disproportionation rather than dimerization. The thermogravimetric analysis results clearly show that the polymer possesses very good thermal stability required for a photosensitive polymer. The high T_g value of the polymer is due to the presence of inflexible and bulky side chain groups. The photoreactivity studies of the polymers in various solvents strongly suggest fast conversion of photoreactive groups during UV irradiation as required for a photopolymer. The photocrosslinking reactions of the polymers carried out in the presence of a triplet

photosensitizer show no significant change in the rate of disappearance of $>C=C<$ in chalcone moieties. Thus, poly(BCPM) with pendant chalcone unit possesses a higher rate of photocrosslinking even in the absence of sensitizer and it may find potential applications as an excellent negative photoresist for photocurable systems.

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