

## The effect of comonomer on the photocrosslinking property of 1-(4-(7-Chloroquinolin-4-ylamino)phenyl)acrylate

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### Abstract

A series of polymer, poly(CPA), poly(CPA-co-AA), poly(CPA-co-HEA), poly(CPA-co-MA), poly(CPA-co-S), poly(CPA-co-AM) and poly(CPA-co-VA), was prepared by solution polymerization technique, using 1-(4-(7-Chloroquinolin-4-ylamino)phenyl) acrylate (CPA) monomer and Acrylic acid (AA), Hydroxyethylacrylate (HEA), Methacrylic acid (MA), Styrene (S), Acrylamide (AM) and Vinylacetate (VA). The formation of these polymers was confirmed by proton NMR and FT-IR techniques. The molecular weight ( $M_w$ ) of these polymers was found to be around 5000 g/mol. The synthesized polymers showed two stages thermal decomposition which was centered around 220 and 350<sup>o</sup>C respectively. The UV absorption technique is used for the study of photocrosslinking property of the polymers. The rate of photocrosslinking of CPA moiety in copolymers was enhanced compared to that of the homopolymer.

**Keywords:** Homopolymer, copolymer, thermal study, UV spectroscopic, photocrosslinking

### 1. INTRODUCTION

A polymer with a backbone of photosensitive moiety i.e. chalcone or cinnamic ester, etc., usually undergoes crosslinking on UV light. The crosslinked polymer [1] has got good resistance towards solvents, resolving power, thermal stability, high tensile

strength and photosensitivity. Mechanical properties of the polymer have been modified upon crosslinking. Modification of mechanical properties of crosslinked polymer has directly proportional to the crosslink density [2]. Polymer containing chalcone moiety in its main/chain has undergone  $2\pi-2\pi$  cyclo addition reaction on UV irradiation due to the fact that the chalcone has  $\alpha$ ,  $\beta$  unsaturated carbonyl system. Because of this unsaturation, adjacent polymer unit undergoes the above said cycloaddition reaction. Watanabe and Ichimura [3] described that the mixing up of two different polymers having substituted cinnamoyl group can enhance the photosensitivity of the polymers. He successfully enhanced the photosensitivity of the poly(vinyl cinnamate) by this method. Crosslinked polymer membranes have been used as gas separating materials in recent days due to the fact that the crosslink decreases chain mobility. UV crosslinked aromatic polyimides had a drastically higher selectivity than their linear analogs [4]. The UV crosslinked polymer membranes effectively separate the mixtures of  $\text{CO}_2/\text{CH}_4$ . The reason behind this excellent selectivity of the mixture is, crosslinking significantly improves the resistance to plasticization by  $\text{CO}_2$  [5] or crosslink disturbs polymer crystallization [6]. Therefore, understanding the phenomenon behind the crosslinking, especially the comonomer effect on the rate of crosslinking is vital to make the tailor made materials. In our investigation, we have chosen acrylated polymer containing chalcone moiety in its side chain as our investigating materials and different copolymers were made using commercially available monomers to find out the effect of comonomer on the crosslinking percentage.

## 2. MATERIALS AND METHODS

4-Hydroxybenzaldehyde and acrylic acid was used as received from Aldrich Chemicals. 1-(4-(2chloroquinolin-5-ylamino)phenyl)ethanone (CE), was synthesized using 4,7-dichloroquinoline and 1-(4-aminophenylethanone (Merck) and Triethylamine (TEA) was received from SD Fine Chemicals. The monomer 4-(3-(4-((7-chloroquinolin-4-yl)amino)phenyl)-3-oxoprop-1-en-1-yl) phenyl acrylate (CPA) used for the synthesis polymer was reported in our previous article [7]. Ethylmethylketone (EMK), Acrylic acid (AA), Hydroxyethylacrylate (HEA) and Acroloyl chloride were used as received from Merck and used as such. ALPHA BRUKER FT-IR spectrophotometer was used and the spectra were recorded using KBr pellet.  $^1\text{H}$  NMR spectra of the samples were run on a Bruker FT-NMR spectrophotometer operating at 500 MHz's using  $\text{CDCl}_3$  as a solvent and tetramethylsilane (TMS) as an internal reference. UV studies were done using LABINDIA model UV 320 instrument by dissolving polymer samples in Tetrahydrofuran (THF). TGA was done using a Mettler 3000 thermal analyzer operating at the heating rate of  $10^\circ\text{C}/\text{min}$  in the air. The molecular weight of the polymer was obtained with a Shimadzu instrument with THF as an eluent at a flow

rate of 0.3 ml/min. Muller-Hinton broth and Muller-Hinton agar were obtained from Himedia and used as such.

## **2.3 Synthesis of polymer**

### **2.3.1 Synthesis of poly (CPA)**

CPA (1.0g) and 0.03g of BPO (3 wt.%) were placed in a polymerization tube containing 10 ml of MEK. The polymerization tube was degassed and heated at  $70\pm 1^{\circ}\text{C}$  in a thermostated water bath for 24 h. Poly(CPA) was precipitated by adding the reaction mixture to a large excess of methanol with rapid stirring. Yield = 0.9g (90%).  $^1\text{H}$  NMR ( $\delta$  ppm): 7-8 (13H, m), 7.1 (1H, d), 7.0 (1H, d) and 0.9-1.3 (3H, m). FT-IR( $\text{cm}^{-1}$ ): 3413 (Ar-NH-Ar), 3030 (aromatic CH-stretching), 2962 (aliphatic CH-stretching), 1742 (-C=O of ester), 1697 and 1646 (cis & trans C=O) and 1619 (aliphatic CH=CH).

### **2.3.2 General procedure for the preparation of copolymer.**

Copolymer was prepared using solution polymerization technique. Monomer 1 (CPA) and monomer 2 were taken in a polymerization tube containing MEK as a solvent and BPO (2wt. %) as a free radical initiator. Nitrogen gas was passed through the polymerization tube to make inert. The polymerization was carried out at  $70\pm 1^{\circ}\text{C}$  for 24h. The polymer solution was then precipitated in methanol and the precipitate obtained was then filtered in sintered crucible, washed with methanol and weighed. This method was used for the preparation of the following.

### **2.3.3. Synthesis of poly (CPA-co-AA)**

(0.004 mol) 1.38g of CPA and (0.004 mol) 0.28g of AA, 10 mL of MEK and 0.02g (2wt.%) of BPO were used for the synthesis of poly (CPA-co-AA). Yield = 0.88g.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7.8 (13H, m) 7.1 (1H, d), 7.0 (1H, d) and 1-1.5 (m, 6H alkane). FT-IR ( $\text{cm}^{-1}$ ): 3413 (Ar-NH-Ar), 3030 (aromatic CH-stretching), 2962 (aliphatic CH-stretching), 1742 (-C=O of ester), 1649 (C=O) and 1618 (aliphatic CH=CH).

### **2.3.4. Synthesis of poly (CPA-co-HEA)**

(0.004 mol) 1.38g of CPA and (0.004 mol) 0.46g of HEA, 10 mL of MEK and 0.02g (2wt.%) BPO were used for the synthesis of poly(CPA-co-HEA). Yield =1.1g.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7-8 (13H, m), 7.1 (1H, d), 7.0 (1H, d), 4.6 (1H, b), 3.6 (2H, d), 3.4 (2H, d) and 1-1.5 ( 6H, m). FT-IR ( $\text{cm}^{-1}$ ): 3336 (-OH), 3036 (aromatic CH-stretching), 2986 (aliphatic CH-stretching), 1740 (-C=O of ester), 1670 (C=O) and

1618 (aliphatic CH=CH).

### 2.3.5. Synthesis of poly (CPA-co-MA)

(0.004 mol) 1.38g of CPA and (0.004 mol) 0.344g of MA, 10 mL of MEK and 0.02g (2wt.%) of BPO were used for the synthesis of poly(CPA-co-MA). Yield = 0.88g.  $^1\text{H}$  NMR ( $\delta$ , ppm): 11 (acetic OH), 7.1-8.1 (aromatic 13H, m and vinylic 2H) and 1.2-2 (alkane m, 6H alkane). FT-IR ( $\text{cm}^{-1}$ ): 3371 (Ar-NH-Ar), 3211 (OH-stretching), 3084 (aromatic CH-stretching), 2982 (aliphatic CH-stretching), 1726 (-C=O of ester), 1671 (C=O) and 1605 (aliphatic CH=CH).

### 2.3.6. Synthesis of poly (CPA-co-S)

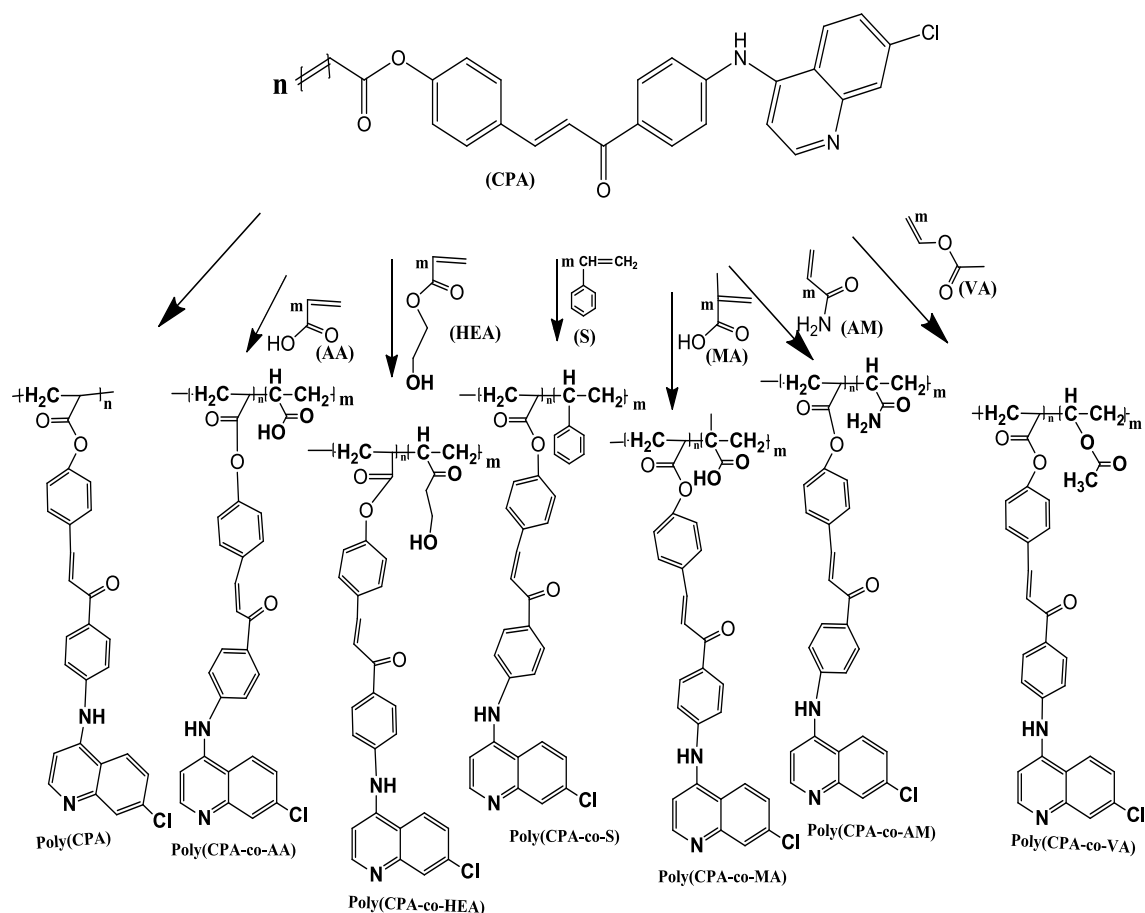
(0.004 mol) 1.38g of CPA and (0.004 mol) 0.416g of S, 10 mL of MEK and 0.02g (2wt.%) BPO were used for the synthesis of poly(CPA-co-HEA). Yield = 1.0g.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7-8.2 (aromatic 13H, m), 7.1 (1H, d), 7.0 (1H, d) and 1-2 (alkane 6H, m). FT-IR ( $\text{cm}^{-1}$ ): 3443 (NH-stretching), 3053 (aromatic CH-stretching), 2927 (aliphatic CH-stretching), 1723 (-C=O of ester), 1679 (C=O) and 1603 (aliphatic CH=CH).

### 2.3.7. Synthesis of poly (CPA-co-AM)

(0.004 mol) 1.38g of CPA and (0.004 mol) 0.308g of AM, 10 mL of MEK and 0.02g (2wt.%) of BPO were used for the synthesis of poly (CPA-co-AM). Yield = 0.78g.  $^1\text{H}$  NMR ( $\delta$ , ppm): 6.9-8.2 (aromatic 13H, m and vinylic 2H, d) 4 (NH, ) and 1-1.9 (m, 6H alkane). FT-IR ( $\text{cm}^{-1}$ ): 3343 (Ar-NH-Ar), 3035 (aromatic CH-stretching), 2929 (aliphatic CH-stretching), 1720 (-C=O of ester), 1672 (C=O), 1651 (NH-C=O) and 1605 (aliphatic CH=CH).

### 2.3.8. Synthesis of poly (CPA-co-VA)

(0.004 mol) 1.38g of CPA and (0.004 mol) 0.344g of VA, 10 mL of MEK and 0.02g (2wt.%) BPO were used for the synthesis of poly(CPA-co-VA). Yield = 0.9g.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7-8.4 (aromatic 13H, m and vinylic 2H, d), 4 (NH, b), 3.4 (alkane H) and 0.8-1.4 (alkane 6H, m). FT-IR ( $\text{cm}^{-1}$ ): 3340 (NH-stretching), 3042 (aromatic CH-stretching), 2992 (aliphatic CH-stretching), 1722 (-C=O of ester), 1672 (C=O) and 1605 (aliphatic CH=CH).



**Scheme : 1.** Synthesis of poly(CPA), poly(CPA-co-AA), poly(CPA-co-HEA), poly(CPA-co-MA), poly(CPA-co-S), poly(CPA-co-AM) and poly(CPA-co-VA).

#### 2.4. Photocrosslinking studies

The polymer samples were dissolved in tetrahydrofuran (HPLC grade) and the samples were irradiated using a mercury lamp (UV source) at room temperature. The distance between the lamps to that of the sample was  $15\text{cm}^{-1}$ . The photocrosslinking properties of the polymer samples were measured by changing in the UV absorption intensities of the chalcone type moiety present in the polymer chain. The rate of disappearance of  $>\text{C}=\text{C}<$  of the pendent  $\alpha,\beta$ - unsaturated ketone unit of the polymer was followed by measuring the UV absorption intensity of the solution.

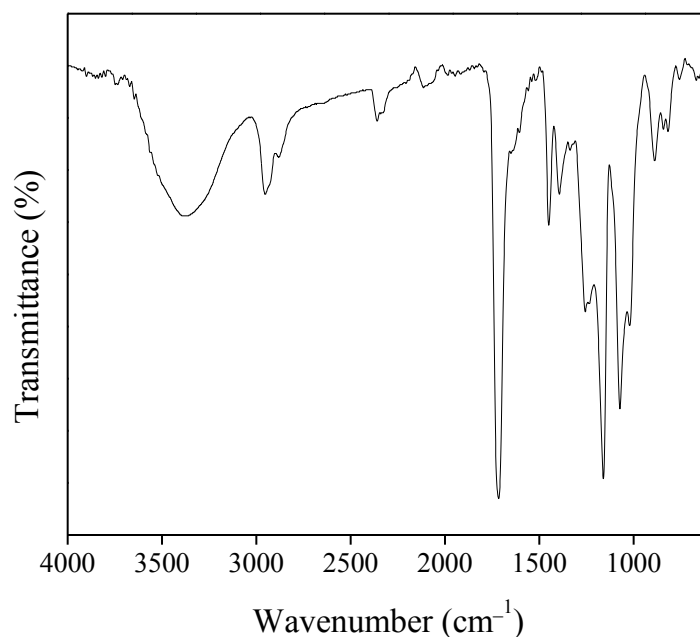
$$\text{Rate of conversion (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

Where  $A_0$  and  $A_t$  are the absorption intensities due to  $>\text{C}=\text{C}<$  chromophore after irradiation of times of  $t = 0$  and  $t = t$  respectively. The following copolymer

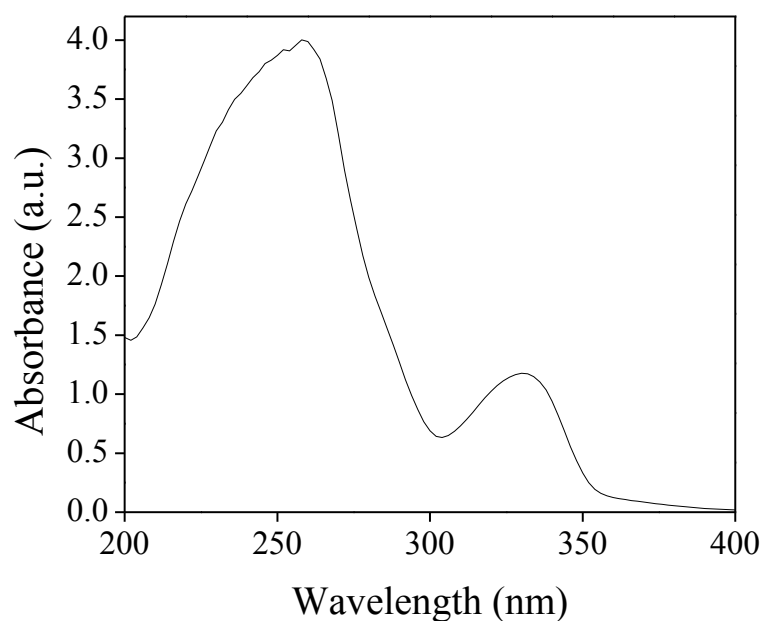
systems were studied for the photocrosslinking by UV irradiation (0-1200 sec).

### 3. RESULTS AND DISCUSSIONS

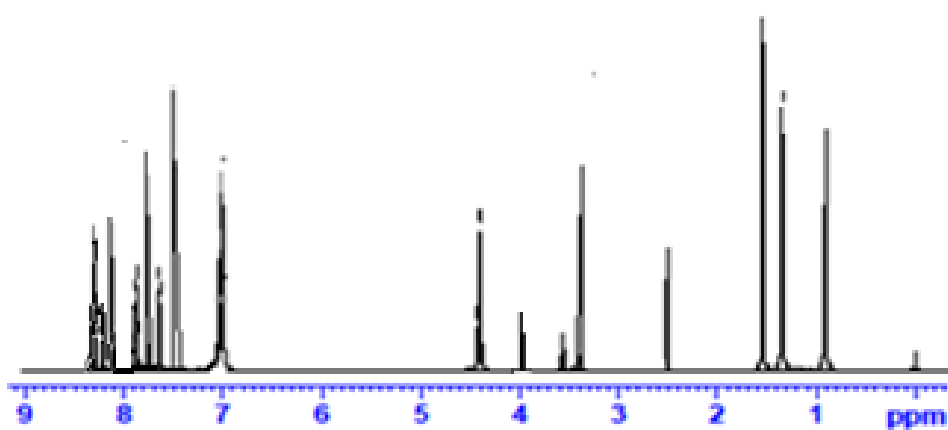
Homopolymer poly(CPA), copolymer, poly(CPA-co-AA), poly(CPA-co-HEA), poly(CPA-co-MA), poly(CPA-co-S), poly(CPA-co-AM) and poly(CPA-co-VA) were prepared by free radical polymerization technique. Synthesized polymers were characterized by FT-IR,  $^1\text{H}$  NMR and UV to confirm the structure. Figs. 1 to 3 is the FT-IR, UV and proton NMR spectrum of poly(CPA-co-HEA) respectively, and these spectrum is the representative of the synthesized polymer series. The obtained values for other polymers were present in the synthesis section. The stability of the polymer on heating was measured by TGA analysis and reported in this paper. The molecular weight of the polymer was determined by GPC. For all the polymers, the weight average molecular weight was around 5000 g/mol (Table 1). The polydispersity values of the polymers were less than 2, quantitatively suggesting that the polymer was terminated by disproportion method, which was typical of acrylates.



**Fig. 1: IR Spectrum of poly(CPA-co-HEA)**



**Fig. 2: UV Spectrum of poly(CPA-co-HEA)**



**Fig. 3:  $^1\text{H}$  NMR Spectrum of poly(CPA-co-HEA)**

### 3.1. Solubility

The solubility data of the polymer samples were presented in the table 1. It shows that the copolymers were soluble in DMSO, dimethylformamide, and tetrahydrofuran, but insoluble in less polar solvents like chloroform, water, methanol and partially soluble in ethanol. The copolymer was not soluble in nonpolar solvents like benzene, n-hexane and carbon tetrachloride.

**Table 1:** Solubility data of the CPA monomer and its polymers

Sample Name	H <sub>2</sub> O	MeOH	EtOH	CCl <sub>4</sub>	CHCl <sub>3</sub>	DMSO	DMF	Acetone	C <sub>6</sub> H <sub>6</sub>	THF	n-Hexane
CPA	-	+	+	+	+	+	+	+	+	+	-
Poly (CPA)	-	-	±	-	-	+	+	-	-	+	-
Poly(CPA-co-AA)	-	-	-	-	-	+	+	±	-	+	-
Poly(CPA-co-HEA)	-	-	-	-	-	+	+	-	-	+	-
Poly(CPA-co-S)	-	-	-	-	±	+	+	-	-	+	-
Poly(CPA-co-MA)	-	-	-	-	±	+	+	±	-	+	-
Poly(CPA-co-AM)	-	-	-	-	-	+	+	-	-	+	-
Poly(CPA-co-VA)	-	-	-	-	-	+	+	-	-	+	-

+ = Soluble, - = Insoluble and ± = Partially soluble

### 3.2. UV studies

UV- visible spectrum of the poly(CPA-co-HEA) is depicted in the fig. 3 as a representative of the polymer series. It shows two characteristic peaks of absorption around 260 and 330 nm, correspond to aromatic and vinylic (>CH=CH<)  $\pi$  to  $\pi^*$  transition respectively. The entire synthesized polymer also showed two characteristic peaks and the obtained values were present in the table 2.

### 3.3. Molecular weights

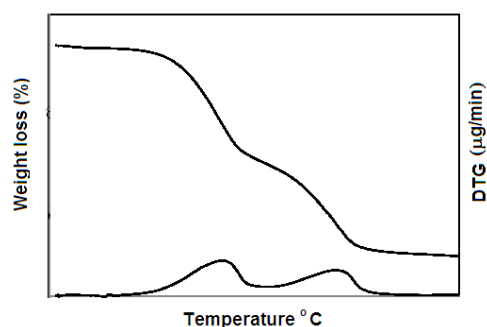
Molecular weights were determined using GPC method. For poly(CPA-co-HEA), the weight average molecular weight is  $M_w = 4.95 \times 10^3$ , the number average molecular weight is  $M_n = 2.65 \times 10^3$  and the polydispersity index is  $M_w / M_n = 1.87$ . Similar trend is observed for other polymer sample in this series and presented in the table 2. The observed polydispersity values confirm that the termination is by disproportionation method ( $M_w / M_n < 2$ ). Acrylates are generally undergoes termination by disproportionation method.

### 3.4. Thermal analysis

Thermogravimetric analysis was used for estimating the percentage weight loss of the copolymer against temperature. The TGA and differential thermo gravimetric curves of poly(CPA-co-HEA) was shown in the fig 4 and the percentage weight loss at



different temperatures were presented in the table 2. These results show that the poly(CPA-co-HEA) undergo decomposition in two stages. The first decomposition temperature revolved around 220°C and the second decomposition temperature centered on 355°C. A similar trend was observed for other polymer samples and the values were presented in the table 2. This type of two stage decomposition was reported earlier for similar type of polymeric systems [2].



**Fig.4.** TGA and DTG spectrum of poly(CPA-co-HEA).

**Table 2:** TGA, molecular weight, UV data of the synthesized materials.

Polymer	TGA		Molecular weight			UV data	
	1 <sup>st</sup> decomposition temperature (°C)	2 <sup>nd</sup> decomposition temperature (°C)	M <sub>n</sub> x10 <sup>3</sup>	M <sub>w</sub> x10 <sup>3</sup>	M <sub>w</sub> /M <sub>n</sub>	Aromatic C=C	Vinylic C=C
Poly(CPA)	220	350	2.88	4.85	1.68	263	332
Poly(CPA-co-AA)	225	335	3.10	5.40	1.74	254	326
Poly(CPA-co-HEA)	220	355	2.65	4.95	1.87	260	330
Poly(CPA-co-MA)	210	310	2.85	4.10	1.44	256	324
Poly(CPA-co-S)	215	315	3.56	5.12	1.46	276	340
Poly(CPA-co-AM)	220	320	3.87	6.13	1.58	266	330
Poly(CPA-co-VA)	218	315	3.50	5.17	1.48	264	334

### 3.5. Photocrosslinking properties of the synthesized polymers:

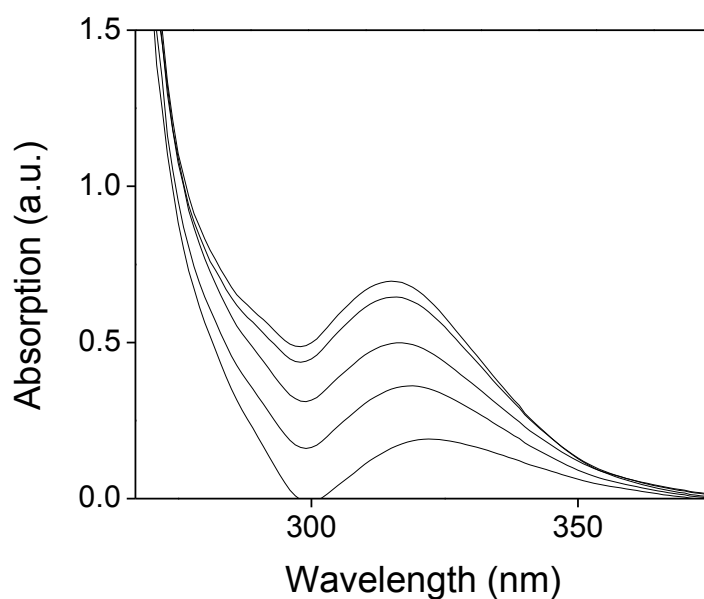
#### 3.5.1. Photocrosslinking studies of the polymer having CPA as a constituent of the polymer chain

A CPA based polymers contain photo sensitive chalcone moiety in its side chain and the photocrosslinking properties of the CPA polymers were studied in detail. The changes in the UV absorption pattern of the poly(CPA-co-HEA) was presented on the Fig. 5. All the polymers shown the similar absorption maximum around 315nm due to the  $\pi$ - $\pi^*$  transition of  $>C=C<$  of the pendant chalcone group present in the polymer side chain. When the polymer solution was irradiated using a UV lamp, we found the decrease in the intensity of the absorption maximum around 315nm. The decrease in the intensity of absorption maximum was due to the formation of the cyclobutane ring by  $2\pi$ - $2\pi$  cycloaddition reaction of the olefinic double bonds, which is present in the pendant chalcone units in the side chain of the polymer. The scheme 2, revealed the possible way in which the chalcone polymers were crosslinked when subjected to UV light.

The formation of cyclo-addition of the olefinic bond destroys the conjugation in the  $\pi$ -electron systems. For this reason, we observed the decrease in the intensity of the absorption maximum around 315nm upon irradiation with UV light on the polymer solution. However, we found that there is no isobestic point in the range of 270-280nm corresponds to the cis-trans isomerisation. This clearly suggests that upon UV irradiation, the polymer undergoes cycloaddition reaction and not cis-trans isomerization. It further confirms that the crosslinking was precedent over the cis-trans isomerism (Scheme 2). The photoisomerization of the polymer chain could be ruled out in this case due to the fact that we had only one crosslinkable double bond and which was involved in cyclisation reaction. Several literature showed the isobestic points for the polymer containing two crosslinkable double bond [8]. Also, the photocrosslinking was carried out in the polymer and therefore the question of disruption of the chromophore aggregates did not arise here as there was no ordered arrangement in the solution. This further proves that the decrease in the intensity of the UV absorption was due to cyclization and not by cis-trans isomerization. The photosensitivity of the polymer samples was measured as a rate at which the double bond disappears upon irradiation. The photocrosslinking conversion of various polymers having CPA as a constituent of the polymer chain was shown in the Table 3. The rate of disappearance of the olefinic bond of the polymer solution after 1200sec of irradiation follows the order of poly(CPA-co-HEA) > poly(CPA-co-MA) > poly(CPA-co-AM) > poly(CPA-co-AA) > poly(CPA-co-VA) > poly(CPA-co-S) > poly(CPA).

**Table 3:** Rate of disappearance of olefinic bond present in the polymers having CPA as a constituent of the polymer chain

I.T (sec)	Poly(CPA)		Poly(CPA-co-AA)		Poly(CPA-co-HEA)		Poly(CPA-co-S)		Poly(CPA-co-MA)		Poly(CPA-co-AM)		Poly(CPA-co-VA)	
	A(305)	C%	A(315 nm)	C%	A(311 nm)	C%	A(306 nm)	C%	A(312 nm)	C%	A(307 nm)	C%	A(305 nm)	C%
0	1.7149	0	0.8828	0	0.6767	0	2.7985	0	1.3619	0	2.1493	0	1.7099	0
300	1.6766	2.23	0.8336	5.57	0.6228	7.96	2.4925	10.92	1.2285	9.81	1.9237	10.51	1.6134	5.6
600	1.5071	12.12	0.7363	11.61	0.4793	29.17	2.2174	20.77	0.9265	31.97	1.7731	17.5	1.4911	12.81
900	1.3937	18.73	0.3608	59.13	0.3263	51.78	1.5879	43.26	0.4313	68.33	1.2828	40.32	1.1792	49.14
1200	0.8690	49.33	0.2949	66.61	0.1429	78.91	1.1168	60.11	0.2949	78.35	0.4923	78.01	1.0468	61.40



**Fig.5.** Shift in the UV absorbance spectrum of Poly(TCP-co-AM) after irradiation period of 0 to 1200 sec.

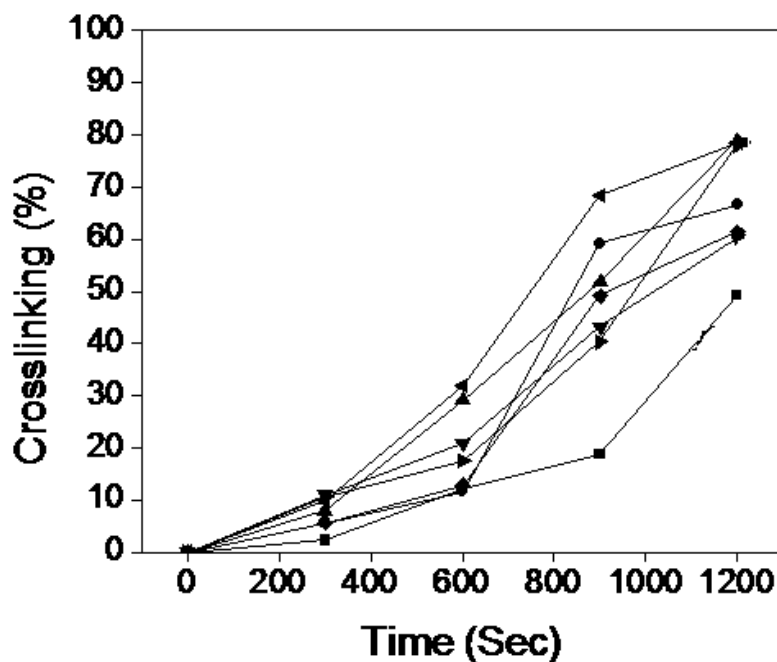


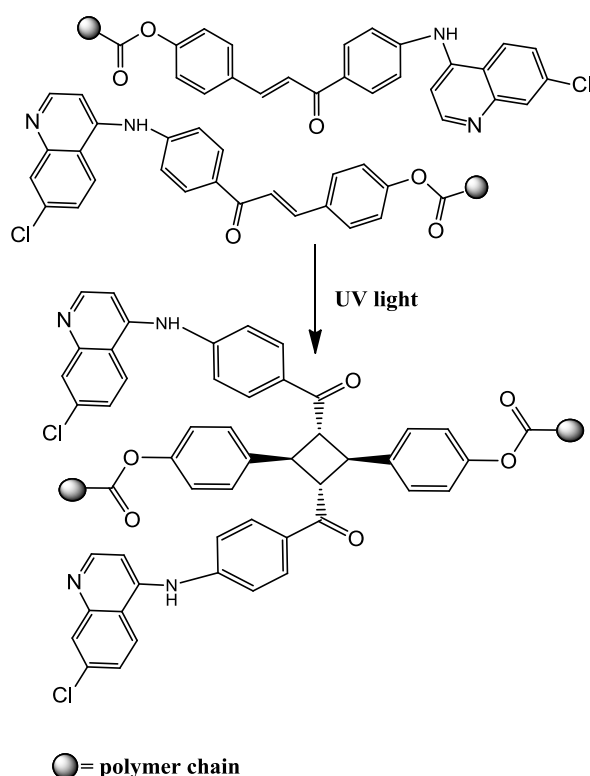
Fig. 6. Rate of disappearance of  $>C=C<$  chromophore of Polymers

### 3.5.3. Effect of comonomers on the rate of photocrosslinking contains CPA

Fig.6. revealed the comparative rate of disappearance of the  $CH=CH$  present in the polymer chain. From this figure we could find that the rate of disappearance of double bond in the copolymers was higher than the poly(CPA) clearly suggesting that the special orientation of the polymer chain in the solution play a major role in deciding the rate of crosslinking. The rate of disappearance of the double bond of poly(CPA-co-HEA) was very high when compared with other polymer systems like poly(CPA), poly(CPA-co-AA), poly(CPA-co-S), poly(CPA-co-MA), poly(CPA-co-AM) and poly(CPA-co-VA).

The observed enormous increase in the rate of photocrosslinking (almost complete disappearance of the double bond) of double bond in the copolymer having a HEA as a comonomer could be due to the presence of aliphatic chain between the crosslinkable double bond which can facilitate the crosslinking process much faster than the aromatic counterpart (in the case of styrene as a comonomer). The comonomers HEA present in the polymer chain provides the flexibility to the polymer backbone and thereby providing proper orientation for the cyclobutane ring formation. The other copolymer system also showed higher photocrosslinking rate than the poly(CPA). The rate of photocrosslinking was increased in the order of poly(CPA-co-HEA) > poly(CPA-co-MA) > poly(CPA-co-AM) > poly(CPA-co-AA) > poly(CPA-co-VA) > poly(CPA-co-S) > poly(CPA). Although we might not be able

to quantify the assistance of the comonomers on the rate of photocrosslinking, we were convinced to say that the comonomer with a smaller molecular size will favor the photocrosslinking. In our investigation, we successfully increased the rate of photocrosslinking from 49.33% (for poly(CPA)) to 78.91% (for poly(CPA-co-HEA)) (Table 3). This shows that in bulky systems like CPA, the introduction of flexible (or small) molecules into the polymer backbone will increase the rate of photocrosslinking of the polymer sample.



**Scheme 2: Effect of UV light on CPA Polymers**

#### 4. CONCLUSION

A series of polymers, poly(CPA), poly(CPA-co-AA), poly(CPA-co-HEA), poly(CPA-co-MA), poly(CPA-co-S), poly(CPA-co-AM) and poly(CPA-co-VA), was prepared by solution polymerization technique. The synthesized polymers were characterized by UV, IR and NMR techniques. The weight average molecular weight of the synthesized polymers was low around 5000 g/mol. Thermal stability of the polymers were very high, first and second decomposition temperature lies around 220 and 350°C respectively. The UV data showed the characteristic peaks for aromatic and vinylic absorption around 260 and 330 nm respectively. The synthesized copolymer shows the high crosslinking percentage than the homo polymer.

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