Photo and Electrically Switchable Behavior of Azobenzene Containing Pendant Bent-Core Liquid Crystalline Polymers

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ABSTRACT: New class of photo and electrically switchable azobenzene containing pendant bent-core liquid crystalline monomers (AZBM 1, 2, and 3) and their polymers (AZBP 1, 2, and 3) are reported. The synthesized precursors, monomers, and polymers were characterized by FT-IR, ¹H, and ¹³C NMR spectroscopy. Thermal stability of polymers was examined by thermogravimetric analysis and revealed stable up to 260 °C. The mesophase transition of monomers and polymers are observed through polarized optical microscopy (POM) and further confirmed by differential scanning calorimetry (DSC). The electrically switching property of monomers and their polymers were studied by electro-optical method. Among the three monomers AZBM 1, 2, and 3, AZBM 1 and 2 exhibit

INTRODUCTION Ferroelectric and antiferroelectric liquid crystals are interesting materials due to their unusual electric properties useful for modern optoelectronics, piezoelectric, pyroelectric, optical devices, and display technology.¹⁻⁴ Ferroelectric and antiferroelectric behavior is identified from bentcore (BC) molecules.^{5,6} The switching property arises due to the smectic phase of BC molecule and the switchable mesophase attributed to polar character and supramolecular chirality of the BC molecule. In addition to the polar order, if the long axes of molecules are tilted with respect to layer normal, the phase is designated as SmCP phase (where P stands for polar order). If the polar axes are the same in adjacent layers, the SmCP phase behaves to be ferroelectric (F) while the polar axes alternate from layer to layer in the ground state, SmCP is antiferroelectric (AF). These BC molecules have attracted much attention due to their interesting new type of liquid crystalline phases which have properties somewhat different from those exhibited by conventional and non-conventional liquid crystals.7-10 Bent-core molecule exhibits variety of phases (B₁-B₈), these B phases is called as banana phases, which depends on linking group, number of aromatic ring, lateral substitution, and terminal alkyl chain.^{11,12} Among them B₂, B₅, and B₇ phases are electrically switchable. In general, antiferroelectric (AF) switching and **AZBM 3** exhibits ferroelectric (F) switching behavior. On the other hand, low molecular weight polymers (**AZMP 1, 2**, and **3**) show weak AF and F switching behavior. The photo-switching properties of bentcore azo polymers are investigated using UV-vis spectroscopy, *trans* to *cis* isomerization occurs around 25 s for **AZBP-1** and 30 s for **AZBP-2** and **3** in chloroform, whereas reverse processes take place around 80 and 90 s. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 936–946

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shorter terminal alkyl chain containing BC molecules exhibit B_1 phase (Colr) and are non-switchable phase, whereas longer alkyl chain BC molecule exhibit SmCP phase (B_2 , B_7). In the B_2 phase, polar switching can be observed as AF/F switching based on polarization of the BC molecule. B_2 phase exhibits, four types of arrangements based on orientation of tilt and polarization in successive layers, results in SmC_SP_A, SmC_AP_A, SmC_SP_F and SmC_AP_F (where the subscripts S, A of C denote synclinic, anticlinic).^{13,14}

Liquid crystalline polymers (LCPs) are the hottest research topic in the field of liquid crystals. Due to their unusual properties (anisotropic, optical, electrical, and mechanical), LCPs have been used widespread in commercial applications, such as high-strength fibers, thermoplastics, displays, optical storage devices, medical application, etc.^{15–18} Among LCPs, the bent-core liquid crystalline polymers (BCLCPs) possess macroscopic polar order with variety of useful properties, such as dielectric, piezo, and pyroelectricity.^{12,19,20} Hence, the developments of BCLC material in to polymeric molecules are the interesting research topic utilitarian in potential application. In general, most of the bent-shaped polymers are reported as main-chain^{21,22} as well as side-chain polymers.^{23–25} The side-chain bent-core polymers are derived

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from 1,3-phenylene unit with five aromatic rings, symmetric²⁴ as well as asymmetric,²⁵ wherein the polymerizable functional groups are generally used as 1,3-diene,²⁶ methacrylates or acrylates group,²³ and siloxane group.²⁷ Interestingly, side-chain bent-core liquid crystalline polymer predominantly demonstrate rich mesomorphism compare with main-chain²⁸ as well as side-chain²⁹ and dendronized liquid crystalline polymers^{30–36} and which are classified as follows side-chain bent-core liquid crystalline polymer (i) (SBCLCPs),¹⁵ (ii) bent-core mesogen-jacketed liquid crystalline polymers (BMJLCPs),³⁷ (iii) central linked bent-core liquid crystalline polymer (CBCLCPs),³⁸ and (iv) hydrogenbonded side chain bent-cores liquid crystalline polymers (HBCLCPs)²⁶ were reported based on the polymeric back bone attached with position of bent-core mesogen pendant. Though BCLCs have been extensively investigated, bent-core side-chain polymers were scarcely achieved with barely detectable polar switching properties.^{23,26}

This work illustrates the novel BC monomers and their BCLC polymers, which are constructed with different linking groups such as azo, azomethine, and ester with higher alkyl chain (dodecyl spacer) on both terminal chain as well as spacer. However, none of the polymers consisting of the above linkage have so far been reported to exhibit dual switching behavior namely photo and electrically switchable liquid crystalline polymers. Bent-shaped compounds were reported to exhibit variety of mesophase like B₁, B₂, B₄, B_x, and N_{μ} with azo and azomethine linkages.^{39–43} In this article, we have focused bent-core liquid crystalline polymers (BCLCPs) and these bent-core molecules behave with respect to polymeric back-bone. The BCLCPs combined with azo and imino functional groups is an important development in the switchable material. As expected, this material is found to form banana mesophases. An imino linkages introduced in this molecule is more conducive to exhibit mesomorphism. The azobenzene is considered to be a prototype molecular switch thus the BCLCPs behave as dual switch with light as well as electric field.

EXPERIMENTAL

Materials

Solvents ethanol, methanol, dichloromethane, ethyl acetate, chloroform, and acetone were purified by the reported procedure.⁴⁴ 4-Aminophenylacetamide (Sigma-Aldrich, India), phenol, sodium nitrate, potassium hydroxide, 4'-hydroxybiphenyl-4-carboxylic acid, sodium hydroxide, potassium carbonate, hydrochloric acid (Merck, India), 4-hydroxybenzal-dehyde, 3-hydroxybenzaldehyde, resorcinol, potassium dichromate, potassium iodide, *N*,*N*-dicyclohexylcarbodiimide (DCC), benzyl chloride, palladium carbon (10%), 12-bromo-1-dodecanol, 12-bromo-1-dodecane, methacrylic acid, and 4-(dimethylamino)pyridine (DMAP) (Aldrich) were used as received.

Measurements

The infrared spectra of BCLCPs were obtained on a Perkin Elmer FT-IR spectrometer using KBr pellets. 1 H and 13 C NMR spectra were recorded on a Bruker 400 MHz spectrom-



eter in CDCl₃ with TMS as an internal standard. DSC measurements were performed at a heating rate of 5 °C/min, the monomers and polymers taken in an aluminum pan with a pierced lid, in dry nitrogen atmosphere with an empty pan as reference on TA instrument. Gel permeation chromatographic (GPC) measurements were performed with Shimadzu GPC and THF used as the eluant at a flow rate of 1.0 mL/ min. All GPC data were calibrated with polystyrene standards. The samples were dissolved in THF (10 mg/mL) and filtered through a 0.45 μ m PTFE filter before the measurements. The LC texture of monomers and polymers are observed using a Euromex polarizing optical microscope (POM) equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. Samples were placed in between two thin glass cover slips and melted with heating and cooling at the rate of 2 °C/min. The photographs were taken from cannon 1000 D camera, the spontaneous polarization (Ps) in the SmCP phase measured by a triangular wave method in a planner-aligned cell using a digital oscilloscope (Agilent, model MSO6012A) and an arbitrary waveform generator (Agilent, model 33220A) coupled with a power amplifier (Trek, model 601). The absorbance spectra of polymers were measured on a Shimadzu UV-1650 spectrophotometer using chloroform as solvent. The photoisomerization of azobenzene between the E and Z-form was carried out using a 6W high-pressure Hg lamp (Sankyo, Japan) for UV irradiation (365 nm), (Hitachi, Japan) for visible light (560 nm).

RESULTS AND DISCUSSION

Synthesis

Asymmetric BCLCPs can be synthesized from asymmetric bent-core mesogens and connected with polymerizable functional groups. Asymmetric BCLCs have fascinated in recent years, because they exhibit a new phase behavior achieved by selective cleavage of protected groups at different chemical conditions. Recently, asymmetric BCLCs were synthesized with high yield can be readily achieved with selective functional groups. In this work, three different monomers and respective of polymers were achieved to explore the structure-property relationship effect on mesophase. The three different BCLC monomers are constructed based on number and nature of aromatic ring; asymmetry is introduced in the bent-core molecules using different linking groups such as azo, azomethine, and ester linkage. Here, asymmetric bent-core mesogens is connected with polymeric back-bone through dodecyl spacer as well as terminal chain. The synthesis of three different monomers and respective polymers is shown in the Schemes 1, 2, and 3. The detailed synthetic procedure of precursors, monomers, and polymers are given in Supporting Information. Since the monomers have poor solubility in methanol, normal precipitation process is not sufficient to remove unreacted monomers. Further purification was achieved by using the column chromatography technique and dried in vacuum over P2O5 at 70 °C for 24 h. Chemical structures of these monomers and polymers were confirmed with ¹H and ¹³C NMR analysis, the characteristic resonance of the vinyl group around



 $\label{eq:constraint} \begin{array}{l} Reagent: i) \ NaNO_2 / \ HCI, \ 0^\circ C, NaOH; \ ii) \ K_2CO_3 / \ KI \ / \ Acetone \ / \ Bromododecanol; \ iii), \ HCI \ / \ EtOH \ / \ reflux; \ iv) \ K_2CO_3 / \ KI \ / \ Acetone; \ v) \ DCC \ / \ DMAP \ / \ DCM; \ vi) \ Jones \ reagent; \ vii) \ Pd \ / \ C \ / \ EtOAc; \ viii) \ HCI \ / \ EtOH \ / \ reflux; \ ix) \ TEA \ / \ THF; \ x) \ AIBN \ / \ THF \ / \ 60^\circ C \end{array}$

SCHEME 1 Synthetic route of AZBM-1 and AZBP-1.

6.09 and 5.53 ppm can be clearly seen is assigned to methacryl protons of each monomer. BCLCPs were successfully synthesized using free radical polymerization method from its monomer. The vinyl group proton is vanished after polymerization broad resonance signal around 1.69 ppm assigned to resonance signal of side-chain methylene protons, whereas the JOURNAL OF POLYMER SCIENCE Chemistry





SCHEME 2 Synthetic route of AZBM-2 and AZBP-2.

signal at 2.10 ppm in all monomers corresponds to methyl protons, shifted up field to 0.88 ppm in the polymers confirming the completeness of polymerization reaction. All the synthesized monomers and polymers are soluble in DMF, DCM, CHCl₃, partially soluble in acetone and insoluble in ethanol, methanol, and benzene.

Mesomorphic Properties of the Monomers and Their Polymers

The transition temperature of BCLC monomers and polymers are observed by DSC and phase transition confirmed by POM. On cooling from the isotropic phase, the monomers (**AZBM-1, 2**, and **3**) exhibit SmCP textures with fluid likes mesophases. Figure 1 depicts the mesomorpic properties of monomers (**AZBM 1-3**). The **AZBM-1** evidences filamentary pattern with banana leaf-like texture which is highly fluid mesophases with mesophase transition higher than the other monomers²² and indicating that **AZBM-1** was constructed with six-aromatic ring and other monomers (**AZBM 2** and **3**) were constructed by five-aromatic ring. The monomer (AZBM-2) exhibit SmCP with fluid like mesophase on heating but the filamentary growth pattern with strips and ribbons with fringe pattern (SmCP) was observed during cooling from isotropic^{23,45} and revealed that AZBM-2 is enantiotropic in nature. The AZBM-2 indicates somewhat lower mesophase transition temperature than AZBM-3. Though AZBM-2 and 3 monomers are five-ring system, the presence of biphenyl moiety in the AZBM-3 is responsible for higher transition temperature when compared with AZBM-2.

During heating **AZBM-3** demonstrated a banana leaf-like texture. While cooling, filamentary like pattern was developed from droplet in isotropic phase, filamentary texture was transformed into broken fan like texture (SmC)²² and further cooling no phase transition, except crystallization which is depicted in Figure 1(a,b). All three monomers exhibit SmCP mesophase with different transition temperature depends on number and nature of aromatic ring in the bent-core molecules and terminal alkyl chain lengths.^{12,23,46,47} From POM study, all the polymers (**AZBP-1**, **2**, and **3**) exhibited grainy





Reagents i) Ethanol / Con H₂SO₄ / reflux; ii) K₂CO₃ / KI / Bromododecane / DMF; iii) KOH / Ethanol / reflux; iv) DCC / DMAP / DCM; v) Ethanol / reflux; vi) TEA/THF; vii) AIBN/THF/60 °C

SCHEME 3 Synthetic route of AZBM-3 and AZBP-3.

like texture while cooling from the isotropic phase at a rate of 5 $^{\circ}$ C/min. as shown in Figure 2.

The polymers **AZBP-1**, **2**, and **3** depict grainy or thread like texture can also be viewed in small birefringence domains when compared with their monomer texture and the domain sizes in polymers are much lesser due to the high viscosity of the polymeric materials. The **AZBP-1** grainy/threaded is fluid like mesophase when compared with other polymers, the high viscosity of the polymeric materials is attributed

more number of aromatic ring (six ring) where as other polymer has five-ring system.^{22,23} The monomers and polymers display different mesophase and transition temperature and these depends on structure-property of the molecules might be influenced by nature of central-core, number of aromatic ring and the chain length.

Figure 3 indicates the DSC thermograms of **AZBM-1**, **2**, and **3** measured at the rate of 5 $^{\circ}$ C/min for first heating and cooling. All the monomers indicate two transition peaks during



FIGURE 1 POM microphotograph SmCP phase is observed for monomers (a) **AZBM-1** at 101 °C, (b) **AZBM-2** at 95 °C, (c) **AZBM-3** at 100 °C, and (d) SmC phase with broken fan like texture of AZBM-3 at 100 °C.

heating and cooling cycle, which is suggesting that all the monomers are enantiotropic in nature. Here, the lower temperature and higher temperature peaks correspond to crystalliquid crystal transition (T_m) and liquid crystal-isotropic transition (T_c) , respectively. LC texture of SmCP phase of these monomers confirmed by electro-optical experiment and phase transition temperatures and enthalpies value are summarized in Table 1. The polymers also show two transition peaks $T_{\rm m}$ and $T_{\rm c}$. Apart from this, a weak glass transition could be observed at 60-70 °C which is shown in Figure 4 and DSC analysis reveals that polymers are enantiotropic in nature. The phase transition temperatures of the polymers are summarized in Table 2. The mesophase transition temperature of polymer (AZBP-1) has shown slight difference between the other polymers of AZBP-2 and 3. The three polymers follow similar mesophase transition temperature trend as that of their monomers (AZBM-1, 2, and 3).

Thermal Stability of Polymers

The thermal stability of the polymers (**AZBP-1**, **2**, and **3**) were evaluated using TGA at a heating rate of 20 °C/min and depicted in the Figure 5. The corresponding data of polymer **AZBP-1**, **2**, and **3** are listed in Table 2. The azobenzene polymers indicate 10% weight loss around at 290–360 °C and 50% weight loss at 390–435 °C indicating their good thermal stability. The results disclosed that the polymers were stable up to 260 °C and fol-

lowed "three-stage" decomposition; the decomposition might be started with cleavage of azomethine, then cleavage of azo group ascribed from evolution of nitrogen gas and final stage decomposition ascribed to the pyrolytic cleavage of ester linkage of the aromatic backbone.⁴⁸ The decomposition of the polymers was almost completed at 700 °C and no further weight loss was observed. The thermal stability of the polymers increases in the order of AZBP-1> AZBP-3>AZBP-2. The presence of number of aromatic ring and biphenyl were expected to introduce rigidity into the polymer which consequently bring up the thermal stability. If the number of ring increases in AZBP-1 rigidity increases and is thermally stable when compared with other five-aromatic ring polymers AZBP-3>AZBP-2, among this AZBP-3 shows somewhat higher stability which is due to the presence of biphenyl moiety present in the polymer. The char yield was calculated by measuring the amount of residual substance present at 700 °C during the TGA analysis. The results of TGA data revealed that azobenzene-based polymers exhibited high thermal stability and char yield (Table 1).

Electro-Optical Investigations of Monomer and Polymer

The investigation on electrical-switching behavior of monomers **AZBM-1**, **2**, and **3** were subjected to electrical field using electro-optical method. The **AZBM-1** is filled with transparent sandwich type ITO cell (indium-tin oxide -coated glass plates) with thickness 8 μ m and sample filled by





FIGURE 2 POM microphotograph of grainy/ threaded like texture is observed for polymers (a) **AZBP-1** at 120 °C, (b) **AZBP-2** at 105 °C and (c) **AZBP-3** at 110 °C.

capillary action in isotropic phase and cooled slowly from the isotropic phase (1 °C per min.). The current responses were measured across a 1 k Ω resistance under a triangular wave voltage of 70 V and frequency of 75 Hz. The filamentary texture patterns of SmCP phase is transformed to a broken-fan texture while applying A.C. electric field and this fan texture remains even after removal of electric field, which clearly indicates the presence of spontaneous polarization in the smectic layers and the polarization tends to align along the applied electric field in the SmCP phase. Two polarization current peaks per half cycle were observed at a very low threshold voltage, if the voltage is increased, the peak



FIGURE 3 DSC thermograms of monomers (AZBM-1, 2, and 3).

intensity increases and the field induced transition are reversible indicating the antiferroelectric switching (SmCP_A) as exhibited in Figure 6(a). The similar electro-switching responses found in **AZBM-2** [Fig. 6(b)], all these observations are quite similar to those obtained for the SmCP_A.^{12,23,49}

Similarly, the **AZBM-3** was filled in an ITO cell with a thickness of 7.5 μ m is then subjected to electric field. The current response of **AZBM-3** was measured under a triangular wave voltage of 40 V and frequency of 75 Hz which results the single polarization current peaks per half cycle were observed even at low frequency. This indicates the ferroelectric-switching behavior of mesophase.^{50,51} The switching current response trace obtained for **AZBM-3** is displayed in Figure 6(c). It is noteworthy to mention that while comparing the polarization current profiles, compounds **AZBM-1**, **2** demonstrates antiferroelectric-switching behavior; on the other hand, **AZBM-3** establish ferroelectric switching behavior depends on structure-property of the molecules influenced by nature of central-core, number of aromatic ring and the



FIGURE 4 DSC thermograms of the polymers (AZBP 1, 2, and 3).

TABLE I Phase Transition Temperature (*T* in °C) of Monomers (**AZBM-1–3**) by DSC

		DSC (°C)							
Monomer Code	Cr		SmCP		lso				
AZBM-1	*	97.9 [15.2]	*	112.8 [15.9]	*				
AZBM-2	*	76.9 [15.9]	*	101.4 [17.4]	*				
AZBM-3	*	91.8 [36.8]	*	105.9 [09.4]	*				

Cr, crystalline phases; SmCP, polar smectic C phase; lso, lsotropic phase; "*" phase exists.

chain length. The switching current response trace obtained for **AZBM-1** and **2** is testified in Figure 6(a,b). The spontaneous polarization (*Ps*) of **AZBM-1** and **2** are measured from its switching current of their SmCP phase and found to be 90, 109 nC/cm². It was observed that all the monomers (**AZBM-1**, **2**, and **3**) are prone to polymerize under the A.C. electric field and, hence, all the data were measured using freshly prepared cells, and the measurement time was limited to be <5 min.²³

Electro-optical investigations of polymers were also carried out in similar ITO cells as previously discussed. The AZBP-1 is filled in ITO cell there is no change in LC texture when observed using POM during applying electric fields at low voltage, if increasing electric-field above 110 V, a very weak switching behavior is observed. The polarization current of AZBP-1 in response to an applied triangular-wave field shows two small humps per half wave function [Fig. 7(a)], indicating perhaps an antiferroelectric switching behavior. Most of the LCPs did not switch upon applying electric field while weak switching behavior was observed in low molecular weight polymers. AZBP-2 also shows electrical switching responses with weak antiferroelectric behavior [Fig. 7(b)].²³ Similarly, electrical switching experiment was carried out on AZBP-3 which shows ferroelectric switching behavior [Fig. 7(c)]. The ferroelectric behavior of AZBP-3 is found from presence of one small hump per half cycle when applied electrical field. All these observations were quite similar to those obtained for the SmCP mesophase exhibited by the polymers.^{26,29,50-52} Whereas in the low intensity of the switching humps indicates that not all the molecular dipoles were switched during the electro-optic measurement because of high viscosity of the polymer samples.23



FIGURE 5 The thermal stability of the polymers (AZBP-1, 2, and 3) were evaluated using TGA at a heating rate of 20 $^{\circ}$ C/ min.

Photo-Switching Studies of Bent-Core Monomer and Its Polymer

The photo-switching property of AZBP-1 was performed in chloroform using UV-vis spectroscopy with absence and presence of UV light illumination. The absorption spectra of azobenzene containing bent-core polymers (AZBP-1, 2, and 3) are pictured in Figure 8. The absorption spectra of AZBP-1, 2, and 3 shows three absorbance maxima at 256–261 nm, 366-367 nm, and 446-447 nm, respectively. The strong absorbance in the UV region at 366-367 nm corresponds to π - π * transition of the E isomer and a weak absorbance in the visible region at 446–447 nm represent to $n-\pi^*$ transition of Z isomer.^{28,33,53-56} The absorption maximum at 264 nm is not important in photo-switching, remaining two absorption peaks were considered for photoisomerization processes. The AZBP-1 is illuminated using UV light with 365 nm at different time intervals and the absorption spectra were immediately recorded. The absorption maximum at 366 nm slowly diminishes whereas the absorption maximum around 446 nm gradually increases, which indicates that E isomer transformed to Z isomer. After 30 s illumination, there is no remarkable change in absorption spectrum which confirms the saturation of $E \rightarrow Z$ isomerization processes. The existence of photoisomerization is further confirmed by two isobestic points existed at 327 and 435 nm.^{28,38,55,56} Figure 8 shows the E/Z photoisomerization of AZMP-1- 3 upon exposure of UV light. The photoisomerization of AZMP-1 takes

TABLE 2 Thermal Property, Molecular Weight, and Absorption Maxima of Polymers (AZBP-1-3)

Polymers	Yield (%)	Tg	T _m	T _c	T _d	Char yield at 700 °C (%)	$ar{M}_{\sf n}$	$ar{M}_{w}/ar{M}_{n}$	λ max (nm) in chloroform	λ max (nm) in film
AZBP-1	74	77	107.7	129.1	273	19	11, 143	1. 31	366, 446	366
AZBP-2	75	70	94.5	113.6	260	11	11, 742	1.57	366, 446	366
AZBP-3	70	74	100.7	122.2	265	15	9,979	1. 26	367, 447	367

 T_{gr} glass transition temperature; T_m , melting temperature; T_c , clearing temperature; T_d , decomposition temperature; \overline{M}_w , weight-average molecular weight; \overline{M}_n , number-average molecular weight; $\overline{M}_w/\overline{M}_n$, molecular weight distribution.





FIGURE 6 Switching current response of monomers. (a) **AZBM-1** observed at 105 °C, 70 V, 75 Hz, (b) **AZBM-2** observed at 95 °C, 40 V, 75 Hz, the occurrence of two peaks in each half period of the applied triangular wave is an indication of an antiferroelectric switching, and (c) **AZBM-3** observed at 95 °C, 40 V, 75 Hz, the presence of one peak is indication of an ferroelectric switching.

place at 30 s whereas other polymers **AZMP-2** and **3** take place at 35 s. Here, the **AZMP-1** has six-member ring and other polymers has five-member ring. Generally, six-member ring system is rigid in nature which can undergo easy photoisomerization when compare with five-ring system. Whereas **AZMP-2** and **3** shows similar photoisomerization attributed that both are five-ring system with similar structure. The photoisomerization studies reveal that the **AZMP-1** shows somewhat faster photoisomerization than other polymers. The time taken for photoisomerization depends on the nature of linking group (electron withdrawing group/donating group) and size of the substituent in the azobenzene moiety.^{38,43,48,53}

The reversible photoisomerization behaviors of BCLCPs are observed using visible light illumination or keeping the solution in dark. The resultant solution (Z isomer) of all the BCLCPs is placed in the dark environment; the absorption band in the range of 366–367 nm was regained slowly attributed to the slow thermal *cis* to *trans* back isomerization of azobenzene unit at ambient temperature in dark, this well-known processes of the thermal back reaction confirms the BCLCPs are thermally reversible behavior. Similarly, the Z isomer of **AZBP-1** sample were irradiated with 560 nm visible light which causes the *cis* to *trans* back isomerization very rapidly compared with that at ambient temperature in dark.^{28,38,56} The time required to recover the original state

upon illumination with 560 nm visible light are 80 s for **AZBP-1** and 90 s for **AZBP-2** and **3**. The photoisomerization studies reveal that BCLCPs show *trans* to *cis* photoisomerization take place at 30, 35, and 35 s whereas reversible processes take place at 80, 90 and 90 s. The bent-core monomers and polymers exhibit very strong photoisomerization phenomena with UV as well as visible light illumination and also thermally reversible.

Recently, the researchers focus their attention on solid film to show the photo-switching property for commercial exploitation. Faster photoisomerization and thermal stability is a crucial parameter for the creation of storage devices in solid samples. Hence, the UV-vis spectroscopic properties of the synthesized polymers were investigated in thin film for polymer AZBP-1-3. Figure 8(d) shows the absorption spectra of polymer (AZBP-1) in thin film. The thin film of polymer shows an absorption band at 366 nm nearly same as in solution phase at 365 nm. The polymer film irradiated with 365 nm UV light, the decrease in absorption at 366 nm was observed ascribed to E to Z isomerization at 80 s. After reaching photo-stationary state, the film was irradiated with 560 nm visible light and absorbance increase at 366 nm, there is no remarkable change after 110 s at 450 nm and confirms the photoisomerization processes. The existence of photoisomerization is further confirmed by two isobestic points existed at 328 and 433 nm.^{28,38,55,56} Similarly, other



FIGURE 7 Switching current response of polymers (a) **AZBP-1** observed at 105 °C, 110 V, 75 Hz, (b) **AZBP-2** observed at 95 °C, 110 V, 75 Hz, presence of two small hump is an indication of an antiferroelectric switching, and (c) **AZBP-3** observed at 95 °C, 110 V, 75 Hz, the presence of one small hump or peak is indication of an ferroelectric switching.



FIGURE 8 The absorption spectra of azobenzene containing bent-core polymers (a) AZBP-1, (b) AZBP-2, (c) AZBP-3 polymers in solution, and (d) AZBP-1 in thin film were recorded with different exposure time of UV light. 0 s corresponds to absence of UV light illumination

polymers indicate *trans* to *cis* photoisomerization at 90 s whereas reverse processes take place at 120 s. The time taken to attain the photo-stationary state in thin film is high when compared with that in solution phase indicating that steric effects play a vital role in thin film.^{28,29,57}

CONCLUSION

We have demonstrated the synthesis, mesomorphic, photoand electro-optical properties of asymmetry BCLCMs and its BCLCPs. All the monomers and polymers evidence liquid crystalline phases; the **AZBM-1** and **2** show SmCP phase with antiferroelectric switching (AF) behavior whereas **AZBM 3** exhibit SmCP phase with ferroelectric switching (F) behavior. Similarly, the polymers exhibit grainy like texture and display weak AF and F switching behavior compared with respective of monomers. The monomers and polymers proves thermal properties in the following order of **AZBM-1**> **AZBM-3**>**AZBM-2** and **AZBP-1**> **AZBP-3**>**AZBP-2**, respectively. The photo-switching properties polymers were carried out in solution as well as film. **AZBP-1-3** indicate *trans* to *cis* photoisomerization take place at 30, 35, and 35 s whereas reversible processes occurred at 80, 90, and 90 s in chloroform. Our investigations revealed that the thermal properties as well as the photochromic properties of these azo-substituted polymers vary as the number and nature aromatic ring present in the polymers. The photo- and electro-optical switching behavior of these BCLCPs might be exploited in the field of optical data storage device, molecular switches, and pyroelectric materials.

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