Synthesis, Characterization, and Studies on the Solid-State Crosslinking of Functionalized Vinyl Cinnamate Polymers

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ABSTRACT: Functionalized vinyl cinnamate monomers were synthesized by the reaction between hydroxyethylacrylate (HEA) and substituted cinnamoyl chlorides possessing electron releasing and withdrawing functional groups like chloro, methoxy, and nitro groups at the para position of the aromatic ring. The structures of these monomers were characterized by Fourier transform infrared (FTIR), ^{1}H-, and ^{13}C-NMR spectral techniques. The homopolymers of the synthesized monomers were obtained by the free radical solution polymerization in dimethylformamide (DMF) at 80°C for 12 h using azobisisobutyronitrile (AIBN) as a radical initiator. The sensitivity of these polymers towards light was studied by monitoring the photocrosslinking nature of the polymers by ultraviolet (UV) and FTIR techniques. The effect of the functional groups on the crosslinking efficiency was studied and compared with that of the unsubstituted polymer. The cyclobutane-type addition mechanism involved in the photocrosslinking phenomena was confirmed by the above spectral studies in the functionalized vinyl cinnamate polymers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 441–448, 1998

Key words: vinyl cinnamates; photocrosslinking; functionalized monomers; cycloaddition

INTRODUCTION

Photocrosslinking is one of the phototransformation phenomena that occurred when polymers like vinyl cinnamates were exposed to light. The insolubility of these polymers after the exposure to an irradiation leads to the use of these polymers for variety of applications such as photoresists and in printing plates.[1–4] Polyvinylcinnamates are well-known classical examples and are the forerunners among the negative-type photoresist polymers.

Polymers with pendant cinnamic ester groups have been studied for their photosensitive nature.[5–10] Copolymers comprising hydroxyethylmethacrylate (HEMA), vinyl acetate, and poly(vinyl alcohol) were reported for their photocross-linking ability without any substitution.[11] Paczkowski et al. reported[12,13] that the presence of different functional groups in the pendant chain could influence the photosensitivity, depending on their electron donor or acceptor nature in vinyl cinnamates derived from poly(vinyl alcohol) and various cinnamoyl chlorides. Further, it was reported that the spacer length in the pendant chain and the relative position of the functional group have a profound effect on the photosensitivity. Introduction of functional groups could be more appropriate than other ways, such as employing a sensitizer or preparing a proper mixture of polymeric system for improving the efficiency of the photosensitivity.[14] Many of the vinyl cinnamate polymers studied were obtained either as copolymers of poly(vinyl alcohol) and cinnamoyl chlorides or homopolymers of the monomers synthesized by various phenols and cinnamoyl chloride.[15] Even though the copolymers of vinyl cinnamates have acquired more importance for the application purpose, their photosensitivity is based mainly on

the nature of photoactive —CH=CH— chromophore. Moreover, poly(vinyl alcohol) used in the above systems should be derived from the poly(vinyl acetate) in which the acquirement of maximum hydroxyl content is rarely possible. This article deals with the synthesis and characterization of homopolymers of the monomers prepared by the reaction of hydroxyethylacrylate (HEA) with the functionalised cinnamoyl chlorides aiming to study the effect of functional groups on the sensitivity and the mechanism of crosslinking by FTIR and UV spectroscopic techniques. Functional groups like methoxy, chloro, and nitro were introduced at the para position of cinnamoyl chlorides. The polymers were prepared by free radical solution polymerization using AIBN as an initiator. The effect of functional groups on the photosensitivity was compared with the unsubstituted polymer.

EXPERIMENTAL

Materials

Hydroxyethylacrylate (HEA) was received from Aldrich, U.S.A., and used as such. Analytical-grade cinnamic acid; 4-methoxy, 4-chloro (Pradeep chemicals, India), and 4-nitro (Lancaster, U.K.) cinnamic acids; thionyl chloride; methanol; and triethylamine (TEA) (s.d. fine chem., India) were used without further purification. Benzene and dimethylformamide (DMF) (s.d. fine chem.) were purified for moisture-free conditions. AIBN (s.d. fine chem.) was used after recrystallization.
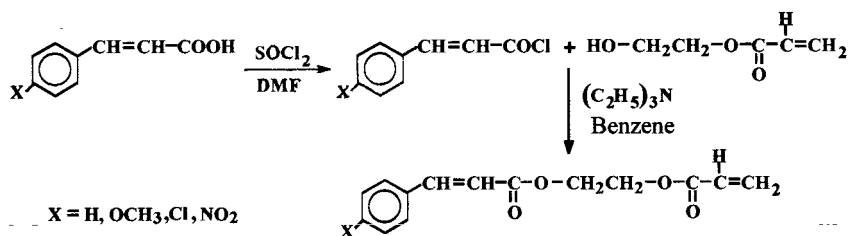
Synthesis of Monomers

The acid chlorides of substituted cinnamic acid were prepared by refluxing it with thionyl chloride and few drops of DMF at 80°C for 30 min initially, and later at 100°C for 20 min. The above freshly prepared acid chloride was added to a three-neck flask equipped with mechanical stirrer and previously charged with HEA, TEA, and ben-

zene. The procedure reported earlier [16] for the synthesis of a similar type unsubstituted monomer was followed for the synthesis of the unsubstituted monomers also in this work. A moisture-free condition was maintained throughout the experiment. The preparation, transfer, and addition of the acid chloride were carried out spontaneously, as the acid chlorides are very sensitive to moisture than the unsubstituted cinnamoyl chloride. The stirring was continued for 12 h. The entire preparation of acid chloride and its esterification reactions were carried out in a nitrogen atmosphere. The precipitated salt, TEA.HCl, was filtered off; and the filtrate was extracted with distilled water and sodium bicarbonate several times. On evaporating the solvent from the organic layer, the monomer, cinnamoyloxyethylacrylate (CEA), was obtained. Similarly, other monomers, chlorocinnamoyloxyethylacrylate (CCEA), methoxycinnamoyloxyethylacrylate (MCEA), and nitrocinnamoyloxyethylacrylate (NCEA) were synthesized. The monomers were purified by column chromatographic method. Silica gel (60–120 mesh size) and a benzene : ethyl acetate (50 : 50) solvent mixture were used as the column packing material and eluting medium, respectively. The synthesis of monomers is shown in Scheme 1.

Spectral Measurements

Fourier transform infrared (FTIR) spectra of monomers were recorded in Nicolet Impact 400 FTIR spectrometer at a resolution of 1 cm^{-1}. The monomers were cast into a thin film between two KBr windows, and the spectra were taken as neat. Bruker MSL 300 MHz Fourier transform nuclear magnetic resonance (FT–NMR) spectrometer was used to record ^{1}H- and ^{13}C-NMR spectra of the monomers using deuterated dimethyl sulfoxide as a solvent. Tetramethylsilane was used as an internal standard. The ultraviolet (UV) spectra were recorded using Shimatzu 160A spectrophotometer. Irradiation was carried out at a distance of 15 cm using a Philips 400 W HP mercury lamp.

Scheme 1 Synthesis of monomers.

Polymerization Procedure

Into a polymerization tube equipped with nitrogen inlet and outlet was placed 0.5 g of the monomer and 2 wt % of AIBN and 10 mL of DMF. The nitrogen inlet and outlet were sealed after passing the dry nitrogen gas through the mixture for 10 min to outgas the air. The mixture contained in the tube was kept in a thermostatic water bath at 80°C for about 12 h. Polymers were precipitated using methanol as a nonsolvent, and filtered and dried in vacuum at room temperature.

RESULTS AND DISCUSSION

Spectral Characterization

The FTIR spectra of MCEA shows the characteristic absorptions at 3031, 3063, and 3083, and 1450, 1497, and 1577 cm^{-1} for aromatic $—CH_{str}$ and $—CH_{def}$ vibrations, respectively. The stretching absorption frequency for the ester carbonyl group is observed at 1717 cm^{-1}, unlike that at 1680 cm^{-1} in the case of acid carbonyl of the corresponding acid. The absorption at 1637 cm^{-1} is responsible for the $—C=C—$ vibration. The vinyl $—CH_{str}$ is noticed at 2836 cm^{-1} as a sharp peak. The absence of broad peak around 3500 cm^{-1} for $—OH_{str}$ of HEA and the two characteristic peaks of $—COOH_{str}$ of the acid at 2520 and 2600 cm^{-1} in the FTIR of MCEA confirmed the formation and the structure of MCEA. The structure of other

monomers, namely, CCEA and NCEA, have no appreciable change in their FTIR spectra as their structures are almost identical. In addition to the above peaks, characteristic peaks at 1526 and 1345 cm^{-1} for $C—N_{str}$ of NCEA and a peak at 772 cm^{-1} for $—C—Cl_{str}$ for CCEA were also observed. The above observations confirm the presence of functional groups in the corresponding monomers. FTIR spectra of MCEA are shown in Figure 1.

The proton NMR absorptions peaks observed for the synthesized monomers gave a good agreement with their corresponding structures. In the ^{1}H-NMR of MCEA (Fig. 2), the two protons of $—CH_2$ group of vinyl segment are not a similar type of protons. They are trans to each other and are resonating at 5.6 and 6.2 ppm, but the close proximity of these protons with $—CH$ protons of $—CH=CH_2$ exhibits a ABX type of coupling pattern resulting in multiplets for each proton resonating at 5.6, 6.0, and 6.2 ppm (see insert in Fig. 2). Another multiplet appearing at 4.3 ppm is caused by the $—CH_2$ group. The two trans $—CH$ protons of cinnamoyl moiety ($—CH=CH—$) gave doublets at 6.3 and 7.6 ppm. These doublets are due to the coupling of $—CH$ protons with each other and appear with the same coupling constant (J) value of 0.053, which is a characteristic peak for trans isomer of cinnamic acid. There are four aromatic protons that are grouped into two (C_6 and C_7) and are observed at 7.2 and 7.4 as multiplets. The disappearance of the multiplets at 5.6
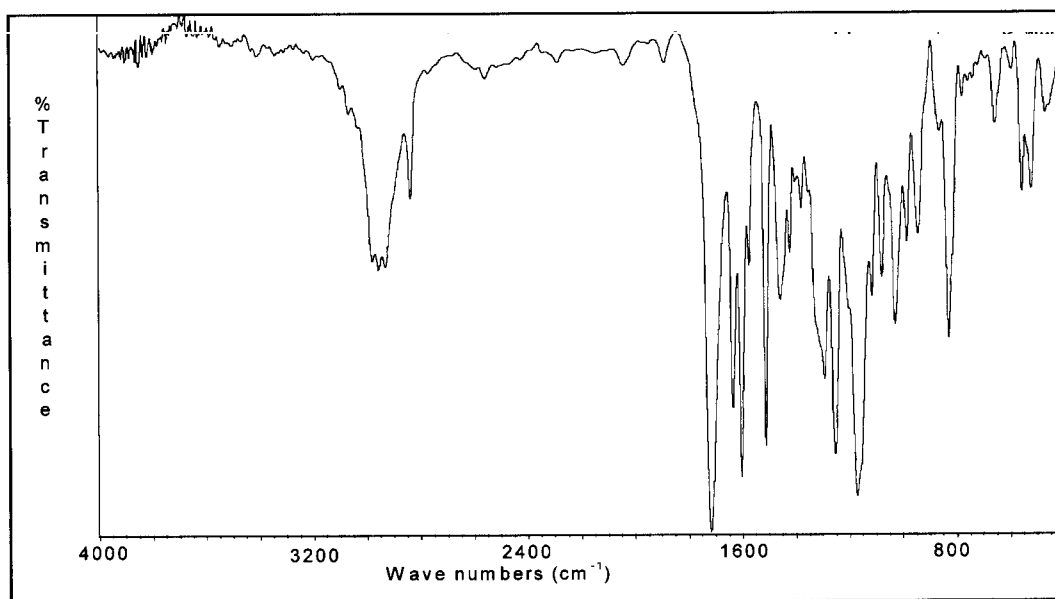

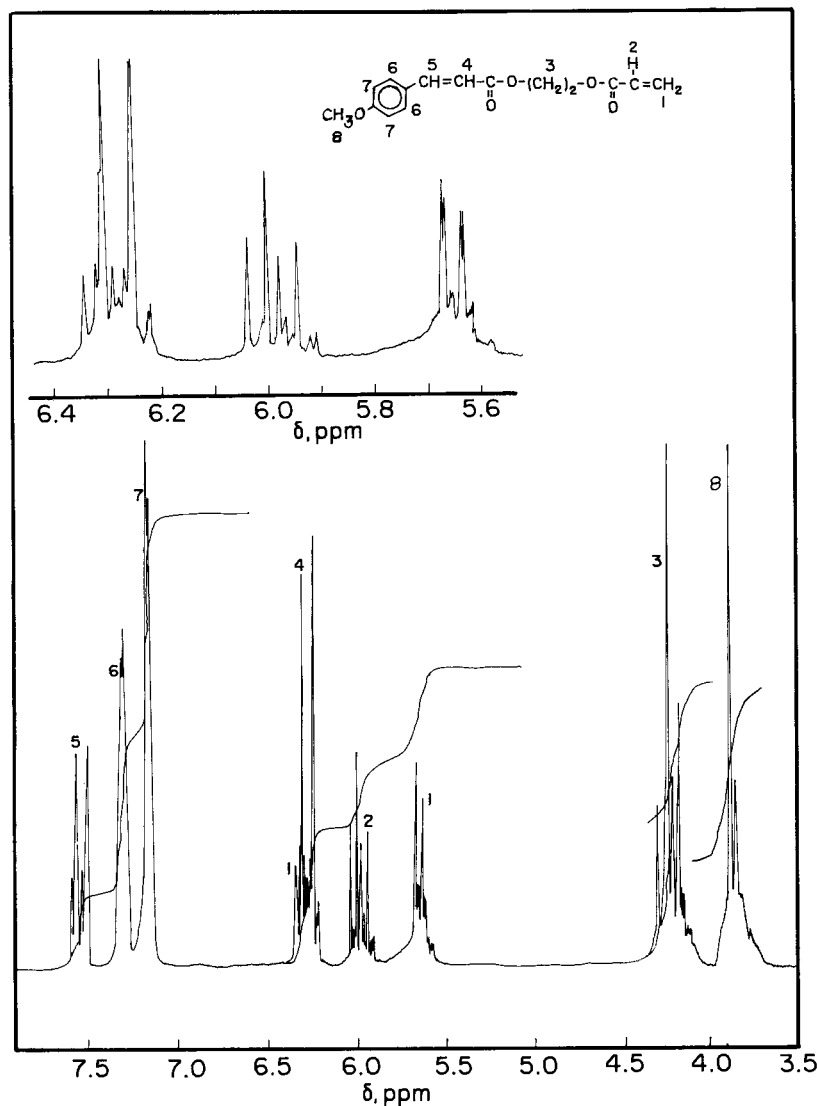
Figure 1   FTIR spectrum of MCEA.

Figure 2 ^{1}H-NMR of MCEA.

and 6.2 ppm was observed in the case of polymer [poly(MCEA)], which is due to the polymerization of vinyl double bonds indicating that the double bond of the vinyl moiety only was getting polymerized, leaving the cinnamoyl double bond unaltered. The complete solubility of the polymer in many of the common solvents indicates that the cinnamoyl double bond is not involved in any crosslinking mechanism during polymerization. This is due to the different electron density of two types of the double bond as reported.[17,18] Additionally, a peak at 3.9 ppm was also noticed for the —CH$_3$ protons of —OCH$_3$ group of MCEA. Similar observations were also noted for CCEA and NCEA.

Similar to ^{1}H-NMR, the structures of the mono-

mers were confirmed by ^{13}C-NMR spectra by observing different types of resonance peaks for various carbon atoms. ^{13}C-NMR differentiated the similar type of groups explicitly than that of FTIR and ^{1}H-NMR. For instance, two well-separated resonance peaks were obtained for carbon atoms of two carbonyl groups of similar type at 165 and 167 ppm. Similarly, two —CH$_2$ groups are identified at 61 and 62 ppm distinctly. The ^{13}C-NMR of MCEA is displayed in Figure 3. Similar observations were also noticed for other monomers. The spectral data of CEA was already reported.[16]

Photocrosslinking Studies by UV

A 1% solution of the respective polymer was prepared in chloroform, spread over the quartz plate
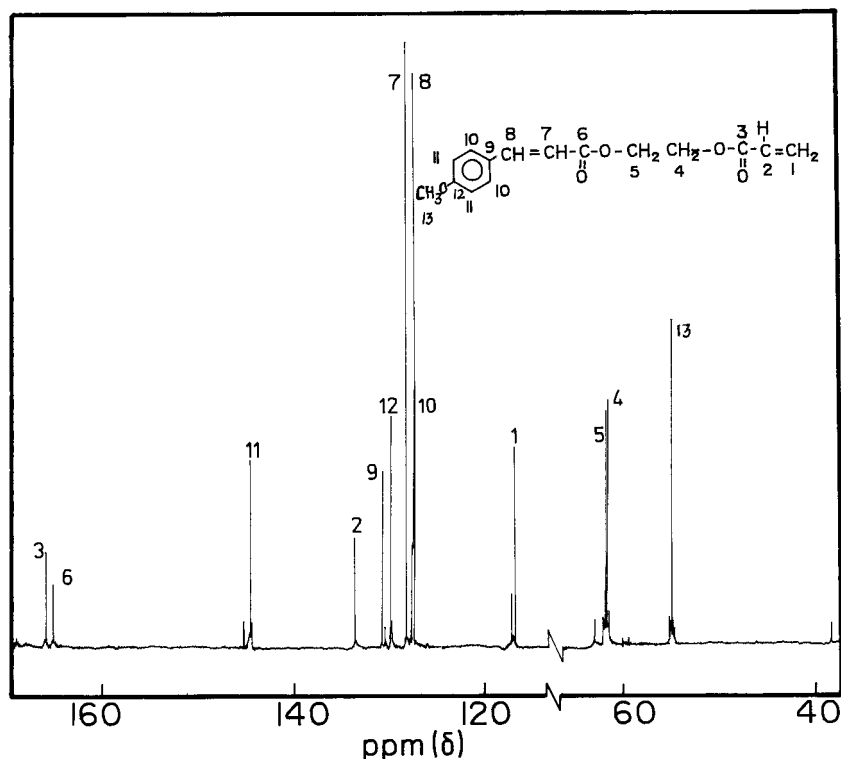
Figure 3 ^{13}C-NMR of MCEA

(5 × 1 cm), and left as such at room temperature. The thin film formed on the quartz plate was subjected for irradiation and UV measurements for selected intervals of time. The photocrosslinking was monitored at 275, 280, 310, and 255 nm for poly(CEA), poly(CCEA), poly(MCEA), and poly-(NCEA), respectively. It is clear from the UV traces of the Figure 4 that the absorbance values were getting reduced as the time of exposure increases without any isobestic point, which is characteristic for the cis–trans isomerization.[11] The

fall in the absorbance value was monitored for the continual irradiation of 0, 10, 15, 20, 30, 45, and 60 min. The crosslinking efficiency was compared by calculating the percentage of conversion of photoactive chromophore (—CH=CH—), which is equivalent to the percentage of crosslinking with the help of the following equation:

$$\% \text{ crosslinking} = A_t - A_o/A_\infty - A_o \times 100$$

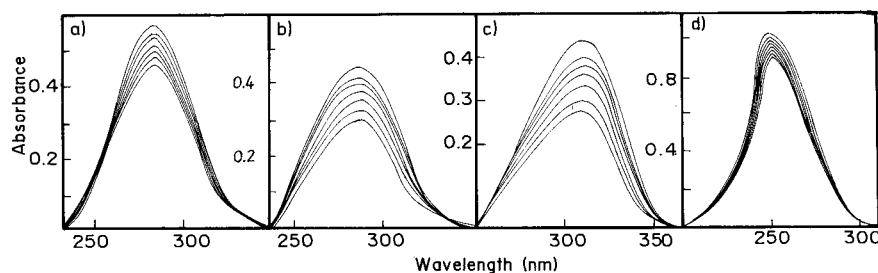where A_o, A_t, and A_∞ are the absorbance values

Figure 4 UV traces showing the decrease in the absorption maximum of the polymers at 0, 10, 15, 20, 30, 45, and 60 min for (a) poly(CEA) (at 285 nm); (b) poly(CCEA) (at 290 nm); (c) poly(MCEA) (at 310 nm); and (d) poly(NCEA) (at 255 nm).
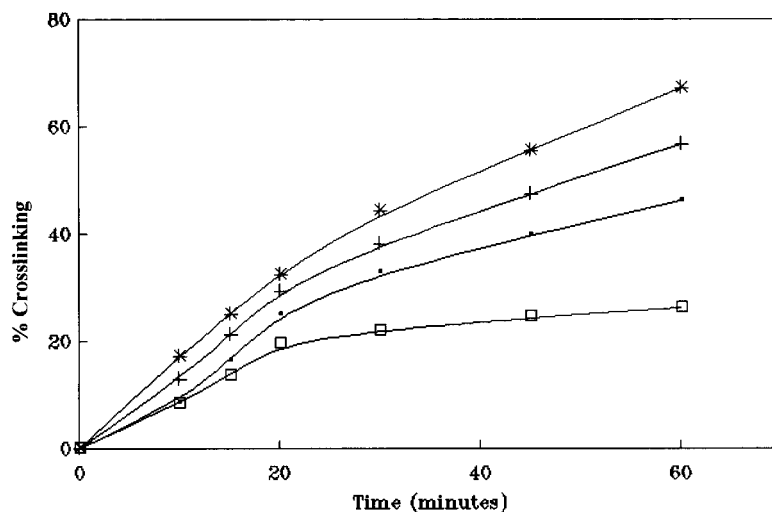
Figure 5 Increase in the percentage of crosslinking of polymers with the increase in the radiation time for poly(CEA) (□), poly(CCEA) (+), poly(MCEA) (*), and poly-(NCEA) (□).

at $0, t$, and a time after which there was no considerable change in the absorbance values. The percentage of crosslinking was then plotted against the time of irradiation as shown in Figure 5.

It could be seen from Figure 5 that the rate of photocrosslinking, in terms of the rate of disappearance of the photoactive —CH=CH— bond, is higher for poly(MCEA) with the value of 67.5%; while poly(CCEA) and poly(CEA) showed 56.6 and 46.3%. In the case of nitro-substituted polymer, poly(NCEA), it is found to be only 26.4% for the same time of irradiation. This is due to the electron releasing nature of —OCH$_3$ and —Cl groups that strengthen the electron density of —CH=CH double bond through an extended conjugation. On the other hand, the stronger electron-withdrawing tendency of the —NO$_2$ group is responsible for the lower crosslinking efficiency of poly(NCEA). Further, it was observed from the Figure 5 that it initially shows a linear rise in the rate of crosslinking, but it was horizontal later. This may be due to the formation of crosslinked networks, which restricts the subsequent penetration of light.

Photocrosslinking Studies by FTIR

Crosslinking was effected by cycloaddition between double bonds of cinnamoyl moieties, which destroys the conjugation in the entire π electron system. Hence, the intensity of the absorption of stretching frequency of this double bond

(—CH=CH—) at 1637 cm^{-1} was followed with respect to the time of exposure to the light by FTIR. The poly(MCEA) solution in chloroform was taken for this experiment. This was spread over a KBr disc, and the solvent was evaporated to form a thin film. This film on KBr was subjected to irradiation for selected intervals of time. The resolution (1 cm^{-1}) and the number of scans (100) during the FTIR measurements was kept constant throughout the experiment. The lowering in the intensity of the peak at 1637 cm^{-1} corresponding to the disappearance of —CH=CH— was monitored; it is depicted in Figure 6. The decrease in intensity of 1637 cm^{-1} peak observed by infrared (IR) studies confirmed that the mechanism of crosslinking is a cycloaddition and not due to the trans–cis isomerization, as the latter would lead to retaining the double bond of the cinnamoyl moiety. Similar observations were noticed for all other polymers. It was observed that the complete disappearance of the peak at 1637 cm^{-1} was not possible, even after a prolonged irradiation time because the formation of crosslinks on the surface of polymer makes it difficult for the subsequent penetration of the light. This trend is similar to the UV observations, in which the absorbance values are not reaching zero.

Further, on looking closely at the structure of the polymer before and after irradiation, it could be noticed that before irradiation both carbonyls (from acrylic and cinnamoyl segments) are not similar and gave a split lead to the appearance of

a shoulder at 1710 cm^{-1} in the carbonyl absorption at 1727 cm^{-1}. This is due to the fact that the double bond strength of the carbonyl bond adjacent to cinnamoyl moiety becomes high because of the extended conjugation through cinnamoyl double bond, aromatic double bonds, and electron donating methoxy group so that it absorbs at a lower wave number of 1710 cm^{-1}. On crosslinking, the shoulder at 1710 cm^{-1} disappeared, leading to the appearance of one carbonyl absorption at 1727 cm^{-1} due to the conversion of the cinnamoyl double bond into single bond. After crosslinking, both carbonyl bonds are similar (ester type and no more extended conjugation). This has been represented schematically in Scheme 2.

There are two mechanisms possible for photocrosslinking phenomena, and polyvinyl cinnamates are susceptible to (2 + 2) π electron cycloaddition and not cis-trans isomerisation as reported earlier.[8] This is established for functionalized vinyl cinnamates also. Figure 6 showed the decrease in the —CH=CH— peak at 1637 cm^{-1} on irradiation, substantiating that the double

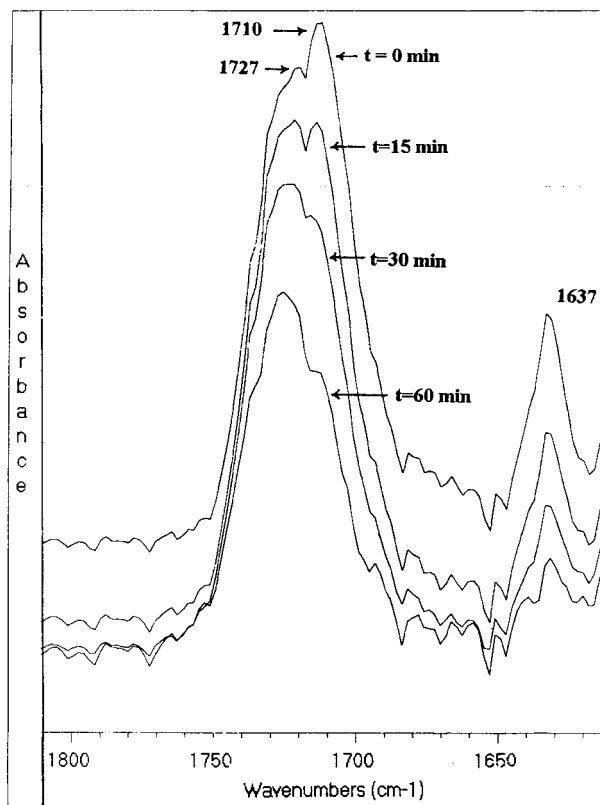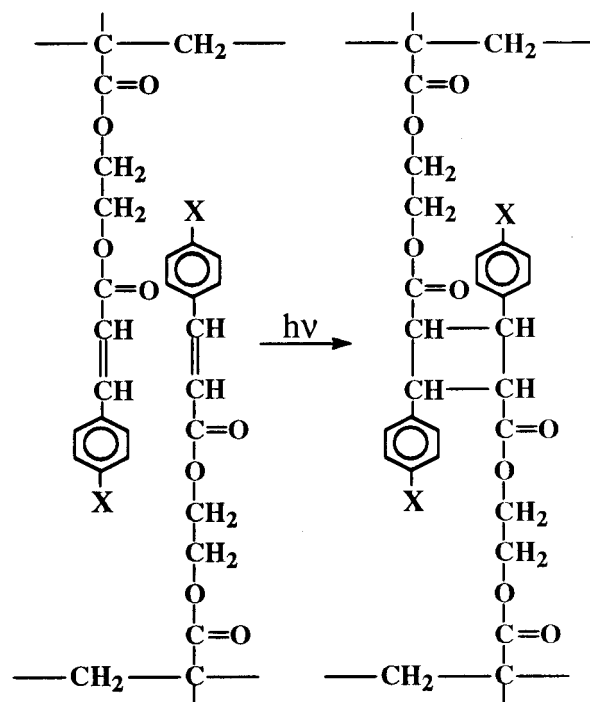**Scheme 2** Photocrosslinking in polyvinyl cinnamate polymers.

bond of cinnamoyl segment is involved in the crosslinking mechanism. This is further confirmed by comparing the ratio of the area of the peaks of —C=O$_{str}$ with —C=C—$_{str}$ at 1727 and 1637 cm^{-1}, respectively (area of —C=O$_{str}$/area of —C=C—$_{str}$) during crosslinking. The plot (Fig. 7) of the above ratio against the irradiation time shows a gradual increase of the ratio (C=O$_{str}$/—C=C—$_{str}$), confirming the cycloaddition mechanism.

CONCLUSION

Photocrosslinking studies by UV and FTIR spectroscopy revealed that the electron-releasing groups like —OCH$_3$ and —Cl increase the photosensitive nature while a electron-releasing group like —NO$_2$ decreases the same compared with that of the unsubstituted polymer. This is due to the presence of electron-donating functional groups at the para position, which increases the electron density of cinnamoyl double bond through conjugation. Among the polymers studied, methoxy-substituted polymer showed higher photosensitivity. Absence of an isobestic point in the UV experiments and IR studies carried out confirmed that the
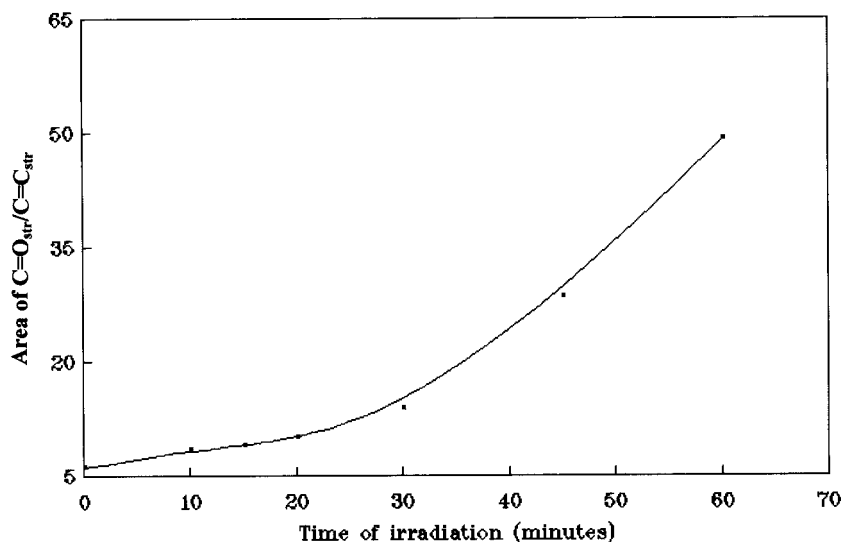

Figure 6 FTIR traces showing the decrease in the intensity of —C=C$_{str}$ peak at 1637 cm^{-1} and the disappearance of the shoulder peak at 1710 cm^{-1} on increasing the radiation time for poly(MCEA).

Figure 7   Increase in the ratio of the area of $—C{=}O_{str}/—C{=}C_{str}$ on increasing the radiation time for poly(MCEA).

crosslinking occurring through the 2 + 2 cycloaddition mechanism.

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