

Polymer Communication

# Main chain helical transformation induced through UV light in arylidene polymer

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## Abstract

Arylidene polymers are showing a preferred main chain conformation in the solution phase when subjected to the circular dichorism (CD) analysis. Probably the first time a non-azo, achiral and acrylate derivative of arylidene compound when subjected to polymerization is oriented itself in a definite helical form. Ultraviolet (UV) light cross-linking of these polymers induces the main chain asymmetric transformation from one preferred conformation to another conformation. Concentration independent nature of the conformational change was observed and the CD spectrum showing a blue shift at 270 nm due to loss in the conjugation of the molecule upon irradiation with UV light.

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*Keywords:* Circular dichorism; UV light; Cross-linking

## 1. Introduction

Many groups worldwide have incorporated additional functional groups into polymers having conjugation in order to make materials that respond to a chemical event by a detectable change in their properties. As part of the wider research programme aimed at developing polymeric materials whose conformations can be switched by photo-irradiation, we now report an arylidene polymer whose conformation can be changed upon irradiation with UV light. In polymer and supramolecular chemistry, the control of helicity has been attracting greater attention due to the wide variety of applications in material science, chemical sensitizing and enantio selective catalyst. Acrylated type polymers comes under the classification of stable helical polymers even in the solution form [1,2]. These acrylated type polymers exhibiting a highly ordered arrangement of the polymers and the helical conformation of the main chain plays an important role for the separation of enantiomers. Thus, acrylated polymers can be used as a chiral stationary phase in HPLC.

Though the acrylated polymers having side chain azobenzene chromophore showing a definite helical conformation was reported by several research workers [3–7], there are only a few reports available about the circular anisotropy was induced by the circularly polarized light as the source of chirality [3,8]. Also the kinetics of the transformation of the helical reversal was not studied in detail.

## 2. Experimental

4-{-3-(4-Hydroxybenzylidene)-2-oxocyclohexylidene}methyl}phenyl acrylate (HBA) and poly(HBA) were prepared by adopting the procedure given in the literature [9]. Polymer ( $M_w = 2.53 \times 10^4$ ) concentrations were prepared in the range of  $10^{-4}$ – $10^{-6}$  M and employed for both CD and UV studies. UV cross-linking of the polymer was carried out by dissolving the polymer in HPLC grade THF and irradiating this sample using high intensity UV lamp kept at a distance of 15 cm from the tested sample. Cross-linked polymer solution was then immediately (simultaneously) employed for both UV absorption and CD studies. UV absorption measurements were conducted on a Shimadzu model 160A spectrophotometer and CD spectra were recorded at 25 °C on a J-715 spectropolarimeter in a quartz cell of 0.1 cm path length, over the range of 260–300  $\text{cm}^{-1}$ . The rate of cross-linking and the helical

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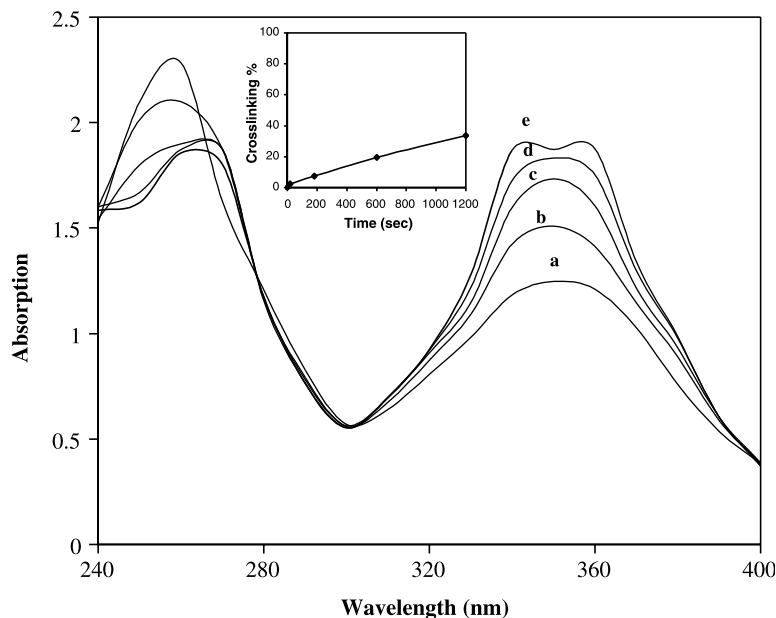


Fig. 1. Change in the UV absorption spectrum of poly(HBA) ( $1 \times 10^{-5}$  M) after irradiation period of (a) 0, (b) 20, (c) 180, (d) 600 and (e) 1200 s. Inset: Rate of disappearance of  $\text{>C=C<}$  chromophore.

transformation was studied by irradiating the polymer sample at different time intervals.

### 3. Results and discussions

The change in the UV spectrum of the polymer upon irradiation with UV light was shown in the Fig. 1. The UV

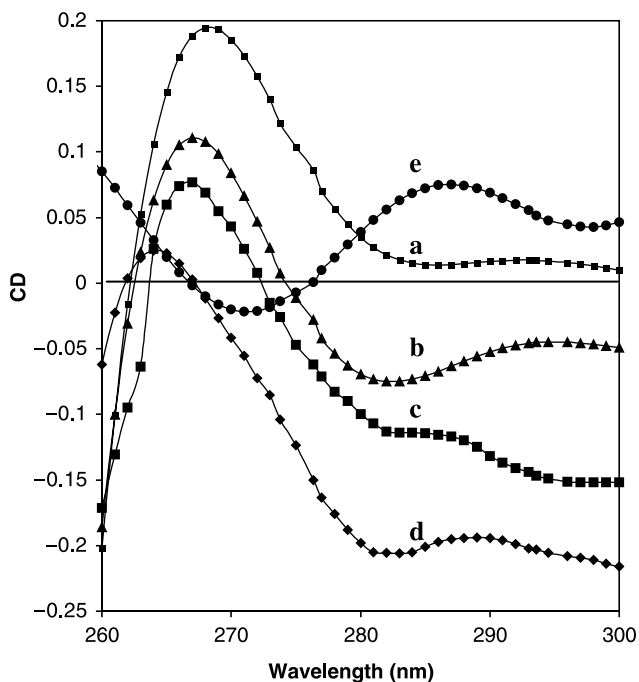


Fig. 2. Change in the CD spectrum of poly(HBA) after irradiation period of 0, (b) 20, (c) 180, (d) 600 and (e) 1200 s.

absorption maximum appears at 348 nm decreases as the irradiation time increases which is due to the  $2\pi-2\pi$  cyclodimerization of the two types of  $\text{>C=C<}$  cinnamoyl units present in the polymer side chain. This type of cyclodimerisation was reported earlier [10] in the case of a single pendent cinnamoyl unit. The photodimerization will precede over the *cis-trans* isomerization since the photocross-linking studies were carried out in solution phase. Further, from the graph of time versus % of cross-linking (inset Fig. 1), we found that the photocross-linking of the polymer was not completed even after 20 min of irradiation. This may be due to the chain fragmentation reaction and intramolecular cross-linking of the polymer which accompanying the photocross-linking process. The CD spectrum of the arylidene polymer was shown in the Fig. 2. This shows that the helical preference of the polymer chain was inverted upon irradiation with UV light as reported by several research workers [11,12]. Cross-linking induced change in the sign of the CD spectra is due to the helical inversion of the main chain responding towards the irradiation light. The CD spectrum shows that the high optical activity of the polymer essentially due to the conformational dissymmetry of the macromolecule [13] provided by the long and highly conjugated side chain present in the polymer chain [5]. Also, the change in the chiro-optical property of the polymer upon irradiation is attributed to a change in the conformation of the main chain of the polymer. The presence of long, highly conjugated side chain is favouring the adoption of the chiral transformation of chain section of the macromolecule with the prevailing handedness [13,14] upon cross-linked with UV light (Fig. 3). The schematic diagram of main chain helical transformation was shown in Fig. 4. This was

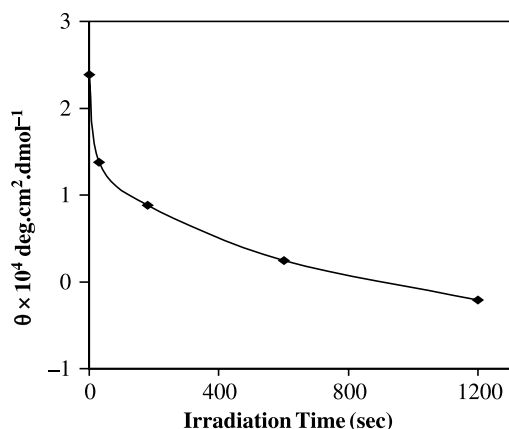


Fig. 3. Change in the molar ellipticity value at 270 nm upon irradiation with UV light.

demonstrated by the strong Cotton effect change at 270 nm ( $\pi-\pi^*$ ) upon irradiation with the UV light. A blue shift was observed at 270 nm upon irradiation with UV light suggesting that the polymer sample losing its conjugation as the irradiation time increases due to the cycloaddition of the double bond present in the polymer side chain. This was also supported by the graph present in the inset Fig. 1. Furthermore, the molar ellipticity value change can be visualized as a rate at which one chiral conformation was changed to another conformation upon irradiation. This shows that the polymer sample was reversed its preferential handedness upon irradiation time of  $\cong 930$  s (Fig. 3). Also, the cross-linking induced change in the sign of the CD spectra results from the inversion of the helicity of the polymer main chain was observed by the naked eye [1]. The colour of the polymer sample has changed from orange to yellow upon irradiation indicating that the polymer was under going helical inversion upon irradiation with UV light. The colour change of the polymer solution due to the loss in the conjugation of the double bond upon cross-linking can be ruled out due to the fact that the substantial quantity of uncross-linked product (about 67%, see inset

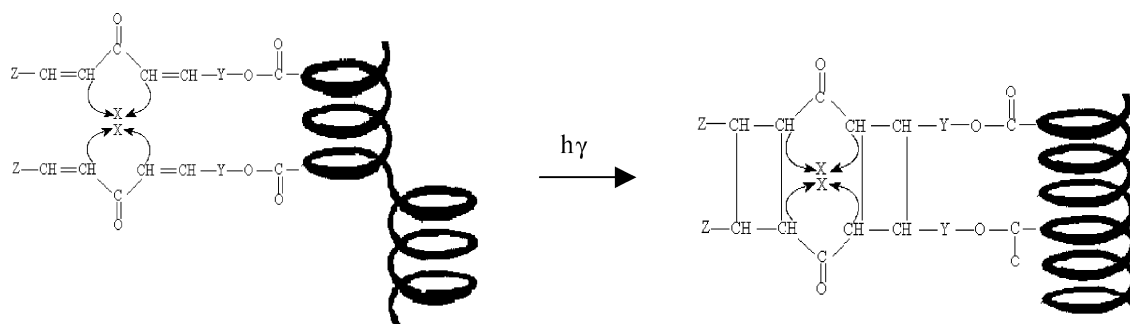
Fig. 1) exists even after 20 min of irradiation. Concentration independent chiral transformation is observed in this system over a range of  $10^{-4}$ – $10^{-6}$  M. This shows that the chiral transformation was observed due to the  $2\pi-2\pi$  cycloaddition of the double bond present in the polymer chain and not by the *cis-trans* isomerization as described in our previous paper [9]. This type of phenomenon was also observed by other workers (supported by the absence of isobestic point or cross over point in the CD spectrum of the polymer sample) [10]. This suggests that a chiral structure is incorporated in each individual polymer chain appears to be responsible for the CD signal [15].

#### 4. Conclusion

The core message of this paper is that the acrylate derivative of arylidene compounds when subjected to polymerization is showing a definite helical conformation in the solution form. The preferred main chain helical conformation was reversed upon irradiation with UV light via cross-linking of the double bonds (cyclobutane ring formation) present in the arylidene compounds. Also, the helical transformation was observed through naked eye. To the best of our knowledge this is the first example that an acrylate derivative of a non-azo, achiral, arylidene compound showing definite helical conformation.

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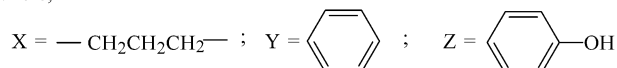


Fig. 4. Schematic representation of the isomerization of main chain helical conformation induced by the UV irradiation.

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