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Optical Switching, Photophysical, and Electrochemical Behaviors of Pendant Triazole-Linked Indolylfulgimide Polymer

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ABSTRACT: Triazole-linked 2-indolylfulgimide polymer has been synthesized and its photochromic switching behavior has been characterized by NMR, IR, GPC, TGA, DSC, and UV–Vis spectroscopy. The synthesized photochromic polymer showed absorption peak maxima at 386 and 510 nm wherein the absorption at 510 nm was attributed to charge transfer from triazole ring nitrogen to carbonyl carbon of fulgimide unit. Fluorescence lifetime studies on exciting at 550 nm reveals triexponential behavior with fluorescence decay around 0.1, 1 and 4.2 ns, which correspond to open (E), closed (C) form of fulgimide and triazole ring, respectively. Whereas exciting at 470 nm evidences biexponential fit with fluorescence decay around 0.1 and 2.2 ns, which corresponds to the closed (C) form and triazole ring, respectively. Fluorescence decay of triazole ring was found to be influenced by the excitation wavelength. The cyclic voltammogram of open form of polymer depicts irreversible reductive wave at −1.4 V. On illumination with 360-nm light, the reduction wave of polymer was shifted toward less cathodic wave at −0.9 V; this leads to formation of the closed form of fulgimide unit. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1138–1146, 2011

KEYWORDS: biexponential; charge transfer (CT); click chemistry; electrochemistry; fluorescence; fluorescence lifetime; functionalization of polymers; 2-indolyl fulgimide; optical switching; photochromism; photoreactive effects; photochemistry; triexponential fit

INTRODUCTION Recent years, optical data storage is becoming significant and everyone seek to store their data like multimedia technology, scientific information in the form of compact disk, memory stick, hard disk, etc. The write–read–erase mechanism of data storage is a key factor in storing the information. Photochromic materials are promising as recording media for optical memory because they erasably or rewritably store data in photon mode. As the data-recording mechanism is based on the photochemical reaction of each molecule in the matrix, extremely high spatial resolution should be achievable. The organic photochromic materials have been responding with light and repeatedly change from chromatic state to achromatic state or vice versa, such as isomerization reaction with light by fulgide, ring opening/closing reaction, and redox reaction used by spiropyran and diarylethenes.[1] Light can induce circulation of π electrons for the electrocyclic reaction to occur. As per Woodward-Hoffman electocyclic reaction fulgide/fulgimide molecule can undergo conrotatory mode of E-configuration to C-configuration, which occurs via thermally irreversible or photochemically reversible. Light is responsible for coloration and decoloration of these molecules. Photochromic compounds can undergo reversible transformation between two distinct chemical configurations on exciting with different wavelengths of light. In any case, a photochromic transformation is always accompanied by profound absorbance changes in the visible region.[2] The two configurations may display distinct physicochemical properties such as refractive indices, dielectric constants, oxidation–reduction potential, and geometrical structures. The instant property changes by photoirradiation without processing lead to their use in various optoelectronic devices, such as optical memory, optical switching, displays, and nonlinear optics.[3,4] The photostationary state emits fluorescence, and it can be exploited to molecular electronics and information storage. Thermally irreversible fulgides/fulgimides exhibit good thermal stability of their photoisomers and show high photostability during repeated illumination cycles.[5,6] The photoresponsive character associated with this fascinating class of organic molecules has suggested a wealth of potential applications in a wide diversity of areas, ranging from biomedical research to information technology.[7] It has been viewed in rewritable optical memories and photofunctional switching applications.[8]

In particular, photochromic polymers meet the requirements in many practical applications ascribed to their excellent photoreponsive behavior in the solid state (thin film).[9–11]

Belfield et al.[12] investigated the laser-induced two-photon photochromism of indolylfulgide doped with a copolymer of phosphorylated poly(vinylbenzyl chloride (VBC)-*co*-methyl methacrylate (MMA)); a thin film was prepared by spin coating onto a glass substrate and it can be used in two-photon holographic and multilayer three-dimensional (3D) information storage. Photochromic materials were used in 3D optical memory devices, based on two-photon absorption. Concentrations of 10^{-1} M and higher are needed for the device to perform at the required writing and reading efficiencies.[13] To achieve the high concentrations of photochromism in the polymer matrix, Rentzepis and coworkers[14] synthesized photochromic crosslinked copolymers by attaching the photochromic fulgimide molecules to the polymer chain and copolymerizing it with methyl methacrylate and characterizing their switching properties. Cu (I)-catalyzed ligation of organic azides and terminal alkynes belong to a group of reactions referred as "Click Chemistry," a term coined by Huisgen et al.[15] These compounds are well known for their biological properties such as antiallergic,[16] antiviral applications and also in materials chemistry.[17] However, no work has been reported regarding the click chemistry with indolylfulgimide polymer. This work deals with synthesis of triazole-substituted indolylfulgimide polymer, and their optical switching, photophysical, thermal, and electrochemical properties were studied.

EXPERIMENTAL

Materials

Diethylsuccinate, acetone, *t*-butyl alcohol, potassium-*tertiary*-butoxide, sodium hydride, sodium hydroxide, methacrylic acid, hydroquinone, and 2,2′-azobis(isobutyronitrile) (AIBN) (Merck, Germany) were used as received. Methanol, ethanol, phenol, THF, diethyl ether, chloroform, triethylamine, dimethylformamide (DMF) (SRL, India) and other solvents were purified by reported procedures.[18] 2-[1,3-Dimethyl-2-indolylmethylene]-3-isopropylidenesuccinicanhydride was synthesized based on a similar reported procedure.[19] Methacryloylchloride was prepared according to procedure reported elsewhere.[20] Hexamethyldisilazane (HMDS) and 3-chloropropylamine hydrochloride (Fluka, Switzerland) were used as supplied.

Synthesis of Propargyl Methacrylate

Propargyl alcohol (4.75 g, 84 mmol) was dissolved in dry THF (0.25 mL); triethyl amine (10.1 g, 100 mmol) was added to a reaction vessel and stirred under nitrogen for 30 min keeping the temperature below 10 °C. Methacryloylchloride (9.3 g, 89 mmol) was then added at the same temperature and stirred overnight at room temperature. The reaction mixture was monitored by thin layer chromatography. After completion of the reaction, mixture was poured into ice cold water and extracted with ethyl acetate, washed several times with water, brine and dried over anhydrous sodium sulfate. The solvent was evaporated by rotary evaporator and purified by column chromatography using hexane as eluent to obtain a colorless liquid product, yield: 8.3 g (80%). FTIR (KBr, cm^{-1}): 3297 (—C≡C—H), 2980, 2877 (—CH$_2$—), 2147 (—C≡C—).

^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 1.8 (s, 3H), 2.5 (s, 1H), 4.2 (s, 2H), 5.6 (s, 1H), 6.1 (s, 1H) (Supporting Information Fig. S1). ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 20.2, 51.0, 62.8, 78.4, 125.5, 138.9, and 168.1(C=O) (Supporting Information Fig. S2). Anal. calcd for C$_7$H$_8$O$_2$: C, 67.73, H, 7.70. Found: C, 67.74, H, 8.0.

Synthesis of 1-Azido-3-aminopropane

1-Chloro-3-aminopropane hydrochloride (6.5 g, 49.9 mmol) and sodium azide (9.75 g, 149 mmol) in water (40 mL) were heated at 80 °C for 15 h. After removing most of the water under vacuum distillation, the reaction mixture was cooled in an ice bath; diethyl ether (50 mL) and then KOH pellets (4 g) were added keeping the temperature below 10 °C. The organic phase was separated, and the aqueous layer was further extracted with diethyl ether (2× 20 mL). The combined organic layers were died over K$_2$CO$_3$ and concentrated to give oil which was purified by bulb-to-bulb distillation to obtain a colorless liquid. Yield: 3.43 g (70%). FTIR (KBr, cm^{-1}): 2097 (—N$_3$), 3390 (—NH$_2$).

^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 1.7 (m, 2H), 2.5 (t, —CH$_2$— J = 7.1), 2.8 (t, J = 7.1, 2H), 3.4 (s, 2H) (Supporting Information Fig. S3). ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 32.0 (CH$_2$), 40.4 (CH$_2$), and 50.1(CH$_2$) (Supporting Information Fig. S4). Anal. calcd for C$_3$ H$_8$ N$_4$: C, 35.99, H, 8.05, N, 54.96. Found: C, 34.53, H, 7.83, N, 53.96.

Synthesis of 2-[1,3-Dimethyl-2-indolylmethene]-3-isopropylidene-*N*-(3-azidopropyl) Succinimide

A flask is charged with a solution of 2-indolylfulgide (1 g, 3.5 mmol) in benzene (15 mL). Through a dropping funnel, 3-azidoamine (0.35 g, 3.5 mmol) in benzene (4 mL) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. To this reaction mixture, zinc chloride powder (0.47 g, 3.5 mmol) was added in one portion. Subsequently, the reaction mixture was raised to reflux temperature, followed by the addition of HMDS (0.36 mL, 4.9 mmol) in benzene (5 mL), through dropping funnel, over a period of 10 min. This reaction mixture was then refluxed for 20 h. The benzene was removed by rotary evaporation. The crude product was purified by flash silica gel chromatography column (9:1 hexane–ethylacetae as eluent) to afford dark red syrup (0.635 g, 50%). FTIR (KBr, cm^{-1}): 1745 (C=OO), 1727, 1690 (—C=O), 1630 (—CH=C—C=O), 1605 (—C=C—(CH$_3$)$_2$), 1712 (N—C=O), 3023 (—CH$_3$), 2094 (—N$_3$), 2982(—CH$_2$—).

^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 1.6 (m, 5H), 1.82 (s, 6H), 2.29 (s, 3H), 3.21 (t, J = 4.8 Hz, 2H), 3.99 (s, 3H), 4.40 (t, J = 5.8 Hz, 2H), 7.02 (s, 1H), 7.37 (m, 1H),7.52 (m, 1H), 7.55 (s, 1H), 7.57 (s, 1H) (Supporting Information Fig. S5). Anal. calcd for C$_{22}$H$_{26}$N$_5$O$_2$: C, 66.83; H, 6.14, N,17.84. Found: C, 66.84; H, 6.10, N, 17.44.

Synthesis of 2-[1,3-Dimethyl-2-indolylmethene]-3-isopropylidene-*N*-[3-(4-methacryloyloxymethyl-1H-[1,2,3] triazole-4-yl)propyl] Succinimide

To solution of 2-[1,3-dimethyl-2-indolylmethene]-3-isopropylidene-*N*-(3-azidopropyl) succinimide (0.7 g, 1.92 mmol) and

propargyl methacrylate (0.239 g, 1.92 mmol) was dissolved in t-butanol–H_2O (3:1) mixture; 30 mol % of $CuSO_4 \cdot 5H_2O$ (0.14 g, 0.57 mmol) with 10 mol % of sodium ascorbate (0.07 g, 0.192 mmol) were stirred at room temperature for 18–28 h. The reaction was monitored by thin layer chromatography. The mixture was poured into cold water, and the resulting solution was extracted with chloroform (3× 50 mL). The combined organic phase was dried with sodium sulfate, concentrated, and purified by column chromatography over silica gel using chloroform as eluent, yield: 0.6 g (70%). FTIR (KBr, cm^{-1}): 1748 (C=OO), 1734, 1693 (—C=O), 1637 (—CH=C—C=O), 1609 (—C=C—(CH$_3$)$_2$), 1714 (N—C=O), 3024 (—CH$_3$).

^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm) : 1.9 (m, 16H), 3.9 (t, J = 5.0 Hz, 2H), 4.3 (t, J = 5.6 Hz, 2H), 5.2 (s, 2H), 5.5 (s, 1H), 6.1 (s, 1H), 6.8 (s, 1H), 7.2 (d, J = 6.8 Hz, 2H), 7.3 (s, 1H), 7.5 (s, 1H), 7.6 (s, 1H) (Supporting Information Fig. S6). ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 25.1, 26.3, 27.2, 28.4, 30, 50, 58.1, 68.6, 103, 114.4, 122.2, 124.3, 126.7(aliphatic), 128, 130.5, 133, 135.7, 142, 143.5, 153.9(aromatic), 158.9, 166,167,168 (—C=O) (Supporting Information Fig. S7). Anal. calcd for C$_{28}$H$_{31}$N$_5$O$_4$: C, 67.05, H, 6.23, N, 13.96. Found: C, 66.54; H,6.10, N, 13.50.

Synthesis of 2-[1,3-Dimethyl-2-indolylmethene]-3-isopropylidene-N-[3-(4-polymethacryloyloxymethyl-1H-[1,2,3] triazole-4-yl) propyl] Succinimide

The polymer was synthesized by free-radical solution addition polymerization technique. The homopolymerization of monomer was carried out using AIBN as an initiator. The monomer (0.5 g, 4 mmol) and AIBN (2 wt % of the monomer) were taken in a glass ampoule and dissolved in 2 mL of dry THF. The solution was degassed by several freeze-pump-thaw cycles under vacuum and sealed. The ampoule was then kept at 60 °C for 48 h, subsequently it was opened and the content was poured into 200 mL of methanol. The precipitated solid was separated by filtration and purified by repeated precipitation from chloroform into methanol. M_w = 2,16,698, M_n = 1,95,334, polydispersity index (PDI) = 1.109. FTIR (KBr, cm^{-1}): 1758 (—C=OO), 1734, 1639 (—C=O), 1637 (—CH=C—C=O), 1609 (—C=C—(CH$_3$)$_2$), 1720 (N—C=O), 3030 (—CH$_3$).

^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm) : 1.9 (m, 16H), 3.9 (t, J = 5.0 Hz, 2H), 4.3 (t, J =5.6 Hz, 2H), 5.2 (s, 2H), 6.8 (s, 1H), 7.3 (d, J = 6.4 Hz, 2H), 7.4 (s, 1H), 7.6 (s, 1H), 7.7 (s, 1H) (Supporting Information Fig. S8). ^{13}C NMR (400 MHz, CDCl$_3$, δ, ppm): 20.2, 23.4, 25.1, 26.3, 27.2, 28.4, 30, 50, 58.1, 68.6, 103, 114.4, 122.2, 124.3, 126.7 (aliphatic), 128, 130.5, 133, 135.7, 142, 143.5, 153.9 (aromatic), 158.9, 166,167,168 (—C=O).

Measurements

Viscosity of polymer was measured with an Ubbelohde viscometer in a temperature bath at 30 °C ± 1 using CHCl$_3$ as solvent. Molecular weight determination was performed by GPC in THF at 25 °C reported versus polystyrene standards. The infrared spectra were obtained with a Bruker IFS 66V Fourier Transform spectrometer using KBr pellets. High-resolution ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl$_3$ with TMS as an internal standard. The thermogravimertic analysis (TGA) and DSC measurements were performed on a Mettler Toledo STAR^e system used to scan the polymer in an unsealed aluminum pan as reference at a heating rate of 5 °C/min.

Photoexcitation was carried out using a 150 W Xenon arc lamp (Oriel). Light of the appropriate wavelength was selected either by a monochromator or cutoff filters (Hoya). The quantum yield of the photochromic reaction, ring closure (coloration), and ring opening (bleaching) in solution or in thin film were determined by comparison with photochromic reaction of E-form of polymer in chloroform. Fluorescence quantum yield of the sample was measured relative to fulgimide as described in the literature.[24]

Preparation of Thin Films

A pair of quartz slides were cleaned with water, acetone, and chloroform in an ultrasonic bath for 30 min and dried in a hot air oven at 60 °C for 3 h. The polymer was dissolved in chloroform (10%, w/w, 0.1); the solution was spin coated on the quartz slide (size: 25 × 25 × 1.5 mm^3) and dried in air. The film thickness was adjusted to get the absorbance between 0.05 and 0.10. The photoswitching property was carried out in a discontinuous mode: that is, the samples were exposed to UV radiation from a 500-W high-pressure mercury lamp, kept at a distance of 10 cm from the sample for varying intervals of time. The irradiated film was subsequently subjected to spectral analysis.

Cyclic Voltammetry Measurements

Cyclic voltammogram was carried out in a CH-620B instrument using conventional three-electrode electrochemical cell with platinum foil as auxiliary electrode, Ag/Ag$^+$ electrode as reference electrode, and glassy carbon as working electrode with 0.1 M tetrabutylammonium perchlorate (TBAP) as the electrolyte; all experiments were performed at ambient temperature (25 ± 0.1 °C) in argon atmosphere.

Fluorescence Lifetime Measurements

Time-resolved fluorescence measurements were carried out using (IBH) time-correlated single photon counting techniques by exciting the sample at 375 and 550 nm. Fluorescence decay was measured at 470 and 550 nm. The data analysis was carried out by the software provided by IBH (DAS-6), which is based on deconvolution techniques using nonlinear least square method, and quality of the fit is normally identified by the value $\chi^2 < 1.2$ and weighted residual.

RESULTS AND DISCUSSION

Characterization of Polymer

The triazole-linked photochromic indolylfulgimide polymer was prepared as per the synthetic route presented in Schemes 1 and 2. The molecular weight of the polymer was determined by GPC (see Supporting Information Fig. S9) and found to be M_w = 2,16,698, M_n = 1, 95,334, PDI= 1.109. The thermal stability of polymer was evaluated by TGA under argon atmosphere (Fig. 1), and the thermogram revealed that the polymer was stable up to 300 °C. A single stage decomposition was observed around 410 °C is due to
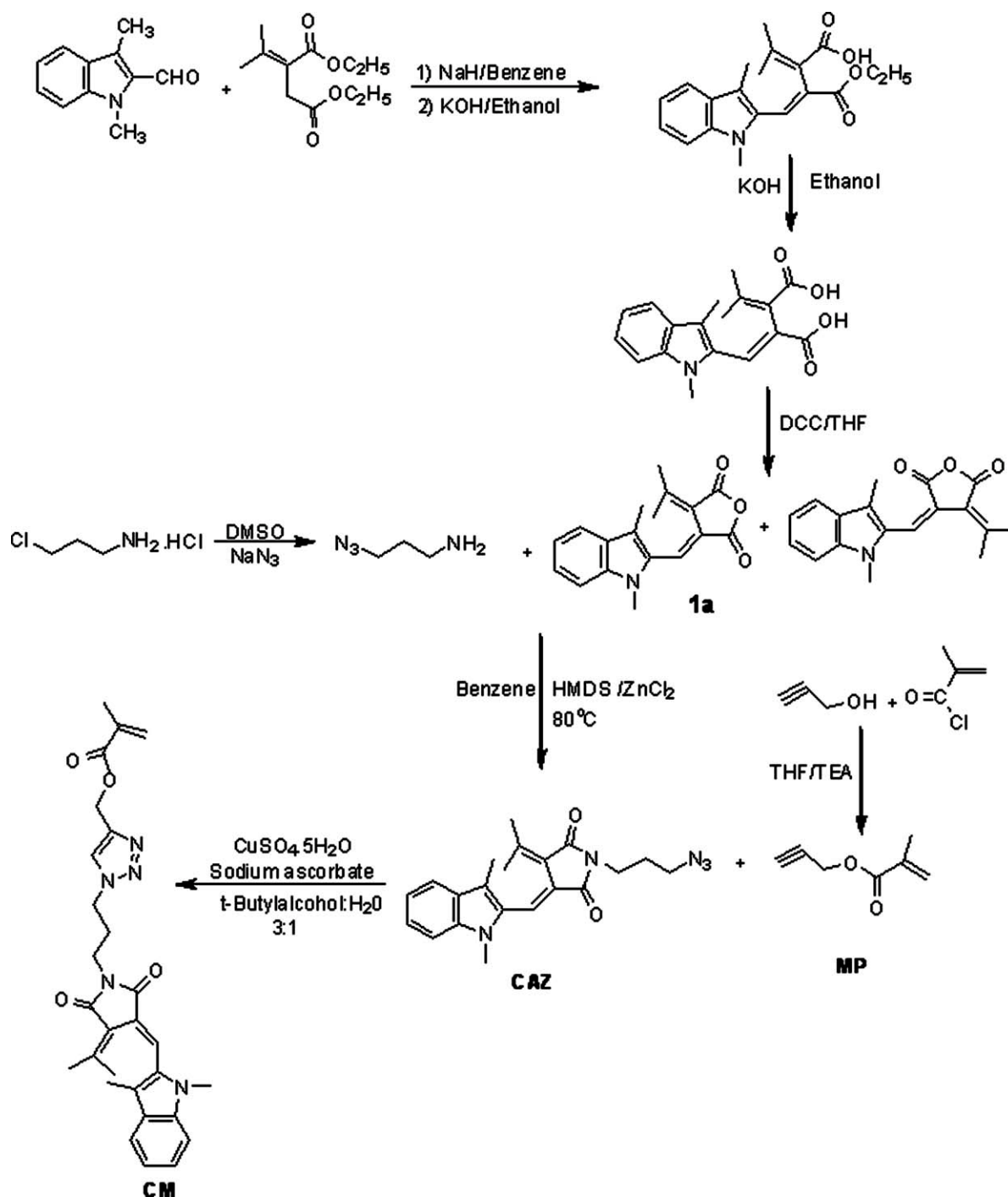
SCHEME 1 Synthesis of precursors.

the breakdown of methacrylic unit and imide group. A high char yield of 29.69% was observed at 750 °C. This high char yield might be attributed to increase of heteroatoms like nitrogen and oxygen. The DSC thermogram of polymer (Fig. 2) indicates a sharp melting point followed by decomposition around 368 °C without glass transition which in turn indicates that the polymer is highly crystalline in nature, attributed to high molecular weight as evidenced by GPC and XRD analysis.

Powdered XRD pattern of polymer was recorded using PAN analytical instrument. The 2θ values were recorded in the range of 10° to 70° (see Supporting Information Fig. S10). It has been observed that the maximum relative intensity peak of XRD pattern was well matched with crystallinity of poly(2-chloromethylpropylene oxide) reported in the JCPDS Powder Diffraction.[22] Based on the observation, the crystallinity of polymer was ascribed to stereo-regular arrangement of bulky side chain.[23] The noticed d-spacing
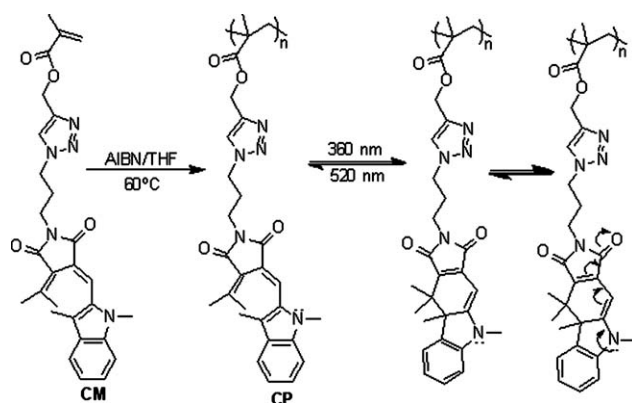
SCHEME 2 Synthesis of polymer.

FIGURE 2 DSC thermogram of polymer in argon atmosphere at a heating rate of 5 °C/min.

values (Table 1) and relative intensity confirms the primary phase of the structure of polymer.

Photophysical Studies of Polymer

The absorption spectrum of the polymer is shown in Supporting Information Fig. S11. The typical $\pi-\pi*$ transitions exhibited a broad absorption band in the UV domain, which corresponds to open (E) form (λ_{max} (CHCl$_3$)/386 nm) of indolylfulgimide moiety. Similar observation was reported by Liang et al.[24] and Saravanan et al.,[25] herein, there is a little difference noticed in absorption peak maxima at 395 and 396 nm for 2-indoylfulgides and 2-indolylfulgimide polymer, respectively.[24]

When absorption spectrum was recorded for polymer dissolved in chloroform, the λ_{max} was noticed at 510 nm that was attributed to charge transfer (CT) from triazole ring to carbonyl carbon of fulgimide. On the other hand, for polymer dissolved in THF and DMF, CT band was not observed at 510 nm (Fig. 3), attributed to the fact that hydrogen bonding between carbonyl carbon of fulgimide and nitrogen present in the triazole ring of polymer is pronounced only in chloroform solution. On irradiation with UV light at 360 nm in the discontinued mode of various time intervals, a peak maximum at 510 nm increases with increasing irradiation time.
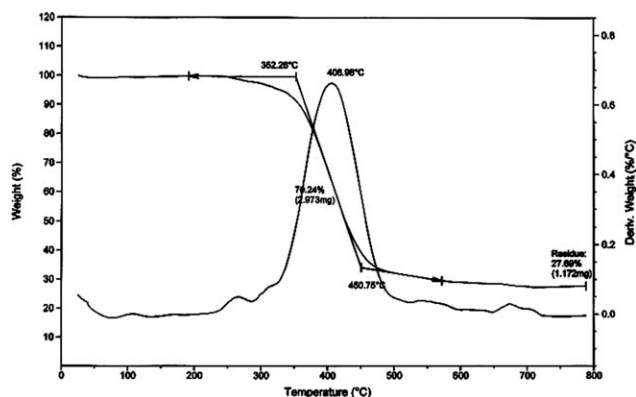

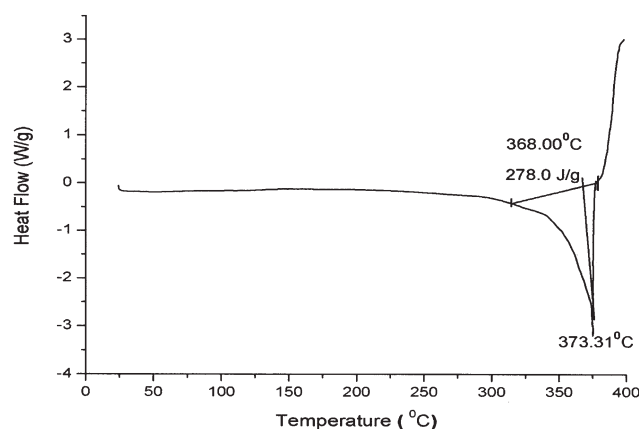FIGURE 1 TGA and DTA thermogram of polymer in N$_2$ atmosphere at a heating rate of 5 °C/min.

However, the triazole ring is not affected during photocyclization process (photostationary state) because it is separated by three-carbon methylene chain. To reach the photostationary state attributed to lone pair of electrons in indole nitrogen, $\pi-\pi*$ transitions of the closed C-isomer of an indolylfulgimide moiety is extended. Indeed, the yellow solution turns pink color, with a concomitant appearance of broad absorption band at 510 nm in the visible region (as given in inset of Supporting Information Fig. S11). Earlier, it has been reported that the photocyclization forces the system into a more planar conformation, thereby increasing conjugation and lowering energy of photochromic unit. On irradiation with 520-nm light in the different time intervals, the C-form reverts back to original position. Alternative irradiations of UV and visible light, the photochromic molecule can behave as a photoswitch. It has been shown that photoswitching property is a pivotal requirement for write and read operations.

The absorption maxima of polymer (in chloroform) in quartz thin film illuminated with 360-nm UV light is shown in Supporting Information Figure S12. It was observed that the absorption maximum appeared at 374 nm in thin film indicates that the E-form of fulgimide moiety was same when compared with that in solution. While increasing illumination time of the thin film polymer, the absorption maximum at 518 nm indicates the C-form of fulgimide moiety. While comparing the absorption maximum of polymer in chloroform

TABLE 1 d-Spacing And Relative Intensity Values of Polymer

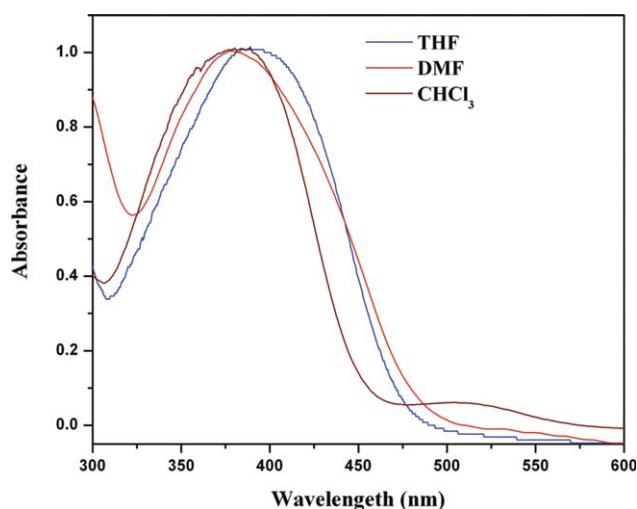| Pos [2θ]	d-Spacing	Relative Intensity (%)
13.63	6.48	85.66
14.33	6.17	100
15.03	5.88	26.75
17.03	5.20	19.83
22.19	4.00	26.65

FIGURE 3 Charge transfer band at 510 nm (chloroform). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and thin film, the absorption maximum of polymer in thin film blue shifted around 12 nm when compared with that of polymer in chloroform, as the polymer in thin film experience a confined environment.

Photoluminescence Spectra of Polymer

The photoluminescence spectra of polymer was recorded in chloroform, and the spectra show an emission maximum at 569 nm, ascribed to CT band emission (shown in Fig. 4). On illumination with light at 360 nm, emission maximum at 569 nm decreases with red shift because of higher fluorescence quantum yield of CT band as compared to that of photoregulated C-form of indolylfulgimide polymer. On other hand, the decrease in full width half maximum (FWHM) of emission
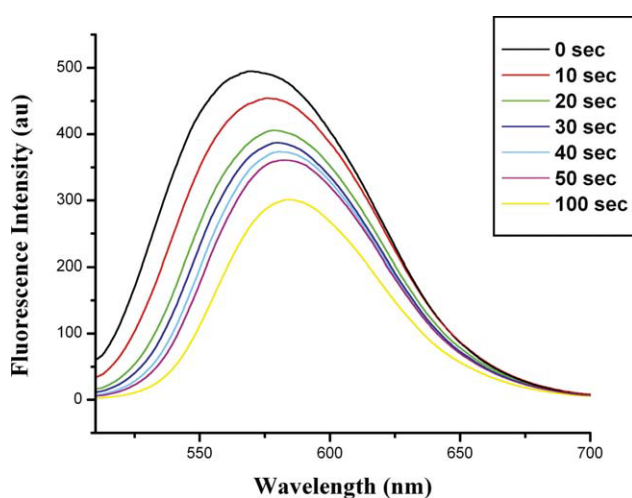

FIGURE 4 Emission spectrum of polymer $\lambda_{ex} = 510$ nm at different time intervals (chloroform). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
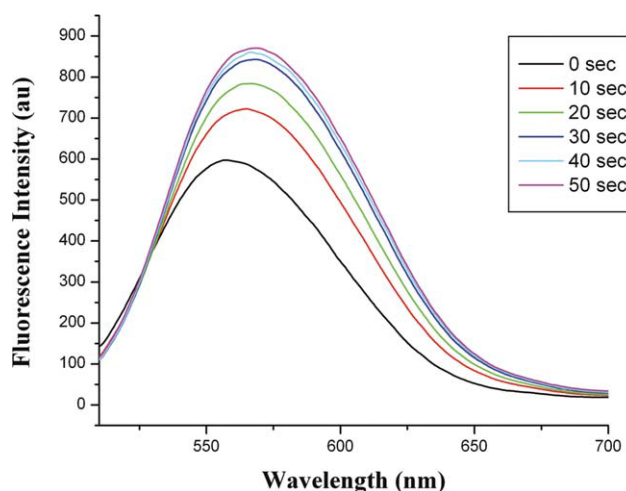

FIGURE 5 Emission spectrum of polymer $\lambda_{ex} = 510$ nm at different time intervals (THF).

peak indicates the increase in emission intensity of C-form of indolylfulgimide at 587 nm during illumination with UV light. The emission spectrum of polymer recorded in THF solvent shows emission peak maximum at 557 nm (shown in Fig. 5). On illumination with UV light, the emission intensity increases with red shift. Based on these observations, it is suggested that, on illumination with light at 360 nm, absorption at 510 nm corresponding to C-form increases, when exciting the sample at 510 nm most of the excitation photon observed by C-form, which leads to decrease in fluorescence intensity. The higher fluorescence quantum yield of C-form in THF was noticed when compared with fluorescence quantum yield of C-form in chloroform. However, with the increase of FWHM emission on illumination of UV light, the C-form of indolylfulgimide emission was red shifted with increasing intensity and constant emission of CT band. The photogenerated C-form of the polymer extends considerably the conjugation across the molecular assembly enhancing the fluorescence intensity with red shift. The red shift around 11 nm was observed on irradiation at 360 nm with different time intervals. This remarkable change in shift revealed that the lone pair of electrons in indole nitrogen extended in the closed form of indolylfulgimide unit. This process is fully reversible. Photochromic component within the same skeleton can be modulated with optical stimulations. Specifically, the electronic structure of chromophores changes with state of the photochromic component when delocalized action is possible across their covalent connector. Under these criteria,

TABLE 2 Fluorescence Quantum Yield of Indolyl Fulgide and Indolyl Polymer

	Acetonitrile	
	λ_{max}, EM (nm)	ϕ^{FL}
Indolylfulgide	618	0.033
Indolyl polymer	590	0.019

TABLE 3 Thermal, Photophysical and Electrochemical Properties of Polymer

	Isomer	λ_{max}^{abs} (CHCl$_3$)[a] (nm)	ε_{max}	λ_{max}^{em} (CHCl$_3$)[b] (nm)	Φ_f[c]	Optical Band Gap (eV)	T_d (°C)
Polymer	E	386	13,400	569	0.010	2.73	373
	C	510	14,400	590	0.19		

[a] Longest wavelength absorption maximum in THF.
[b] Fluorescence emission maximum in CHCl$_3$.
[c] Fluorescence quantum yield relative to Rhodoamine B as standard ($\Phi = 0.65$).

the reversible transformation of photochromic switch results in modulation of emission intensity.[26,27]

Fluorescence Excitation Spectral Studies

The fluorescence excitation spectra of polymer are illustrated in Supporting Information Figures S13 and S14 for polymer in chloroform/THF before and after irradiation with light at 360 nm has been recorded and emission maximum fixed at 550 nm. Fluorescence excitation spectrum had two peak maxima at 476 and 507 nm that corresponds to indolylfulgimide moiety and triazole ring, respectively. This fluorescence excitation was conformed by the exactly matched absorption spectrum of C-form of indolylfulgimide and triazole ring present in the polymer. It confirms that emission occurs from both indolylfulgimide and triazole ring present in the polymer.

Fluorescence Quantum Yield of Polymer

The fluorescence of C-form of polymer consists of broad emission band with its maximum intensity at 587 nm (see Table 2), which is due to the photoregulated colored forms of indolylfulgimide moiety rather than triazole ring present in the polymer. Fluorescence quantum yield of the polymer was calculated and given in Table 3. On comparison with quantum yield of indolyl polymer in E-form (0.05) and C-form (0.11) reported by Liang et al.,[24] in our studies, the quantum yield decrease to 0.02 (E-form) and 0.01 (C-form), respectively. The decrease in quantum yield of polymer is due to highly efficient vibrational relaxation of three methylene groups in the polymer, which leads to interconversion of the nonradiative transitions. However, it is difficult to examine the emission of E-form; we were able to detect emission peak maximum 557 nm, which could be restored by CT band[28] of triazole ring and carbonyl carbon in presence of solvent (chloroform).

TABLE 4 Fluorescence Lifetime Decay Profile of Polymer at Different Time Intervals of Illumination Under 360 nm UV Light

| Time (s)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	B_1	B_2	B_3
0	0.16	1.0	4.2	25.00	23.99	51.01
30	0.10	1.0	4.7	26.85	23.90	49.25
60	0.11	1.0	5.2	16.14	29.99	53.87
90	0.08	0.97	5.0	20.44	23.01	56.55
120	0.08	1.0	4.3	22.19	23.48	54.33

$\lambda_{exc} = 375$ nm, $\lambda_{em} = 550$ nm.

Fluorescence Lifetime Studies

The fluorescence lifetime of triazole-containing indolylfulgimide moiety of the polymer in chloroform on excitation at 375 nm exhibited triexponential behavior with lifetime of 0.1 (25%), 1 (23%) and 4.2 ns (51%) (Supporting Information Fig. S15). Fluorescence lifetime was recorded after irradiation of sample at 360 nm with various time intervals, and fitted values are given in Table 4. From the results, it is observed that the relative amplitude of C-form of indolylfulgimide moiety increased whereas the relative amplitude of E-form decreased. Whereas, triazole ring show no remarkable change in relative amplitude. The observed fluorescence decay revealed that 0.1 and 1 ns corresponds to E-form and C-form of indolylfulgimide, respectively. The fluorescence lifetime of 4.2 ns for the triazole ring is unaffected during the irradiation at 360 nm. To conform, whether the absorption maxima at 510 nm correspond to C-form of indolylfulgimide moiety or CT band of triazole ring and carbonyl carbon of indolylfulgimide moiety, we have calculated the fluorescence lifetime for the same polymer on excitation at 470 nm. The fluorescence decay well fitted in biexponential function with lifetime of 1 and 2.2 ns, which corresponds to closed (C) form of indolylfulgimide and triazole ring of the polymer, respectively.

Electrochemical Studies of Polymer

Cyclic voltammograms of 2-indolylfulgide and 2-indolylfulgimide polymers were recorded 0.1 M TBAP in acetonitrile
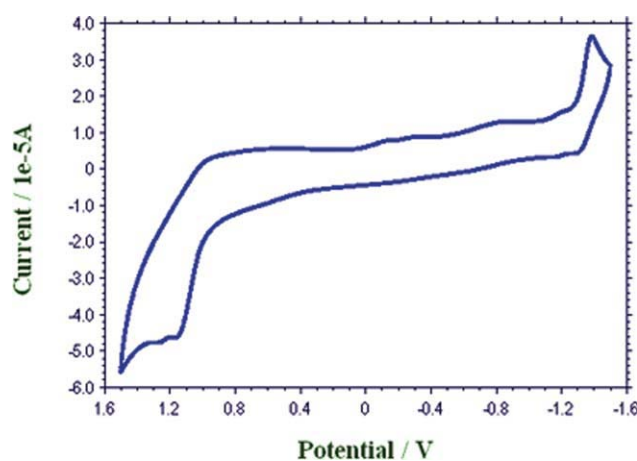
FIGURE 6 Cyclic voltammogram of open E-isomer of polymer in acetonitrile (1×10^{-3} M) and (0.1 M TBAP) on a platinum electrode (vs. Fc/Fc$^+$) with scanning rate of 50 mV s^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 7 Cyclic voltammogram of close C-isomer of polymer in acetonitrile (1×10^{-3} M) and (0.1 M TBAP) on a platinum electrode (vs. Fc/Fc$^+$) with scanning rate of 50 mV s^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
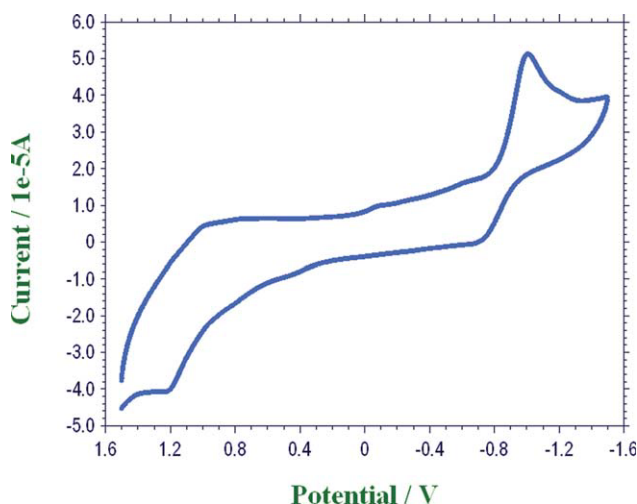
solution at a scan rate of 10 mV s^{-1} as shown in Supporting Information Figures S16, S17 and Figures 6 and 7, respectively. The open form of indolylfulgide shows no characteristic oxidative and reductive peaks. After illumination at 360 nm, the electrochemical signal arising as irreversible cathodic peak at -1.3 V was tentatively assigned to closed form of 2-indolylfulgide. While, the open form of 2-indolylfulgimide polymer shows irreversible reductive peak at -1.4 V, after illumination at 360 nm (time interval of 90 s) two new irreversible reductive peaks appeared at less positive potentials, that is, -1.2 and -0.9 V. Increasing the illumination (time interval of 180 s) at the same wavelength abruptly shows single irreversible reductive peak at -0.9 V and this indicates the formation of photogenerated closed form of indolylfulgidmide polymer. Similar observation was reported by Moriyama et al.[29] for the electrochemical cyclization of diarylethenes. As a result, on photochromic ring-closing reaction, the conversion of the 2-indolyl rings to 5,9b,10,10-tetramethyl-2-propyl-9b,10-dihydropyrrolo[3, 4b]carbazole-1,3(2H,5H)-dione would result in the decrease of the open form, giving rise to a reduced electrochemical signal arising from the open form and the formation of new cathodic peak due to the reductions of the closed form. The occurrence of these new reduction waves at less cathodic peak is in good agreement with the more conjugated nature of the nitrogen present in the fulgimide polymer. The peculiar interaction of conjugated nitrogen with light is essential for making optical devices and optical data storage applications.

CONCLUSIONS

The work summarized the synthesis of 1,2,3-triazole containing 2-indolylfulgimide polymer, which is characterized by spectral analysis. The photophysical, electrochemical, and thermal behavior were analyzed. Herein, the triazole ring present in the side chain leads to increase in the thermal stability of the polymer. In this scenario, emission spectrum of polymer interestingly shows peak maximum at 557 nm, which attributed the CT band of triazole ring to carbonyl carbon of indolyl fulgimide unit. On irradiation with 360 nm, the emission maximum was red shifted from 557 to 590 nm because of formation of photoexcited C-form. We have studied optical switching properties of this material by fluorescence lifetime techniques. On excitation at 375 nm, triexponential behavior was exhibited with lifetime of 0.1, 1, and 4.2 ns. On excitation at 470 nm, biexponential behavior was exhibited with lifetime of 1 and 2.2 ns. Cyclic voltammograms of E-form of polymer show irreversible reduction peak at -1.4 V; during photolysis, the reduction peak at -1.4 V shifted toward less cathodic peak at -0.9 V, which suggested the closed C-form of indolylfulgimide unit. Owing to interesting photophysical, electrochemical and thermal properties, these materials make them potentially useful for applications in optical storage and optical switching devices.

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