

Research Article

Synthesis and Characterisation of Photo-Cross-Linkable Liquid Crystalline Poly(*n*-[*n*'-flurobenzoylstyroxy]alkylmethacrylate)s and Their Fluorescence Lifetime Properties

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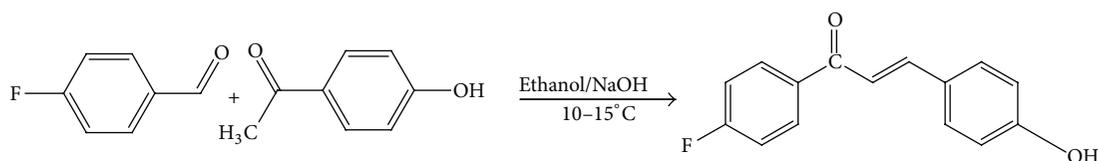
This paper reports a study on photo-cross-linkable polymer containing pendant chalcone moiety exhibiting liquid crystalline as well as fluorescence lifetime properties in detail. The photoresponsive polymers were prepared, and their structure has been characterized by ¹H-NMR, ¹³C-NMR, and UV-Visible spectroscopy. The photo-cross-linking behavior of polymers has been studied by UV-Visible and fluorescence spectroscopy. UV spectral studies revealed that the polymers follow $2\pi + 2\pi$ cyclo addition reactions when they undergo photo-cross-linking under the influence of UV-light. Number and weight average molecular weight of the polymers were determined by Gel Permeation Chromatography (GPC) and polydispersity index value near to 1.5. The thermal and thermooxidative stability of the polymers were determined by Thermogravimetric Analysis (TGA). Thermal transitions were studied by DSC, and presence of mesophases was identified at 147 and 126°C by hot stage polarized light optical microscopy (HPOM). Fluorescence lifetime measurements using the time-correlated single photon counting (TCSPC) method reveal that the average lifetime values decrease from 5.94 ns to 5.32 ns on UV-irradiation were discussed in detail.

1. Introduction

Liquid crystalline polymers have generated considerable interest in recent years, and the photo-cross-linkable LCPs have driven special attention if they contain both mesogen and photoactive groups in their structure [1–5]. The former incorporates LC properties to the polymer, and the later facilitates cross-linking of the chain under the influence of UV radiation. These classes of polymers are very useful in fabricating anisotropic networks, information storage devices [6, 7] and nonlinear optical devices [8]. Many research articles reported photochemical and liquid crystalline behaviours of these polymers using UV-Visible spectral studies and polarised optical microscopic characterisations. In addition to these studies, fluorescence lifetime measurement has been used as a new instrumental technique to support photoreactive behaviour of photo-cross-linkable liquid crystalline polymers.

Fluorescence lifetime measurements encompass tremendously large fields of science. Since the mid-19th century, nearly every great breakthrough in chemistry and physics has aided the development of fluorescence lifetime techniques, and a growing number of discoveries in biology and medicine owe their existence to fluorescence lifetime. A variety of fluorescence detection methods are available for lifetime measurements but the advent of time-correlated single photon counting (TCSPC) [9, 10] has simplified data collection and enhanced quantitative photon counting.

This paper reports newer root for the synthesis of poly(*n*-[*n*'-flurobenzoylstyroxy] alkylmethacrylate)s; the photo-cross-linking and liquid crystalline behaviour of polymers have been well characterised by UV and HPOM studies. We believe that there is no report in recent years on fluorescence lifetime study in combination with UV and liquid crystalline mesophase transition studies about photo-cross-linkable liquid crystalline polymer containing pendant chalcone moiety.



SCHEME 1: Synthesis of HPFSK.

This research work may kindle significant scientific work and practical contribution with respect to the development of unique photo-cross-linkable liquid crystalline polymeric materials.

2. Experimental

2.1. Materials. 4-Fluorobenzaldehyde and 4-hydroxyacetophenone were purchased from Spectrochem Chemicals. 4-bromobutanols, 6-bromoheaxanol, methacryloyl chloride were purchased from Aldrich Chemicals. Ethanol, tetrahydrofuran, ethylacetate, chloroform, and diethylether were purchased from Merck, and all the solvents were distilled as per standard methods. Thin Layer Chromatography (TLC) technique was carried out on Merck aluminium plates with 0.2 mm silica gel. Anhydrous sodium sulphate was used to dry all organic extracts. AIBN was recrystallised using 1:1 methanol and chloroform.

2.2. Measurements. The FT-IR spectra of the polymers were recorded on Perkin Elmer FT-IR Spectrometer RXI. The specimen was prepared in the pellet form using KBr. $^1\text{H-NMR}$ spectroscopic measurement was recorded with Bruker MSC 300 spectrometer. Thermal stability of polymers was investigated by TGA using NETZSCH STA 409 C/CD. The number average and weight average molecular weight of the polymer were determined by PL-GPC 650. Glass transition temperature of polymer was measured from Differential Scanning Calorimeter (DSC) NETZSCH.DSC.204. The photo-cross-linking studies have been done by Perkin Elmer Lambda 35 UV-Visible Spectrometer. The fluorescence spectrum of the polymer has been recorded in FluroMax 2.0. The texture of the prepared sample was studied by Euromax polarizing microscope equipped with a Linken HFS91 heating stage. The sample was prepared by a small quantity of the material being melted between two thin glass cover slips to get uniform film and anisotropic behavior observed by heating as well as cooling with Toshiba digital camera.

2.2.1. Fluorescence Lifetime Measurements. Lifetime measurements were made using time-correlated single photon counting system (TCSPC, HORIBA JOBIN YUVON IBH, UK) by exciting the sample using 280 nm Nano-LED (pulse width: <1 ns) and 460 nm Nano-LED (pulse width: >1 ns), a fast response red sensitive PMT (Hamamatsu Photonics, Japan) detector. The fluorescence emission was collected to 90 degree from the path of the light source. The electrical signal was amplified by a TB-02 pulse amplifier (Horiba) fed to the

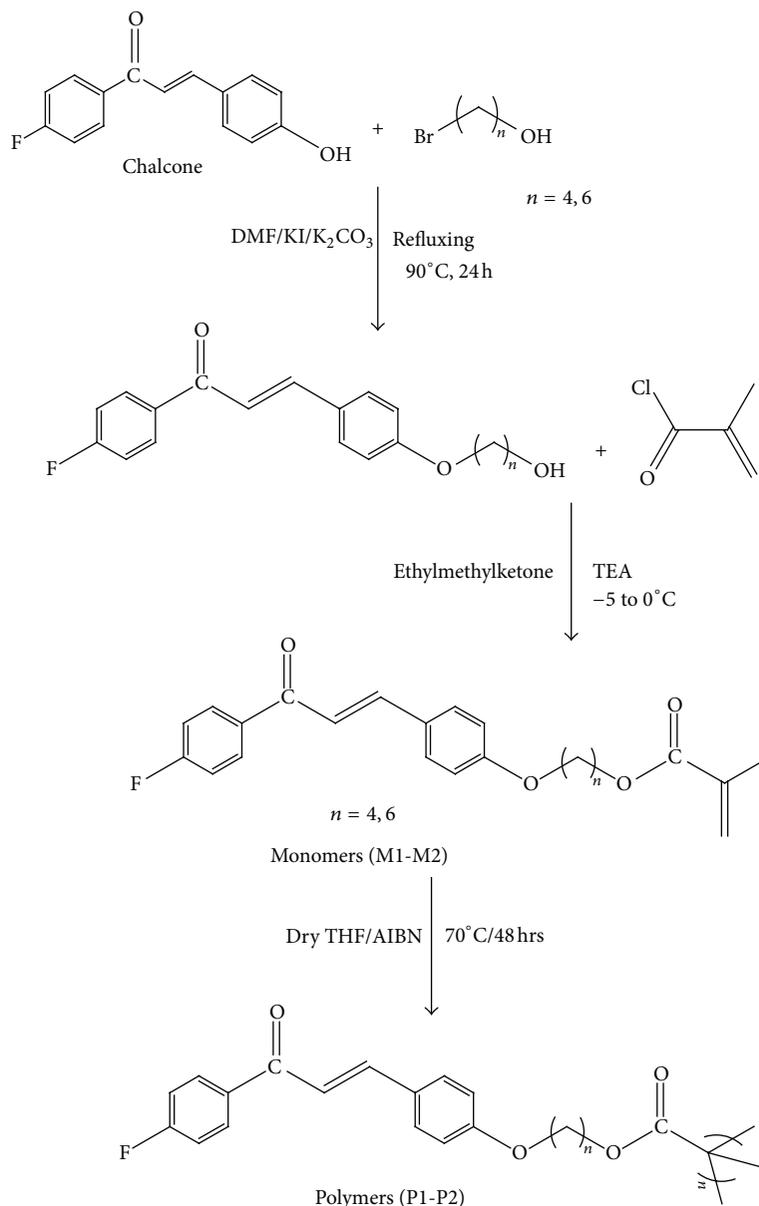
constant fraction discriminator (CFD, Phillips, The Netherlands). The first detected photon was used as a start signal by a time-to-amplitude converter (TAC), and the excitation pulse triggered the stop signal. The multichannel analyzer (MCA) recorded repetitive start-stop signals from the TAC and generated a histogram of photons as a function of time-calibrated channels (55.7 ps/channel) until the peak signal reached 1000 counts. The instrument response function was obtained using a Rayleigh scatter of Ludox-40 (40 wt.% suspension in water; Sigma-Aldrich) in a quartz cuvette at 280 nm excitation and 460 nm excitation. Decay analysis software (DAS6 v6.0, Horiba) was used to extract the lifetime components. The goodness of fit was judged by the chi-square values, Durbin-Watson parameters, as well as visual observations of fitted line, residuals, and autocorrelation functions.

2.3. Synthesis of Pendant Chalcone (Scheme 1). The pendant chalcone compound HPFSK was synthesized according to the reported literatures [11, 12]. The obtained products were purified by recrystallisation in ethanol and then identified using ^1H , $^{13}\text{C-NMR}$, and FT-IR spectra.

2.4. Hydroxyphenyl-4'-fluorostyryl Ketone (HPFSK). In a three-necked flask equipped with a mechanical stirrer and dropping funnel, a solution of NaOH (8 g) in distilled water (40 mL) was added to 4-hydroxyacetophenone (6.80 g, 0.05 mol) in 50 mL of ethyl alcohol. The reaction was cooled using an ice bath (10–15°C). A solution of 4-fluorobenzaldehyde in 50 mL of ethyl alcohol was then added dropwise with constant stirring, and the temperature was not allowed to exceed 25°C. After 12 h, the reaction mixture was neutralized with 2 M HCl to isolate the product. The yellow coloured solid product was filtered and washed several times with ice-cold water. The crude product was recrystallized from methanol into a yellow crystalline product HPFSK (Scheme 1).

FT-IR (KBr pellet, cm^{-1}); 1497 (aromatic C=C); 1590 (olefinic CH=CH); 1650 (keto C=O); 3550 (Ar-OH). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm) (Figure 1); 6.8–8 (2d, 8H, Ar-H), 7.5, 7.8 (2d, 2H olefinic –CH=CH–), and 6.4 (S, 1H, –OH).

2.5. 4-[4'-Fluorobenzoylstyryloxy]butyl Methacrylate (FBSOBMA) (M1) (Scheme 2). In a two-necked round bottom flask, chalcone (HPFSK) (3 g, 0.0123 mol) was dissolved in 100 mL of DMF and stirred well, and K_2CO_3 (3.39 g, 0.0246 mol) and a pinch of KI were added into the above solution and allowed stirring for 30 minutes in



SCHEME 2: Synthesis of monomers and polymers.

an oil bath. The prepared 4-bromobutanol (1.6 mL) was added dropwise into the above mixture and allowed stirring for 24 h at 90°C. The product yellow solid formed was poured into water, filtered, and dried. The crude product 4-hydroxybutyloxystyryl-4'-fluorophenyl ketone obtained was recrystallised from ethanol-water mixture (50 : 50) (yield 65%, 2.5 g).

4-Hydroxybutyloxystyryl-4'-fluorophenyl ketone (2 g, 6.3 mmol) and 1.5 mL of triethylamine were dissolved in ethylmethylketone (150 mL). The above mixture was cooled between 0 to -5°C, and methacryloyl chloride (2 mL in 20 mL of EMK) was added drop wise for an hour with constant stirring and cooling. The reaction mixture was stirred for another 6 hours at room temperature, and the precipitated ammonium salt was filtered off. After drying

over anhydrous sodium sulphate, EMK was evaporated using rotary evaporator. The crude monomer product was purified by column chromatography using ethyl acetate/n-hexane (2 : 8 v/v) as eluent. The monomer FBSOBMA (Figure 2) obtained was pale yellow coloured solid (yield 75%).

¹H-NMR (Figure 2) (CDCl₃, δ in ppm); 7–8.3 (aromatic protons, m, 8H); 7.5 and 7.9 (olefinic double bond, 2d, 2H); 1.3–1.7 and 3.3–4.3 (spacer ethylenic protons m, 8H); 5.8 and 6.5 (vinylic protons, d, 2H); 2.1 (methyl protons t, 3H).

2.6. 6-[4'-Fluorobenzoylstyroxy]hexyl Methacrylate (FBSOHMA) (M2) (Scheme 2). The monomer 6-[4'-fluorobenzoylstyroxy] hexyl methacrylate (FBSOHMA) (Figure 3) was synthesised followed by analogous procedure discussed in the above monomer synthesis using 6-bromo

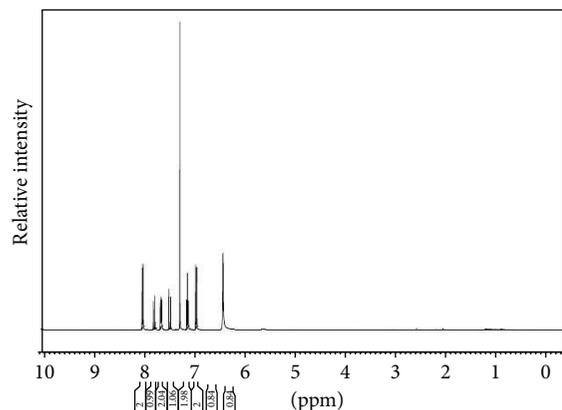


FIGURE 1: $^1\text{H-NMR}$ spectrum of 4-hydroxyphenyl-4'-flurostyryl ketone (HPFSK).

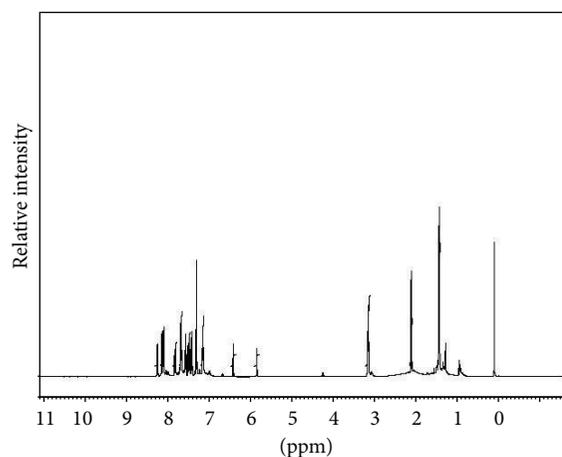


FIGURE 2: $^1\text{H-NMR}$ spectrum of (4-[4'-flurobenzoylstiryloxy] butyl methacrylate) (FBSOBMA) (M1).

hexanol instead of 4-bromobutanol. The monomer obtained was pale yellow coloured solid (yield 67%).

$^1\text{H-NMR}$ (Figure 3) (CDCl_3 , δ in ppm); 6.7–7.9 (aromatic protons, m 8H); 7.5 and 7.9 (olefinic double bond, 2d, 2H); 0.9–1.9 (spacer ethylenic protons m, 12H) 5.8 and 6.3 (vinylic protons, d, 2H); 2 (Methyl protons t, 3H).

2.7. Synthesis of Polymers (Scheme 2). The polymers poly(4-[4'-flurobenzoylstiryloxy] butyl methacrylate) (P1) and poly(6-[4'-flurobenzoylstiryloxy] hexyl methacrylate) (P2) were synthesised by free radical polymerisation. The free radical polymerizations of monomer M1 and M2 were carried out using AIBN as initiator as shown in the schematic representation (Figure 2). The predetermined quantities of monomers were taken with AIBN (5% weight of monomer) in polymerization tube and dissolved with 20 mL of dry tetrahydrofuran (THF). The above solutions were degassed by N_2 gas atmosphere for 10–15 minutes. Then, the polymerization tubes were kept at 70°C for 48 hours and subsequently then poured into methanol to precipitate the polymer. The polymers obtained were separated by filtration and purified

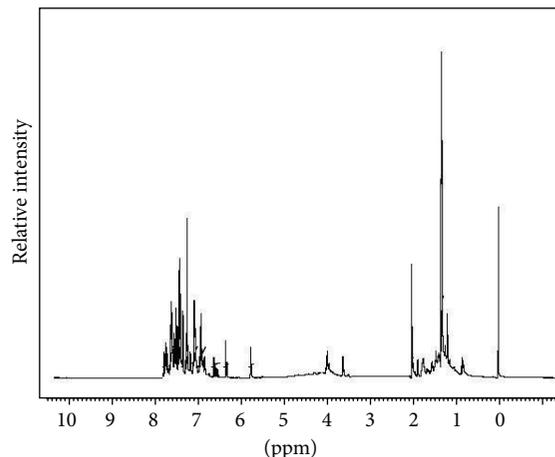


FIGURE 3: $^1\text{H-NMR}$ spectrum of (6-[4'-flurobenzoylstiryloxy] hexyl methacrylate) (FBSOHMA) (M2).

by repeated reprecipitation from chloroform into methanol and then dried in vacuum. The yield obtained was 70%.

3. Photoreactive Measurements

The photoreactivity of polymers was studied by dissolving the samples in chloroform, irradiated with UV-light at 254 nm using photoreactor, and kept at a distance of 10 cm from the light source for different time intervals. After each irradiation period, the UV spectra were recorded using Perkin Elmer scanning spectrometer. The rate of disappearance of double bond in photosensitive group was followed by the expression,

$$\text{Rate of conversion (\%)} = \frac{(A_o - A_t)}{(A_o - A_\infty)} \times 100, \quad (1)$$

where A_o , A_t , and A_∞ are absorption intensities due to the $>\text{C}=\text{C}<$ group after the irradiation time $t = 0$, $t = T$, and $t = \infty$ (maximum irradiation time), respectively.

4. Results and Discussions

4.1. Synthesis and Characterization. The photo-cross-linkable liquid crystalline monomers and polymers were prepared as shown in Scheme 2. The photoreactive chalcone HPFSK was prepared by reacting 4-Fluorobenzaldehyde with 4-hydroxyacetophenone in the presence of NaOH as base. The FT-IR spectrum of HPFSK showed absorption bands at 1497, 1590, and 3550 cm^{-1} corresponding to aromatic, olefinic, and alcoholic group, respectively. The $^1\text{H-NMR}$ spectrum (Figure 1) showed resonance signals at 6.8–8, 7.5, 7.8, and 6.4 ppm corresponding to aromatic, olefinic, and alcoholic protons, respectively. The monomers were synthesised by reacting the intermediate (formed by O-alkylation of chalcone in DMF in the presence of K_2CO_3) with methacryloyl chloride in the presence of triethylamine at $0\text{--}5^\circ\text{C}$ (Scheme 2). The $^1\text{H-NMR}$ (Figure 2) spectrum of M1 showed characteristic peaks at 5.8 and 6.5 ppm due to vinyl and methyl protons. The aliphatic ethoxy protons showed signals between 1.3 and 4.3 ppm. The

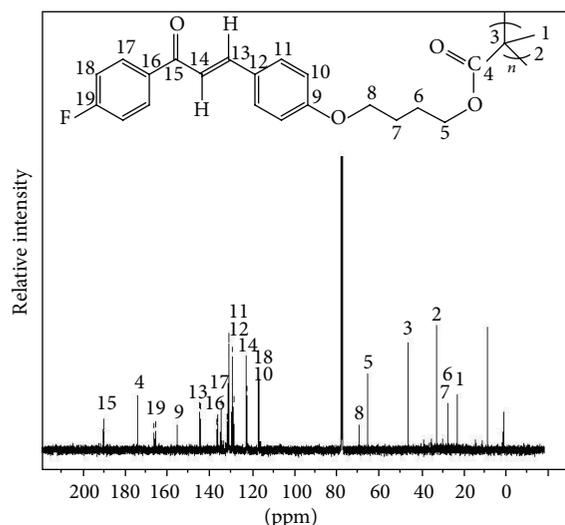


FIGURE 4: ^{13}C -NMR spectrum of poly(4-[4'-fluorobenzoylstyryloxy]butyl methacrylate) (FBSOBMA) (P1).

pendent olefinic double bond was shown by signals at 7.5 and 7.9 ppm. The appearance of multiplet signals between 7.0 and 8.3 ppm is due to aromatic protons. The above same trends were exhibited by M2 (Figure 3) with slight deviations. The photoresponsive liquid crystalline polymers P1 and P2 were synthesized by predetermined amount of monomers in THF at 70°C ; the polymerization was carried out for 48 hours (Scheme 2). The above mixture was precipitated in methanol and filtered off. The precipitated polymer was separated by filtration and purified by repeated reprecipitation from chloroform into methanol. The polymers synthesized were identified using ^{13}C -NMR spectra. The ^{13}C -NMR of P1 is shown in Figure 4. The methyl, vinyl, and tertiary carbons resonate between 23.5 and 70 ppm. The ester and olefinic carbons were identified by the signals at 174.6, 122, and 144.5 ppm, respectively. The signals between 118 and 167 ppm were due to aromatic double-bonded carbons. ^{13}C -NMR spectra polymer P2 is shown in Figure 5. The methyl, vinyl, and tertiary carbons resonate 25.5–69 ppm. The ester and olefinic carbons were identified by the signals at 175.5, 121.5, and 143.5 ppm respectively. The signals 116–170 ppm were due to aromatic double-bonded carbons. The solubility of both the polymers P1 and P2 was tested in various organic solvents. They were soluble in polar aprotic solvents such as DMF, DMSO, Dioxane, and THF and in chlorinated solvents such as chloroform, dichloromethane. It was insoluble in methanol, 2-propanol, and hydrocarbon solvents such as toluene, benzene and n-hexane.

4.2. Molecular Weight. The number average and weight average molecular weight of polymers P1 and P2 were determined by PL-GPC650. The number average molecular weight (\overline{M}_n) and weight average molecular weight (\overline{M}_w) of the polymer P1 were 8.7×10^4 and 13.05×10^4 . The molar mass distribution of polymer is given by polydispersity index (PDI) value 1.50. For the polymer P2, the \overline{M}_n and \overline{M}_w were 8.92×10^4 and

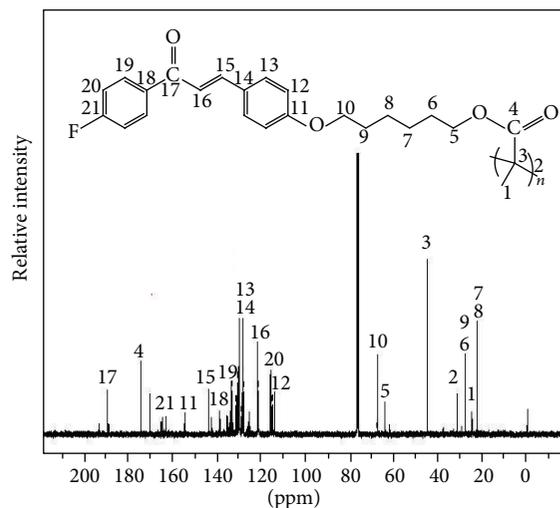


FIGURE 5: ^{13}C -NMR spectrum of poly(6-[4'-fluorobenzoylstyryloxy]hexyl methacrylate) (FBSOHMA) (P2).

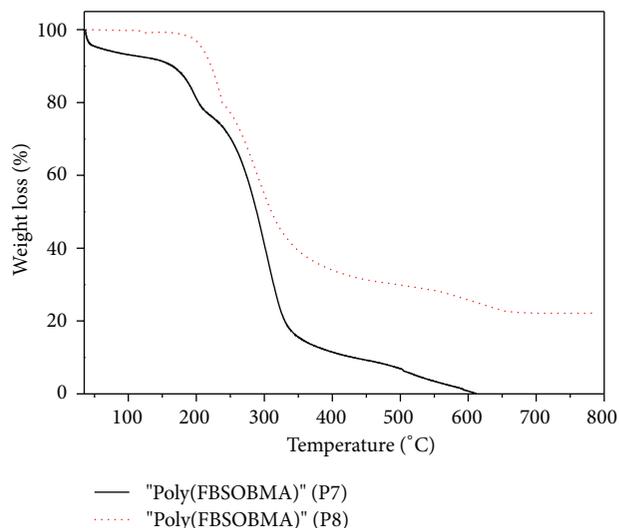


FIGURE 6: Thermogravimetric Analysis of poly(4-[4'-fluorobenzoylstyryloxy] butyl methacrylate) (P1) and poly(6-[4'-fluorobenzoylstyryloxy] hexyl methacrylate) (P2).

13.46×10^4 , respectively, and polydispersity index (PDI) value was 1.51. The theoretical values of PDI for polymer produced via radical combination and disproportionation are 1.5 and 2.0, respectively. The PDI values of polymers P1 and P2 were 1.50 and 1.51, respectively. Both polymers P1 and P2 show the tendency of chain termination by radical combination rather than disproportionation.

4.3. Thermal Properties. The Thermogravimetric Analysis (TGA) of prepared polymers was measured under nitrogen atmosphere in the temperature ranges $30\text{--}700^\circ\text{C}$ in order to investigate the thermal stability. The TGA data are illustrated in Table 1. The data in Table 1 and Figure 6 indicate that the homopolymers decompose at higher temperature, and they

TABLE I: Thermogravimetric Analysis (TGA) and liquid crystalline properties data of polymers (P1 and P2).

S. no.	Polymer	Temperature (°C) at weight loss (%)		T_g (°C)	T_m (°C)	T_i (°C)	$\Delta T = T_i - T_m$ (°C)	Mesophase
		IDT (°C)	50%					
P1	Poly(FBSOBMA)	160	287	Nil	105	147	42	Nematic
P2	Poly(FBSOHMA)	194	310	Nil	97	126	29	Nematic

show single-stage decomposition with good thermal stability. The initial decomposition temperature (IDT) of the polymers P1 and P2 were slightly different from each other due to smaller difference in molecular mass. Both P1 and P2 show 50% weight loss at temperatures 287 and 310°C, respectively, proving the flame retardancy and stability of polymers. These thermal studies have shown that the polymers possess very good thermal and thermooxidative stability required for the negative photoresist polymers.

4.4. Photo-Cross-Linking Studies. The photo-cross-linking studies were carried out to study the changes which occurred in the polymer during UV irradiation to confirm photoresist nature of polymer. The polymer solution was prepared in the concentration range of 10–20 mg/L using chloroform. It was irradiated with UV-light of 254 nm; the photo-cross-linking ability of the polymer was followed by the rate of disappearance of the C=C bond of photosensitive group in the UV spectrum. When the polymers irradiated with UV light of 254 nm, they undergo $2\pi + 2\pi$ cycloaddition and form photodimers as shown in Scheme 3. The absorption intensity decreases rapidly with increasing irradiation time and band disappears almost completely within three minutes of irradiation. The decrease in the UV absorption intensity due to the cross-linking of polymer through $2\pi + 2\pi$ cyclodimerisation of CH=CH- group of 4-fluorobenzoylstyryloxy group leads to formation of cyclobutane ring. The rate of disappearance of double bond in photosensitive group was calculated by the expression [13]:

$$\text{Rate of conversion (\%)} = \frac{(A_o - A_t)}{(A_o)} \times 100, \quad (2)$$

where A_o and A_t are absorption intensities due to the $>C=C<$ group after the irradiation time $t = 0$ and $t = T$ respectively.

The UV spectral changes during photo-cross-linking and photoconversions of polymers are shown in Figures 7 and 8. In the polymers P1 and P2, the pendant chalcone unit and polymeric backbone are linked by flexible methylene spacer units. The photo-cross linking rate of P2 was slightly faster than P1. This rapid cross-linking may be attributed to the spacer unit between the photosensitive group and polymer backbone which provide more flexibility and free movement for the side chain which accelerate the increased rate of cross linking [14].

The photolysis studies of various ethylene spacer containing polymers imparted that the rate of photo-cross-linking depends on the length of the methylene chain so the polymer P7 and P8 follow this trend

$$\text{Hexamethylene} > \text{Butamethylene}. \quad (3)$$

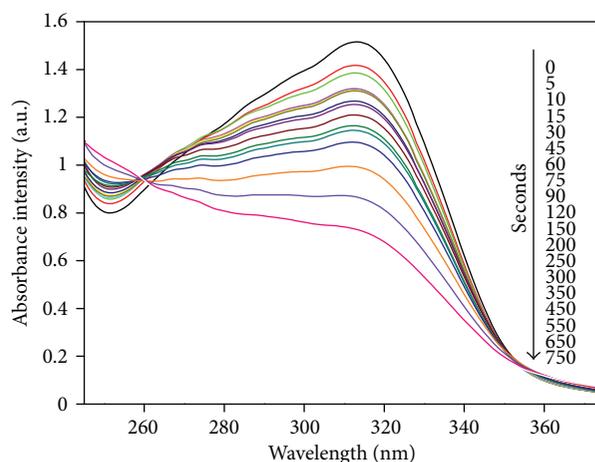


FIGURE 7: UV spectral changes during photo-cross-linking of poly(4-[4'-fluorobenzoylstyryloxy]butyl methacrylate) (P7) at various time intervals in chloroform solution.

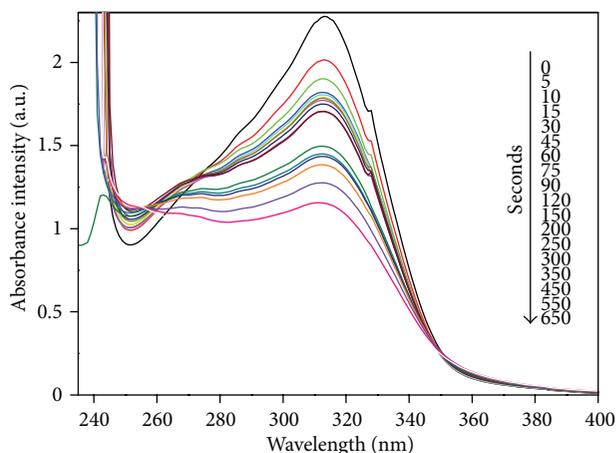
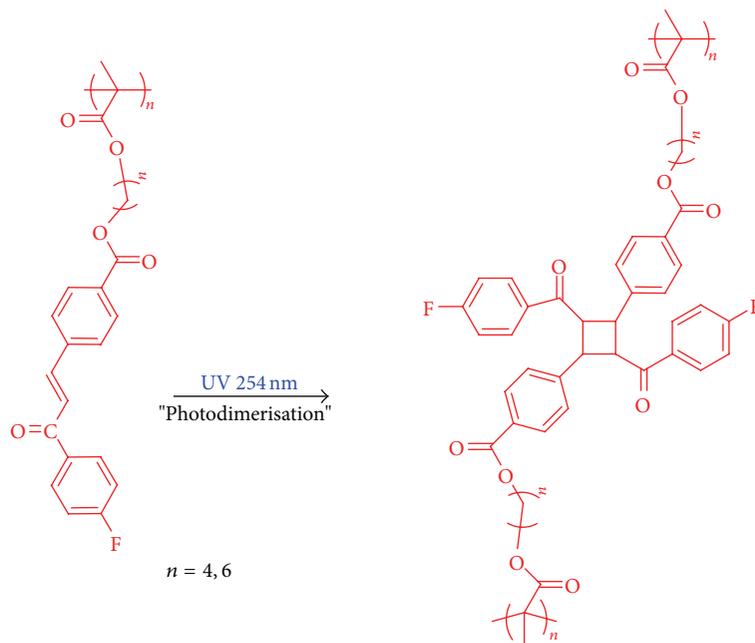


FIGURE 8: UV spectral changes during photo-cross-linking of poly(6-[4'-fluorobenzoylstyryloxy]hexyl methacrylate) (P8) at various time intervals in chloroform solution.

Figure 9 denotes that the rate of disappearance of the C=C of photoreactive groups is slightly fast in P2 than P1 and shows 100% photoconversion, since they have smaller substituents in their pendant unit and there is no intramolecular crosslinking can be formed by the dimerization of adjacent chalcone groups.

4.5. Fluorescence Spectral Studies. The existence of photoresponsive behaviour of polymers can be evidenced by fluorescence spectra. The fluorescence intensity of polymer



SCHEME 3: Photodimerisation of polymers (P1 and P2).

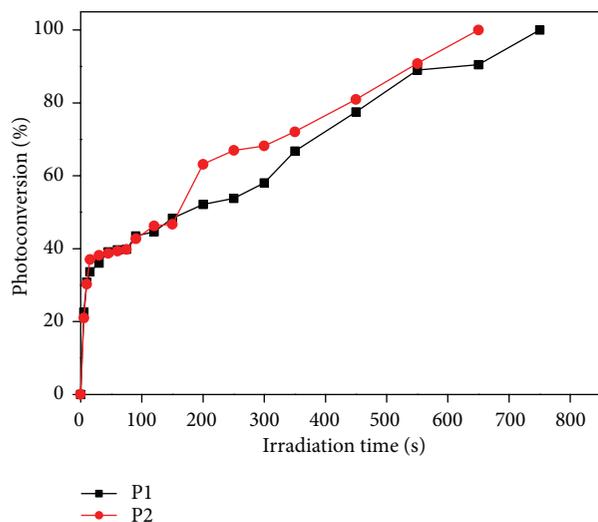


FIGURE 9: Photoconversions on UV-irradiation for polymers P1 and P2.

decreases as the time of irradiation increases. The decrease in intensity is due to $2\pi + 2\pi$ cycloaddition which leads to cyclobutane ring formation by destroying π electron conjugation. From the figures it is noticed that P1 shows gradual decrease in the intensity, whereas P2 shows sudden decrease.

Fluorescence spectral changes during photo-cross-linking of polymers P1 and P2 are shown in Figures 10 and 11. Both polymers P1 and P2 were excited at the wavelength of 348 nm, and they were irradiated with UV-light of 254 nm at various time intervals. The decrease in fluorescence intensity

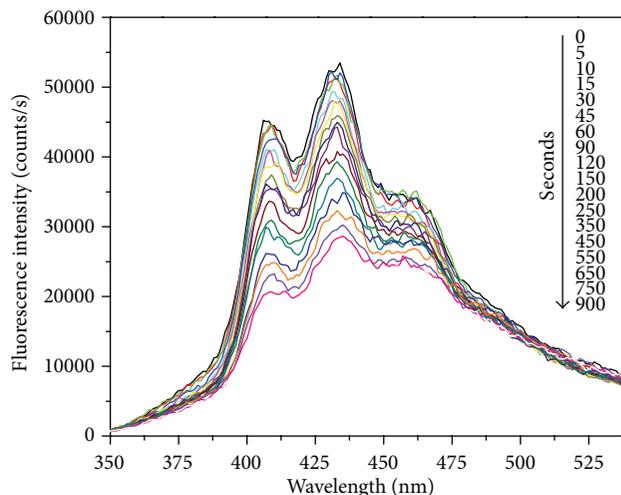


FIGURE 10: Fluorescence spectral changes during photo-cross-linking of poly(4-[4'-fluorobenzoylstyroxy] butyl methacrylate) (P1) at various time intervals in chloroform solution.

was observed till the completion of photo-cross-linking of polymers which is noticed from their decrease in intensity or disappearance of emission peaks. The emission of both polymers P7 and P8 occurred at 430 nm, since they contain similar functional groups and spacer units.

4.6. Morphological Study of Photo-Cross-Linking Polymers. The SEM technique can give high resolution images which enables the visualization of morphological information without losing any accuracy during analysis. The synthesized

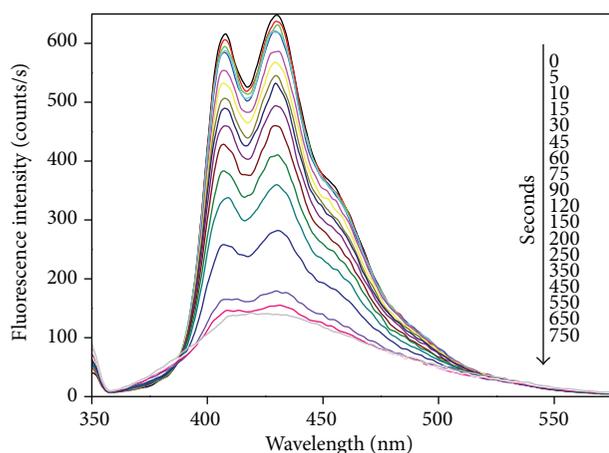


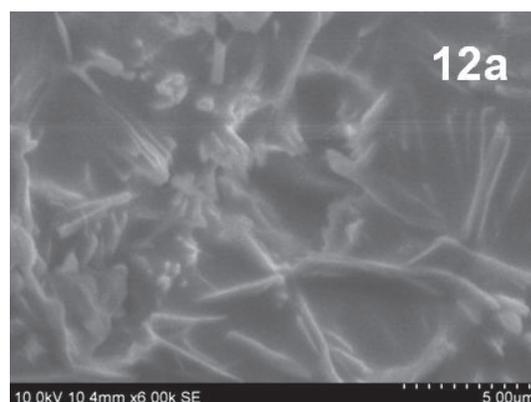
FIGURE 11: Fluorescence spectral changes during photo-cross-linking of poly(6-[4'-fluorobenzoylstyryloxy]hexyl methacrylate) (P2) at various time intervals in chloroform solution.

photo-cross-linkable liquid crystalline polymers were irradiated with UV-light of 254 nm for 30 minutes. The virgin polymers (P1 and P2) and photo-cross-linked polymers (P1 and P8) were characterised by HITACHI Scanning Electron Microscope (SEM) S-3400N model to understand the morphology of both virgin and photo-cross-linked polymers. The SEM images of both virgin and photo-cross-linked polymers shown in Figures 12(a) and 13(b). As observed from the SEM images of Figures 12(b) and 13(b), the photo-cross-linked polymer sample confirms loosely held dispersion of polymeric materials, while virgin polymer exhibits compact stringent dispersion of polymeric surface as described by Mathur and Kumar [15].

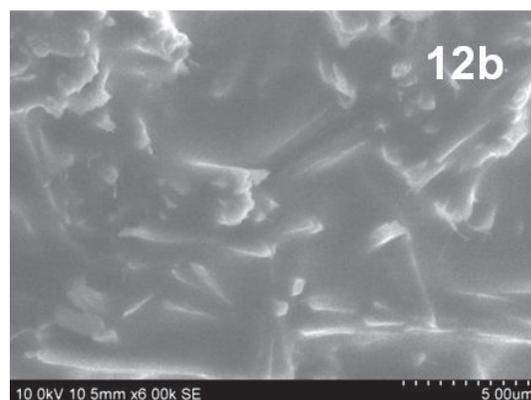
It is inferred from the SEM images that all the virgin polymers P1–P8 have irregular-shaped flakes in their lattice which packed on one over the other in nondirectional manner, and they all have hard and crystal-like surface. But, SEM images of photo-cross-linked polymers from P1 to P8 show uniform size of polymer flakes which were arranged regularly.

It can be clearly observed from the SEM images that their surfaces after photo-cross-linking were smoothed well, and all the irregular crystal with rough surface has been changed into brightened smooth surface. The smoothness in the polymer surface may be due to photodimerisation of polymers. When two polymer molecules undergo cyclobutane ring formation during photo-cross-linking, one polymer molecule bounds to the other through cyclobutane ring. This structural interaction may lead to smoothness and regular or ordered arrangement of polymer lattice after UV-treatment.

4.7. Liquid Crystalline Properties of Polymers. The development of photosensitive media based on liquid crystalline compounds for data recording, optical storage, and reproduction is one of the most rapidly developing areas in the physical chemistry of low molecular mass and polymer liquid crystals [16]. The rigidity of the mesogenic core, the flexible spacer length, and terminal units highly influence the molting



(a)



(b)

FIGURE 12: Scanning Electron Microscope image of (a) virgin polymer poly(FBSOBMA) (P1) and (b) photo-cross-linked polymer poly(FBSOBMA) (P1).

temperature, mesophase temperature, and even molecular arrangement.

In some polymers, they are taking the effect of mesogen and spacer together; a polymer having rigid mesogen and shorter spacer should show the higher transition temperature [17]. The phase transition temperature and mesophase of the polymers are studied by traces of DSC thermogram and HPOM images. Generally in the DSC thermogram, at the highest transition temperature there will be an endotherm corresponding to the transition from LC phase to isotropic phase. The transition in some cases from crystal to liquid crystal is marked by more than one endotherm. When such multiple curves were observed, the one having the highest temperature is attributed to crystal-to-mesophase transition.

The DSC thermograms of Polymers P1 and P2 are shown in the Figure 14 which shows two endotherms observed in the heating scan and in the annealed samples. In general, for the first lowest transition temperature which occur just after the glass transition temperature is melting endotherm, and the second highest transition temperature attributed to nematic phase to isotropic mesophase transition. The polymers P1 and P2 show crystal-to-nematic phase transition at temperatures at 105°C and 97°C, respectively. The polymers

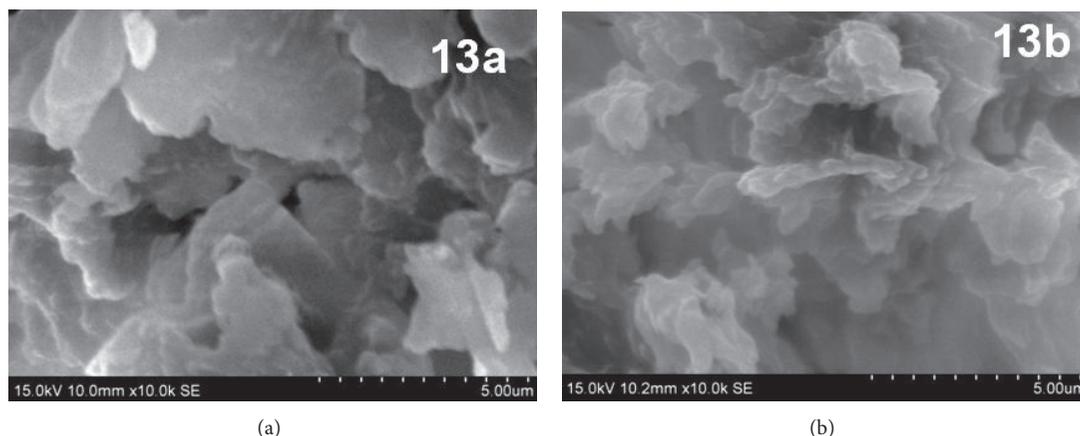


FIGURE 13: Scanning Electron Microscope image of (a) virgin polymer poly (FBSOHMA) (P2) and (b) photo-cross-linked polymer poly (FBSOHMA) (P2).

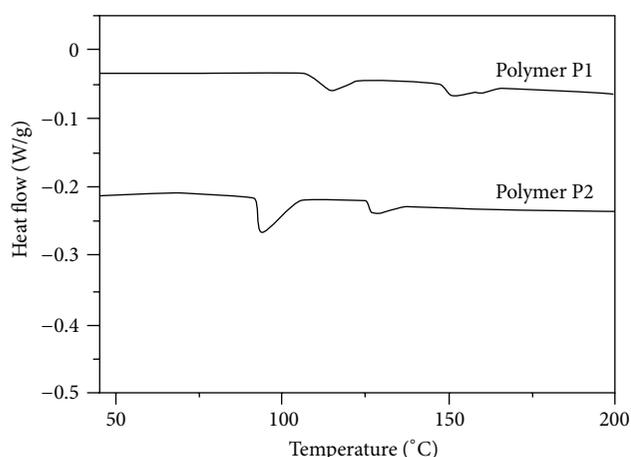


FIGURE 14: Differential scanning calorimetric thermogram of polymers poly(FBSOBMA) (P1) and poly(FBSOHMA) (P2).

P1 and P2 show nematic-to-isotropic phase transition at the temperature 147°C and 126°C, respectively shown in Figures 15 and 16. The liquid crystalline properties of polymer are shown in Table I. The liquid crystalline phases were observed in between the T_m and T_i . The mesophase duration ($\Delta T = T_i - T_m$) was observed in between 42 and 29°C; this indicates that they possess relatively good mesophase stability.

4.8. Fluorescence Lifetime Studies. The time-resolved fluorescence decays of polymers P1 and P2 have been monitored in chloroform. The polymers P1 and P2 were excited at 460 nm. The fluorescence lifetimes of both polymers after and before the UV-irradiation at wavelength of 254 nm have been measured and plotted in Figures 17(a) and 18(c). The χ^2 values which are known as the fitting parameters determining the fine fit for triexponential decay are found to be <1.3, and average lifetime $\langle\tau\rangle$ is calculated using the following equation [18]:

$$\tau_{\text{av}} = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2 + \alpha_3\tau_3^2}{\alpha_1\tau_1 + \alpha_2\tau_2 + \alpha_3\tau_3}, \quad (4)$$

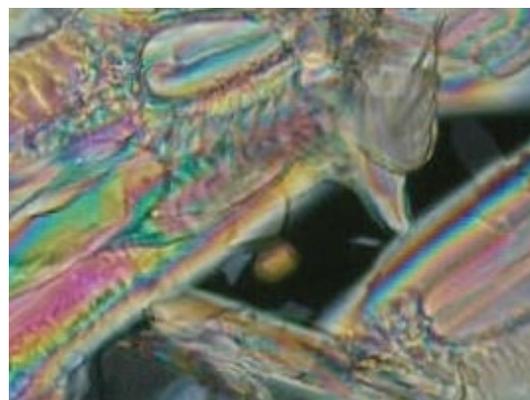


FIGURE 15: Polarised optical micrograph of poly(FBSOBMA) (P1) showing nematic mesophase at 147°C.



FIGURE 16: Polarised optical micrograph of poly(FBSOHMA) (P2) showing nematic mesophase at 126°C.

where τ_1 , τ_2 , and τ_3 are the lifetime values of three emissive states and α_1 , α_2 , and α_3 are called preexponential factors which give abundance of emissive states. The fluorescence lifetime values of photoresponsive polymers P1 and P2 were

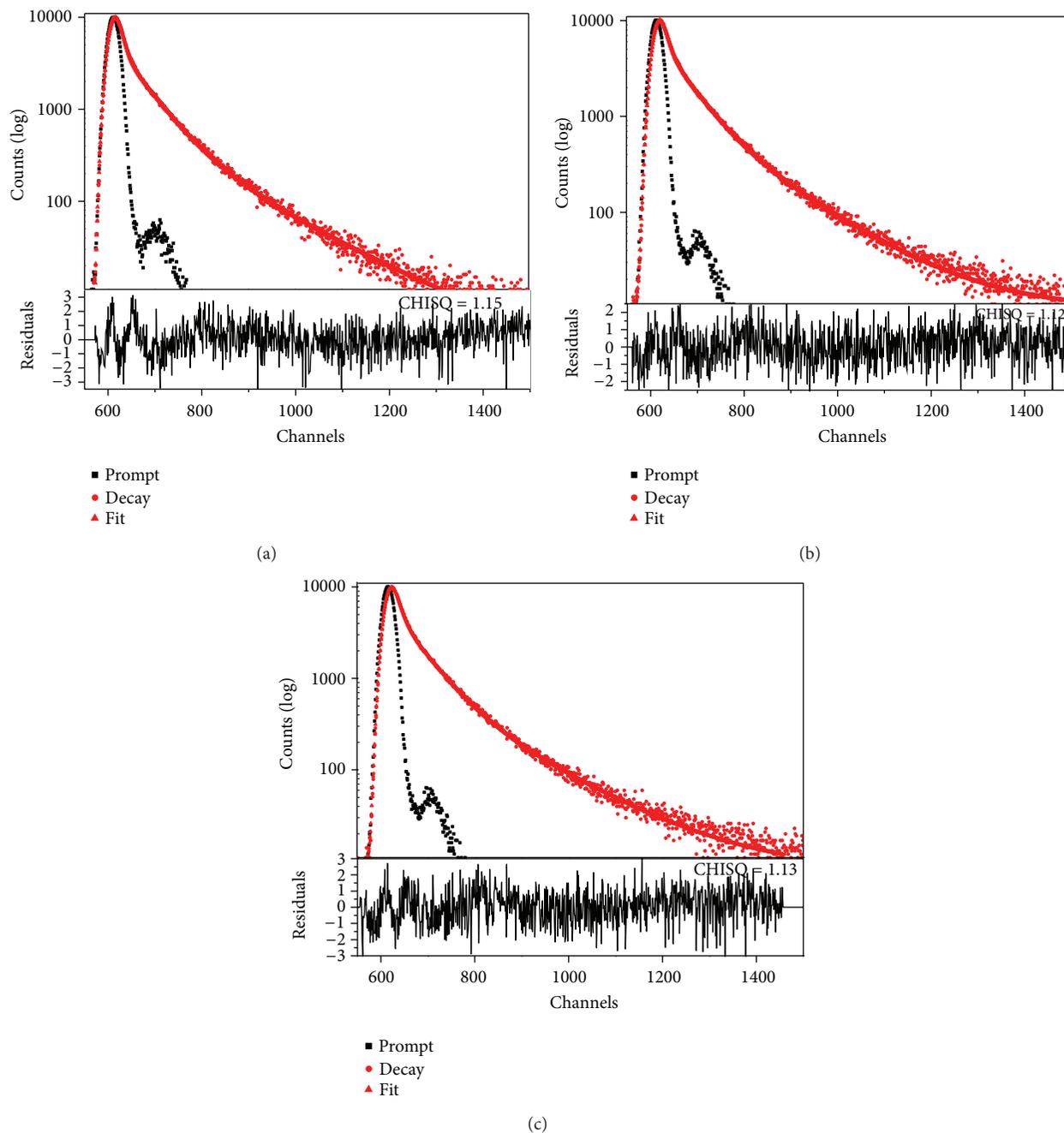


FIGURE 17: (a) Lifetime decay of poly(4-[4'-fluorobenzoylstyryloxy]butyl methacrylate) (P1) before UV-irradiation. (b) Lifetime decay of poly(4-[4'-fluorobenzoylstyryloxy]butyl methacrylate) (P1) after 150 sec UV irradiation. (c) Lifetime decay of poly(4-[4'-fluorobenzoylstyryloxy] butyl methacrylate) (P1) after infinite sec UV irradiation.

given in Table 2. The polymer solutions were prepared in the concentration range 10–20 mg/L using chloroform. The lifetime measurements of two polymers were determined at nonirradiative and UV-irradiative condition at different time intervals. Since the number of molecules with electron donor or withdrawing groups affects fluorescence only partially [19], the polymers show very little lifetime variations before and after UV-irradiations. In both polymers P1 and P2, lifetime

values are decreasing after UV-irradiation at different time intervals 0, 150, and ∞ seconds.

In general, rotation of the part of the molecule participating in fluorescence is the most trivial process of the nonirradiative energy loss and typically occurs in the excited state. Considering the molecules of the bond order in ground state equal to 2, upon excitation the electron from the bonding orbital is promoted to the excited state orbital

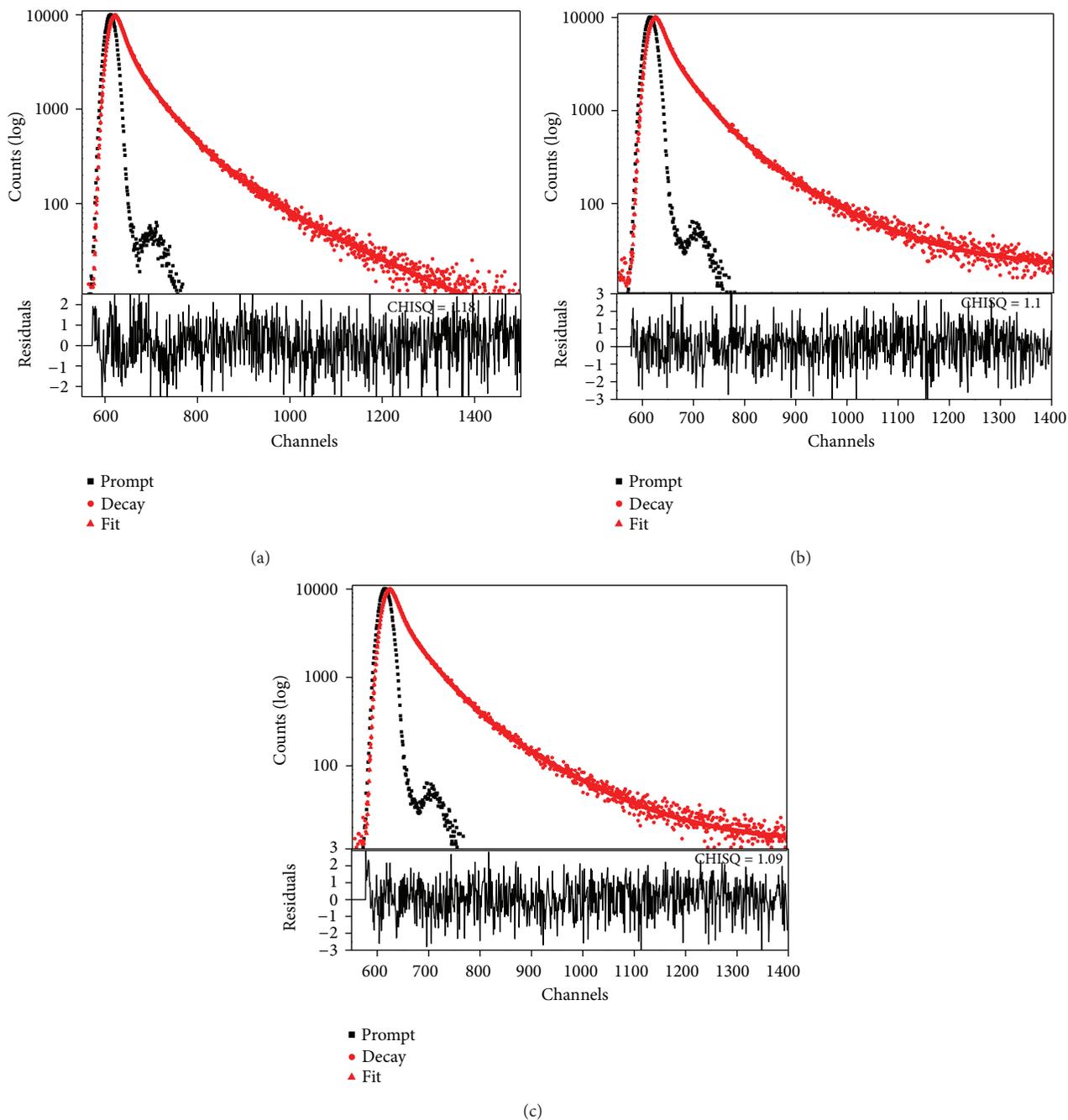


FIGURE 18: (a) Lifetime decay of poly(6-[4'-fluorobenzoylstyroxy]hexyl methacrylate) (P2) before UV-irradiation. (b) Lifetime decay of poly(6-[4'-fluorobenzoylstyroxy]hexyl methacrylate) (P2) after 150 sec UV irradiation. (c) Lifetime decay of poly(6-[4'-fluorobenzoylstyroxy]hexyl methacrylate) (P2) after infinite sec UV irradiation.

TABLE 2: Fluorescence lifetime decay of polymers P1 and P2.

Polymers	λ_A (nm)	λ_E (nm)	UV-irradiation time (sec)	τ_1 (ns)	α_1	τ_2 (ns)	α_2	τ_3 (ns)	α_3	$\langle \tau \rangle$	χ^2
P1	313	430	0	3.07	0.4601	0.4287	0.3657	9.05	0.1742	5.94	1.15
			150	2.72	0.4417	0.4761	0.2899	7.63	0.2683	5.60	1.12
			∞	2.40	0.4349	0.4469	0.2790	7.12	0.2862	5.32	1.06
P2	313	430	0	3.19	0.4946	0.8282	0.3312	9.60	0.1742	6.05	1.18
			150	2.65	0.5065	0.6778	0.2663	7.23	0.2271	4.91	1.10
			∞	2.61	0.4848	0.6154	0.2926	7.01	0.2226	4.77	1.09

producing bond order 1. Such change in the bond order transforms the rigid frame work formed by the double bond to a flexible system of single bond, leading to twisting of molecule around a C-C bond causing subsequent cis/trans isomerisation [20]. Since rotation around the double bonds contributes to a decrease in lifetime, it is logical to suggest that any restriction of rotation, such as rigid environment of the molecules, would marginalize the role of nonradiative path way and lead to subsequent increase of fluorescence lifetime.

Molecules capable of undergoing an electron transfer process possess strong electron donating and occasionally electron withdrawing group [21]. Among withdrawing groups, only nitro group has been used successfully as quenchers other withdrawing groups may affect a little fluorescence lifetime. For example, tetranitrofluorescence has lifetime of 2.4 ns compared with 4.0 ns for fluorescence.

The polymers poly(4-[4'-flurobenzoylstyroxy] butyl methacrylate) (P1) and poly(6-[4'-flurobenzoylstyroxy] hexyl methacrylate) (P2) fluorescence lifetime values before irradiation were 5.94 and 6.05. The molecules capable of undergoing an electron transfer possess strong electron donating and occasionally electron withdrawing group. The exceptions are however numerous, and a number of molecules with electron donor or electron withdrawing group affect fluorescence lifetime partially. So the electronegative nature of fluorgroup substitution at the 4th position of both polymers P1 and P2 might not be affected by the fluorescence lifetime values. Nevertheless, the two polymers showed restriction to free rotation after photodimerisation, and slight polarisation of ester linkage predominates into further decrease of fluorescence lifetime up to infinite photodimerisation. In the polymers P1 and P2 they show χ^2 values near to 1.1 or 1 which indicate all the fits are monoexponential and show the goodness of fitting parameters.

5. Conclusions

The photos-cross-linkable, liquid crystalline polymers P1 and P2 were synthesized by free radical polymerization in THF using AIBN as initiator. The synthesized polymers have been characterized by H^1 -NMR, C^{13} -NMR, and UV-Vis spectral studies. The TGA analysis clearly indicates that the polymers show 50% weight loss near to 400°C which exhibit good characteristics of thermal and thermo-oxidative stability. The polydispersity index (PDI) values 1.50 and 1.51 obtained from GPC indicate that polymerization was terminated by free radical combination. The photo-cross-linking and fluorescence lifetime study of polymers show their indispensable importance in photoresist applications. The liquid crystalline property of the polymers was identified from DSC and confirmed by HOPM images at 147°C and 126°C. From the average lifetime values 5.32 ns and 4.77 ns at infinite UV-irradiation on both P1 and P2 reveal that the photo physical behavior of polymers using the time-correlated single photon counting (TCSPC) method. Thus, the synthesized polymers exhibit both photoresponsive as well as liquid crystalline property, and they might be useful in optical data recording and nonlinear optical (NLO) applications.

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