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Side-chain Polysiloxane Liquid Crystalline Elastomers from Non-mesogenic Components[†]

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ABSTRACT

Synthesis and characterisation of two new azo-based polysiloxane elastomers containing nonmesogenic monomer and different cross-linkers are described. The chemical structure of the synthesised compounds was confirmed through standard analytical techniques. Remarkably, both the elastomers displayed mesophase, despite the monomer and the cross-linker being nonmesogens. The mesophase was characterised by a combination of differential scanning calorimetry, polarising optical microscopy and X-ray diffraction experiments. The X-ray diffraction studies revealed an intercalated lamellar structure for the mesophase. Interestingly, the elastomer containing biphenyl-based cross-linker showed mesophase with an extended thermal range compared to the mesophase displayed by its counterpart containing phenyl-based cross-linker. The photoisomerisation behavior of the elastomers in solution and photoswitchable property in the solid state have been investigated. The monodomain sample of the elastomer showed a reversible, asymmetric bending and unbending behavior upon exposure to UV and visible light respectively, with a faster response time.

INTRODUCTION

During the last decade, there has been an increasing interest in the synthesis of liquid crystal elastomers (LCEs) that combine the anisotropic properties of liquid crystals as well as elasticity of polymeric materials.^{1, 2}Significance of the LCEs was first predicted by de Gennes³, since then a large number of LCEs have been synthesised by several methods. The anisotropic network of the LCEs can be formed *via* cross-linking from various liquid crystalline polymers (main-chain, side-chain and combined polymers) with reactive groups. Among these, side – chainLCEs were found to exhibit wider mesophase range at low temperatures as compared to main – chain LCEs which show higher clearing temperatures and crystallize faster due to the rigid rod – like mesogenic moieties.⁴Mainly two synthetic routeshave been followed to prepare the side-chain LCEs namely-free radical polymerisation of acrylic type monomer ⁵ and hydrosilylation of terminal alkene with linear poly[(methylhydro)siloxanes] or polymer systems with reactive Si-H bonds.^{6,7}The most commonly used technique is siloxane chemistry which was introduced by Finkelmann and his co-workers. In this synthesis, the linear polymer backbone is coupled with the monomer and cross-linker (CL) agent in a single step. This reaction is platinum catalyzed, which results in the grafting of vinyl-terminated monomer and divinylicCL moieties to Si-H bonds of polysiloxane network.⁶A huge variety of LCEs with different monomers and CLs have been reported by this method namely end-on mesogens⁸, side-on mesogens⁹⁻¹¹, photosensitive side groups¹² and main-chain polymers¹³.

In this paper, attention was devoted to the synthesis of new side-chain liquid crystal elastomers (SCLCEs) in which the monomer and CL are attached sideways to the polymer backbone. Among various backbones, polysiloxane backbones are interesting due to their flexibility, low glass transition temperature and more importantly they do not hinder the ordering

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of the attached LC's and enable the formation of LC phases at ambient conditions.¹⁴ Further, incorporation of photochromic moieties as monomer in the LCEs will offer the advantage of studying the light induced structural changes in the elastomer. Azobenzene is the most widely used chromophore due to their interesting *trans*-to-*cis* isomerisation by shining UV light and back conversion to the thermodynamically stable *trans* state by shining higher wavelength of light.¹⁵ There are only a few reports on SCLC elastomers which contain a photoresponsive azo moiety either in monomer or CL or in both. These elastomers were prepared either via free radical polymerization in presence of a thermal initiator^{16 - 18}or through hydrosilylation reaction using a suitable catalyst^{19,20}. The other examples for the synthesis of SCLCEs using a poly(hydrosiloxane) backbones are mentioned below. Finkelmann and his co-workers have described a series of oriented LCEs containing polymethylhydrosiloxane (PMHS) backbone, mesogenic monomers and cross-likers.^{6,9,10} Similarly, Ying Jiang group reported PMHSbased chiral smectic side-chain LCEs, in whichdosage of the cross-linking agent influenced the thermal and mesophase behavior of the elastomers.^{21,22} Further, same group has described the azocontaining chiral polysiloxane LCEs in which the cholesteric polysiloxanes were obtained by reacting cholesteric monomer and phenolic hydroxyl monomer in different ratios with polysiloxanes.²³ After that the chiral azo – containing polysiloxane LCEs were synthesised by esterifying cholesteric polysiloxane with acyl acid of azo diacid. Introducing azo as a crosslinking agent into the polymer network was found to increase the thermal stability. Aditya Agrawal and co-workers have reported a nematic LCE containing PMHS backbone, vinylterminated monomer and a resorcinol-based spacer (11UB) as a CL.²⁴ Additionally, Wandet al. described azo containing polysiloxane based side-chain LCE in which two mesogenic monomer units along with 11UB CL were attached side – on to the PMHS backbone.²⁵ It is interesting to

point out here that most of these reported LCEs contain mesogenic monomer ^{6,9,10,24,25} and in few examples both monomer and CL are mesogens^{21,22}.

Herein, we describe the synthesis of two new polysiloxane SCLCEs which displayed a lamellar liquid crystalline phase despite the monomer and the CL being non-mesomorphic in nature. These SCLCEs contain a same azo-based monomer but differ in cross-linking units. A phenyl centered di-vinyl terminated-CL was used to obtain LCE_1 , while a biphenyl core containing CL was employed in the synthesis of LCE_2 . Synthesis, characterisation, mesomorphic and photo-isomerization behavior of the elastomers LCE_1 and LCE_2 are presented below. Additionally mono-domain LCE sample was also prepared and its photo-actuation behavior was investigated.

EXPERIMENTAL

MATERIALS

Polymethylhydrosiloxane (PMHS $M_w = 1900$)was purchased from Alfa Aesar. 4phenylazophenol, 4, 4'-biphenyldiol, hydroquinone,Karstedt's catalyst (platinum (0)-1, 3divinyl-1,1,3,3 tetramethyldisiloxane complex solution in xylene) and 11-bromo-1-undecene were purchased from Sigma Aldrich and used without purification. Potassium carbonate (K₂CO₃)andpotassium iodide(KI) were purchased from commercial suppliers and used asreceived. The solvents used in the synthesis namely dichloromethane (CH₂Cl₂) and toluene were of analytical grade. As receivedsolvents were dried over molecular sieves (4Å, 1-2mm from Alfa Aesar). All the intermediate compounds were purified by column chromatography on silica gel (60-120 mesh) followed by repeated crystallization.

INSTRUMENTATION AND TECHNIQUES

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Chemical structure of all the synthesised compounds was confirmed through fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopy. FT-IR spectra were recorded using FT/IR-4600 typeA spectrophotometer using KBr pellets. ¹H NMR spectrawererecorded with a Bruker Avance 400 MHz spectrometer (Bruker, Switzerland) using tetramethylsilane (TMS) as an internal standard. Optical properties and phase transition temperatureswere studied through polarising optical microscopy (POM) and differential scanning calorimetry (DSC). DSC measurements were carried out using Perkin Elmer DSC(DSC 6000, Perkin Elmer, US) at a heating rate of 5°C/min and 10°C/minunder a nitrogen atmosphere. The mesomorphic properties were examined using Olympus BX50 POM (Olympus Co., Japan) equipped with a Linkam LTS 420E (Linkam, UK) heating stage with T95-HS Link controller. Xray diffraction studies (XRD) on powder samples were carried out using Panlaytical X'Pert Pro 2008, using Cu-K_q(λ =1.54Å) radiation. The diffraction patterns of the sample were collected on a fast high resolution PIXCEL solid state multichannel detector. Thermal stability of the elastomerswas investigated using PerkinElmer STA 6000 (Waltham, USA)simultaneous thermal gravimetric analyzer (TGA).Photo – isomerisationbehavior of the monomer & elastomers was analysed using Shimadzu UV-2401 PC (Shimadzu Corporation, Japan) UV-Visible spectrophotometer. UV-Vis spectra were recordedusing dilute solutions of the samples in toluene by employing a cuvette of 1cm path length.

Synthesis of monomer, 1-Phenyl-2(4-(undec-10-en-1-yloxy) phenyl)diazene (M)

A mixture of 4-phenylazophenol (5g, 25mmol),anhydrous $K_2CO_3(17.388g, 125 mmol)$ and KI (0.62g, 3.8mmol)in dry butanone (200 ml) was stirred for 30min at 80°C. Thereafter, 11-bromo-1-undecene(6.63 ml, 30.24mmol)was added and heating was continued for an additional 18h until the reaction was complete which was confirmed throughthin layer chromatography (TLC).

The solution was cooled to room temperature and filtered. The solvent from the filtrate was evaporated and the residue obtained was purified through column chromatography on silica gel usinghexane/ethyl acetate mixture (9:1) as an eluent. The product thus obtained on removal of the solvent was further purified by crystallization using ethanol to yield orange crystals as a pure product;(Yield: 71%, m.p. 71°C).**FT-IR** (KBr) v_{max} : 3070, 2920,2849, 1640, 1582, 1502, 1465, 1252, 1110-1000, 980-810 and 685cm⁻¹. ¹H **NMR** (500 MHz, CDCl₃) $\delta_{(ppm)}$ 7.91 – 7.90 (d, ³*J* = 8.5Hz, 2H, Ar-H), 7.88 -7.86 (d, ³*J* = 7.0Hz, 2H, Ar-H), 7.49 (t, ³*J* = 7.0Hz, 2H, Ar-H), 7.44 - 7.42(d,³*J* = 7.0Hz, 1H, Ar-H), 7.00 - 6.98 (d, ³*J* = 8.5Hz, 2H, Ar-H), 5.9-5.7 (m, 1H, -CH=CH₂), 5.1-4.9 (m, 2H, -CH=CH₂), 4.02 (t, ³*J* = 6.0Hz, 2H, Ar-O-CH₂), 2.25-2.04 (m,2H, -CH₂-CH=CH₂), 1.9-1.75 (m, 2H, Ar-O-CH₂-CH₂-), 1.49-1.25 [(m,12H, (-CH₂-)₆].

UV-Vis (toluene): $\lambda_{max} = 348$ nm(π - π * transition) and 444nm(n- π * transition)

Synthetic route to the olefinic monomer along with IR, NMR spectra and a DSC thermogram recorded for the monomer are provided in Electronic supplementary information (ESI)[†] (Scheme S1, Fig. S1-S3)

Synthesis of cross–linker, 1,4-bis (undec-10-enyloxy)-benzene (11UB)(C₁):

The **CL-C**₁was synthesized following a scheme shown in S2 (†ESI).Typically,a mixture of hydroquinone (5g, 45mmol), K₂CO₃ (62g, 450mmol) and KI (1g, 6.8mmol)in 250 ml dry butanone was heated to reflux. A solution of 11- bromo-1-undecene (22ml, 99mmol) was added drop-wise to the reaction mixture and refluxing was continued for further 18h. Thereafter excess butanone was distilled off and the remaining mixture was extracted with CH₂Cl₂.The organic layer was washed with 5% sodium hydroxide solution (2 x 100ml), water (2 x 100ml) and then dried over anhydrous magnesium sulfate. Following this, solvent from the organic extract was

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59 60 evaporated to obtain a residue which was purified by column chromatographyusing CH₂Cl₂as an eluent to give C₁ as a white solid; (Yield: 35%, m.p. 60°C). **FT-IR** (KBr) v_{max}: 3079, 2918, 2850, 1642, 1509, 1469, 1236, 1110 - 1000, 910 and 824cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ(ppm): 6.82 (s, 4H, Ar-H) 5.86-5.75 (m, 2H,-CH=CH₂), 5.02-4.92 (m, 4H, -CH=CH₂), 3.89 (t, ${}^{3}J$ = 10.0Hz, 4H, Ar-O-CH₂-), 2.08-2.01 (m, 4H, -CH₂-CH=CH₂), 1.8-1.6 (m, 4H, Ar-O-CH₂-CH₂-), 1.43-1.31 (m, 24H, (-CH₂-)₁₂). The FT-IR, NMRspectraand a DSCthermogram recorded for C₁ are presented in Fig S4 – S6 ⁺. Synthesis of cross-linker, 4,4'-bis(undec-10-en-1-yloxy)-1,1-biphenyl(BP)(C₂): The synthetic pathway followed to obtain CL-C₂ is provided in Scheme S3[†]. A mixture of 4'-biphenyldiol (3g, 16.1mmol), anhydrous K₂CO₃ (22.218g, 161mmol), KI (0.4g, 4. 2.4mmol)and powdered molecular sieves (4Å, 2g)in dry butanone (150 ml) was heated to reflux. A solution of 11-bromo-1-undecene (8.84ml, 40.3mmol) was added slowly to the reaction mixture and the resulting solution was heated under reflux for an additional 18h.After that, reaction mixture was filtered, solvent from the filtrate was evaporated and the residue obtained was purified through column chromatography on silica gel usingCH₂Cl₂as an eluent. Evaporation

of the solvent from the eluate provided a material which was crystallised using acetonitrile to yield white crystals as the pure product (Yield: 48%,m.p. 105 °C.). **FT-IR** (KBr) v_{max} : 3080, 2920, 2850, 1642, 1500, 1473,1249, 1110, 1000, 911 and 825cm⁻¹.¹H **NMR** (400 MHz, CDCl₃) δ (ppm):7.49 – 7.47 (d,³*J*= 8.8Hz, 4H, Ar-H), 6.97 – 6.95 (d, ³*J* = 8.8Hz 4H, Ar-H), 5.9-5.8 (m, 2H, -**CH**=CH₂), 5.1-4.9 (m, 4H -CH=**CH**₂), 4.0 (t,³*J* = 6.4Hz, 4H, Ar-O-**CH**₂-), 2.2-2.0 (m, 4H, -**CH**=**CH**₂), 1.9-1.8 (m, 4H, Ar-O-**CH**₂-**CH**=**CH**₂), 1.6-1.2 (m, 24H (-**CH**₂-)₁).

The FT-IR, NMR spectra and DSC thermogramobtained for C₂are provided in Fig S7 – S9 ⁺.

Synthesis of poly-domain liquid crystal elastomers(LCE₁ and LCE₂):

LCE₁ was prepared using the azo monomer (**M**) and the bifunctional cross - linker CL-(**C**₁) which were simultaneously attached to a highly flexible polysiloxane backbone through hydrosilylation reaction. The azo monomer**M**(0.5g, 1.4mmol) was dissolved in dry toluene (50ml). To this stirred solution, CL-**C**₁(0.05g, 0.1mmol) and **PMHS** (0.085g, 0.05mmol) were added. The reaction mixture was heated to 65°C under nitrogen atmosphere and 40µL of Karstedt's catalyst (in xylene) was injected. The solution was stirred at 65°C under nitrogen atmosphere until the Si-H absorption peak of PMHS at 2172 cm⁻¹ disappearedcompletely, which was monitored through IR spectroscopy. Thereafter, the yellow-colored solid residuewas collected by repeated precipitation with methanol and then dried under vacuum. (Yield: 63%, m. p. 45°C). **FT-IR** (KBr) v_{max} : 3028, 2919, 2836, 1602, 1512, 1432, 1087, 1027, 890 and 840 cm⁻¹

A similar procedure was followed to synthesise LCE₂, in which CL- C_2 was used as a cross – linking agent in place of CL C_1 .

(Yield: 58%, m.p.46°C).**FT-IR** (KBr) v_{max} : 3028, 2920, 2869, 1612, 1493, 1438, 1079, 1030, 895 and 840 cm⁻¹

A schematic representation of the synthesis of LCE₁& LCE₂ is shown in Scheme1.

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SCHEME 1Schematic representation of synthesis of elastomers, LCE₁& LCE₂

Synthesis of mono-domain LCE

Mono-domain LCE was prepared following a procedure described by Finkelmann⁸. A schematic representation of the preparation of the mono-domain LCE film is shown in Scheme 2. In a typical procedure, the reaction mixture containing azo monomer (0.55mmol), **CL-C2** (0.053mmol) and backbone **PMHS** (0.60mmol) were dissolved in 2ml of toluene. After an ultrasonication process for an about 3-4 min to ensure a homogeneous dispersion, the mixture was cast into a polytetrafluoroethylene (PTFE) mold. Thereafter appropriate amount of Pt-catalyst solution was added into the reaction mixture. The mold was ultra-sonicated for another 5 min to remove air bubbles entrapped in the mixture and then placed in an oven pre-heated to 60°C for 2h to complete the first cross-linking step. After this cross-linking step, the mold was cooled to room temperature and the film was peeled off carefully. This film was dried at ambient condition

for an overnight. Then the film was stretched with a load of about 1.098g at 60°C for 48h and at 150°C for 24h to complete the second cross-linking as shown in the Scheme 2.



SCHEME 2 Schematic representation of synthesis of mono-domain LCE

RESULT AND DISCUSSION

Two new polysiloxane-based LCEs containing an azo monomer but different crosslinking groups are described.LCE₁ contain a phenyl-based CL (C_1) whereas LCE₂ has a biphenyl core in the CL (C_2). Both the monomer and the CLs have terminal vinyl groups and the corresponding elastomers were prepared by grafting these to a siloxane backbone through a hydrosilylation reaction (Scheme1). Interestingly, both of these elastomers displayedmesomorphism despite the monomer and the CLs being non-mesogens. Chemical

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structure of M, C_1, C_2 and the elastomers was confirmed through FT-IR, ¹H NMR and UV-Visible spectroscopic techniques. Thermal properties and mesomorphic behaviour of the elastomers wereinvestigated by TGA, DSC, POM and XRD studies.

Structural characterisation of LCEs:FT-IR and NMR spectra

FT-IR spectra of LCE₁ and LCE₂ with reference to PMHSare shown in Fig. 1(a) and (b) respectively. Polymer PMHS displayed a characteristicvibrational bandat2172cm⁻¹which is due to Si-H stretching mode. In addition, the spectrum also showed sharp bands at 1267, 1086 and 905-832 cm⁻¹ which are due to Si-C, Si-O-Si and Si-O stretching vibrations.^{26,27} After the hydrosilylation reaction, the band at 2172cm⁻¹disappeared which clearly indicated that all the Si-H reactive sites in PMHS have been used for grafting of monomers as well for cross-linking thus resulting in the elastomer. As seen from Fig. 1(a) and (b) both the elastomers exhibited identical IR pattern with vibration bands at 3028 and 2977-2836 cm⁻¹ which are due to aromatic C-H and aliphatic C-H stretching modes. Additional IR bands were observed at 1512-1432, 1087 and 1027, 890-840 cm⁻¹ which can be attributed to Si-C, Si-O-Si, C-O-C and Si-Ostretching vibrations. Thus IR studies evidently confirmed the successful incorporation of monomer andCLto the polysiloxane backbone.



Fig. 1An overlap of FT-IR spectra of (a) LCE₁and(b)LCE₂with that of PMHS

Chemical structure of the elastomers was further confirmed through NMR spectroscopy. ¹H NMR spectra of the azo monomer (**M**), CLsand LCEs are shown in Fig. 2 (i) and (ii).In the spectrum of monomer and the CL, characteristic peaks for olefinic protons appeared at \sim -5.0 and ~5.7 ppmas multiplets[†].During the hydrosilylation reaction, hydrogenation of the double bond takes place along with the addition of silane to terminal carbon of the unsaturated bond resulting in a silane-terminated alkyl chain. Indeed, the NMR spectra of LCE₁ and LCE₂ showed the absence of signals corresponding to olefinic protons of azo monomer and the CLs. The resonance signals for the aromatic protons were observed in the range \simeq 6.8 – 8.0 ppm. Additionally, NMR signal for the methyleneoxy (Ar-O-CH₂-) group was observed at \simeq 3.9 ppm and signals for remaining aliphatic protons were observed in the region \simeq 0-1.9 ppm. Thus,the NMR data confirmed that the monomer and the CL have been successfully grafted onto PMHS backbone.



Fig. 2 (i) ¹H NMR spectra of (a) azo monomer, (b)CL- C_1 and (c) LCE₁



Fig 2(ii) ¹H NMR spectra of (a) azo monomer, (b) CL- C_2 and (c) LCE₂

Solid state ¹³C-NMR

 A solid state 13C-NMR spectrum of the LCEs is shown in **Fig 3**(a) LCE₁ and (b) LCE₂. The observed chemical shift values around 224, 215, 209,194, 186, 179, 155, 150, 141, 133, 128 and 125 ppm were assigned to the carbon atoms present in the phenyl rings with polar groups and unsaturated aromatic carbon atoms. The peaks at upper field in the region 100 - 40 ppm are attributed to the saturated carbon atoms of the aliphatic chains.

Fig. 3 ${}^{13}C$ spectra of elastomers (a) LCE₁ and (b) LCE₂

Gel permeation chromatography (GPC)

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) values for PMHS and elastomers were determined from GPC, calibrated using polystyrene standards. PMHS was found to be a mixture of short oligomers with the major M_w peak value around 750 g/mol (the merchant label mentioned 1900 – 2000 g/mol). M_n and M_w for elastomers, LCE₁ and LCE₂ are shown in Table 1. On the basis of GPC experiments, the polydispersity index (PDI) of the elastomers was calculated to be in the range of 1.02-1.03.

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 Table 1 Molecular weights of LCEs measured by GPC based on calibration using polystyrene standards.

LCEs	$M_{\rm n}$ (g/mol)	$M_{ m w}$ (g/mol)	$M_{ m w}/M_{ m n}$
PMHS	744	749	1.006
LCE1	81421	84443	1.03
LCE ₂	81313	83728	1.02

 M_n is number-average molecular weight; M_w is weight-average molecular weight

Thermal and mesomorphic properties of LCEs:

Thermal stability of the elastomers was investigated using TGAanalysis. As illustrated in Fig. 4(a) & (b)TGA thermograms of both the LCEs showed three degradation peaks at temperatures 334°C, 462°C and 529°C for LCE₁ and at 321°C, 362°C and 526°C for LCE₂ respectively. Temperature at which 5% weight loss of the sample occurred (under N₂) was greater than 300°C for both the elastomers which suggested a high thermal stability for these elastomers.⁹



Fig.4 TGA thermograms of (a) LCE_1 & (b) LCE_2

The phase behaviour and the associated transition temperatures for the elastomers were studied using DSC measurements. DSC thermograms recorded for LCE₁ and LCE₂ are shown in Fig. 5 (a) & (b) respectively. LCE₁ showed a melting transition at 45°C followed by an isotropic transition at around 62°C. Similarly LCE₂ also displayed melting at around same temperature of 46°C and an isotropic transition at 72°C. DSC studies clearly indicated an increased mesophase range for LCE₂ (of 26°C) when compared to that of LCE₁ (17°C). This result indicates that extension of the aromatic core [rigidity] in the cross-linker stabilises the mesophase in the corresponding elastomer. This property is similar to the observation already made for low molecular weight LC compounds. ²⁸



Fig.5 DSC thermograms of LCEs on heating and cooling at a rate of 5° C/min (a) LCE₁ and (b) LCE₂ of second run.

The optical textures of the elastomers were observed under a POM (crossed polarisers). The representative images of the samples held between a normal glass slide and a coverslip are shown in Fig. 6. A grainy yellow texture was observed for both the elastomers upon melting.

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There was no significant change in the texture of the mesophase upon increasing the temperature, however, on shearing the sample in the mesophase, colorful pattern was observed in the direction of shearing. Representative images of LCE₁ and LCE₂ recorded at 55° C and 58° C, on cooling from the isotropic state are provided in Fig. 6(a) and (d) respectively. Further, on shearing the sample, we were also able to observe colourful textures and dark textures in some parts of the sample, as shown in Fig. 6 (b), (c) and (e), (f) for LCE₁ and LCE₂ respectively.



Fig. 6 Optical textures of LCEs sandwiched between a normal glass slide and a cover slip; Top row-LCE₁ and bottom row-LCE₂. a & d - the textures LCE₁ and LCE₂ at 55°C and 58°C respectively, recorded on cooling from the isotropic; b & c- the textures observed for LCE₁ upon shearing; e & f – the textures observed for LCE₂ upon shearing, at the same temperature. Arrows indicate the direction of polariser and analyser.

X-ray diffraction (XRD) analysis

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59 60 XRD technique was employed to further probe the nature of the mesophase displayed by the elastomers. An X-ray diffractogram recorded for LCE₂ at 52°C is shown in Fig.7. The XRD pattern showed a peak in the small angle region having a layer spacing d=20.37Å and a diffuse peak in the wide angle region at $d \sim 4.3$ Å. In addition, a weak intensity peak was also observed at d value of around 8.4 Å. The first order reflection calculated from XRD is close to half of the measured molecular length of the spacer (L=38.2 Å for C₂ respectively, considering an extended all *trans* conformation of the alkyl chains, using ACD/3Dviewer freeware, Fig.S10†). XRD information coupled with the observation of homeotropic regions under POM, suggest a possible lamellar-like arrangement of the elastomeric segments in the mesophase. Based on this, we propose an intercalated smectic A structure (SmA_c) for the mesophase. A schematic representation of the molecular arrangement in the elastomer in which the aromatic cores of the **M** and the CL overlap favorably as shown in Scheme1, matches well with XRD results. Also it is worth mentioning here that, side-chain LC polymers with longer spacers generally exhibit smectic phases.^{29, 30}



Fig. 7 X-ray diffractograms of LCE₂.

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Photo - isomerisation of LCEs:

Photo - isomerisation behaviour of the azo monomer and LCEs was investigated using UV and Visible irradiation. The experiment wasperformed by employing aUV lamp (220V, 50Hz) having an emission wavelength of 254nm. The absorption spectra were recorded using dilute solutions of compounds in toluene $(1.1 \times 10^{-5} \text{mol } \text{L}^{-1} \text{of the monomer and } 0.4 \text{ wt\% of elastomer})$. In the absence of UV illumination, both monomer and elastomers showed a strong absorbance in the UV region at ~348 nm, which corresponds to π - π * transition of the *trans*isomer of azobenzene moiety. In addition, a shoulder peak was also observed in the visible region at 444 nm which is due to $n-\pi^*$ transition of the *cis* isomers. These spectra of the monomer and elastomers are very similar to those of other azo-related compounds.^{15,31}Upon UV-irradiation of 254 nm, intensity of the π - π * transition band at 348 nm decreased as a function of time, while a gradual increase in the n- π^* transition band at 444 nm was observed, which suggested a photoinduced *trans* to *cis*isomerization of the azobenzene moiety.Further, when the visible illumination was ceased, the cisstate was reverted back to the stable trans form, as reported elsewhere.³² The absorption spectra for the monomer displaying this photo - isomerisation, *trans* to *cis* and *cis* to *trans* are given in Fig. S11a⁺ and Fig.S11b⁺, respectively. Similar time dependent absorption spectra for LCE₁ and LCE₂ displaying gradual conversion of *trans* to *cis* isomer upon irradiation with UV light are shown in Fig. 8a and b respectively.



Fig. 8 UV-Vis spectra showing *trans* to *cis* conversion of $LCE_1(a)$ and LCE_2 (b) (in toluene) by shining UV light at 254nm.

The reverse transformation from *cis* to *trans* can be brought about by shining visible light (>540) wavelength. UV-Vis spectra showing the thermal back relaxation of LCE₁ and LCE₂ upon illuminating visible light at an interval of 30 sec are provided in Fig. 9a and b respectively. It can be noted from the figure that time required for photosaturation for *cis* to *trans* conversion is much higher than that of *trans* to *cis* conversion.



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 Fig. 9 UV-Vis spectra displaying cis - trans conversion of LCE₁(a) and LCE₂ (b) in solution(toluene) by shining visible light.

A comparison of peak absorbance at 348nm of the elastomers (LCE₁ and LCE₂) for *trans* to *cis* and *cis* to *trans* conversion as a function of exposure time is shown in Fig.10 a and b respectively. For LCE₁ isomerisation occurred at 90sec while for LCE₂ at 120sec (monomer-180sec, Fig. S11a[†]). Similarly, the back relaxation occurred at 800sec for LCE₁ whereas back conversion took place around 750sec for LCE₂ (monomer-510 sec, Fig. S11b[†]).



Fig. 10 The peak absorbance of LCEs with respect to exposure time for (a) trans - cis isomerisation and (b) cis - trans isomerisation.

The extent of isomerisation of *trans*to *cis* (conversion efficiency, CE) was estimated from the following equation;

$$CE = \frac{A(t)_o - A(t)_\infty}{A(t)_o} \times 100\%$$

Where $A(t_o)$ is absorbance before UV and $A(t_o)$ is absorbance after UV. The CE calculated for the monomer, LCE₁ and LCE₂ are 70%, 59% and 57% respectively.

The difference in thermal *back relaxation* and *UV on* process could be attributed to the structure and properties of the cross-linking agents present in the elastomers. In case of LCE₂, due to the rigidity of the biphenyl CL, the overall response of the molecule (structural orientation/bending) to the UV light is small compared to LCE₁ which contain a single phenyl ring as the core in the CL. The photo saturation depends on the radiation and is almost same in both cases. On the other hand, thermal back relaxation depends on the structural modifications. Since the response of LCE₂ to the UV light is lower than that of the LCE₁ (probably due to the rigid core) therefore the LCE₂ are giving back relaxation comparatively faster than LCE₁.

In general, behavior of a LC elastomer depends on structure of the elastomer backbone, length of the flexible spacers and rigidity of the mesogenic units and cross-linking agents. The flexible spacers decouple the mesogenic core from the backbone and provide the necessary freedom to self-assemble into a LC phase. So far, in majority of the LCEs generally either the monomeror the CL and in some cases both are liquid crystalline. Interestingly, in the present system, a mesogenic elastomer was obtained despite the monomer and the CL being nonmesogenic. This result highlights that, monomer or CL need not be mesogenic to ensure the LC properties in the resulting elastomer, but importance of the favourable interaction between monomer and the CL, decoupling from the backbone, overlapping of the flexible spacers, internal self-organization upon polymerization are deciding factors for an elastomer to show a LC property. Further, we observed that increase in the rigidity of the core (biphenyl *vs* phenyl in the CL) resulted in mesophase stability and also contributed towards the faster switching

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between *cis* to *trans* form in the azo containing elastomer which are advantages for optical storage devices.

Swelling behaviour of LCEs:

In order to characterize the cross-linking degree, the effective cross – link density or the average molecular weight between the two cross – link points (M_c) was determined by swelling experiments. M_c was calculated according to the Flory and Rehner swelling theory.

$$M_{c} = -\rho V_{1} (V_{2}^{1/3} - V_{2}^{2})$$

$$[ln (1-V_{2} + V_{2} + \chi V_{2}^{2}]$$
(1)

Where ρ is the density of the elastomer before swelling, V_1 is the molar volume of the swelling solvent, V_2 is the volume fraction of the elastomer at swelling equilibrium and χ is the elastomer – swelling agent interaction parameter. The volume fraction of polymer network V_2 was calculated as

$$V_2 = 1/Q \tag{2}$$

Where Q is the equilibrium swelling ratio of elastomer by volume, which was determined gravimetrically through the following equation:

$$Q = 1 + (W_2 / W_1 - 1) \rho_p / \rho_s$$
(3)

Where W_1 is the weight of the elastomer before swelling, W_2 is the weight of the elastomer at equilibrium swelling, ρ_p and ρ_s are densities of the elastomer and solvent, respectively. The elastomer – swelling agent interaction parameter χ can be theoretically predicted from the below expression:

$$\chi = (\sigma_1 - \sigma_2)^2 V_I / RT \tag{4}$$

Where σ_1 and σ_2 are solubility parameters of the solvent and elastomer, *R* is the gas constant and *T* is the absolute temperature. Swelling measurements were made in toluene (3ml) with samples of the initial weight, 0.008g for LCE₁ and 0.034g LCE₂. The swelling experiment was accomplished in several days at room temperature to achieve equilibrium. Swollen elastomers, removed from the solvent at regular intervals were dried superficially with filter paper, weighed and placed in the same condition. The measurements were continued until a constant weight was reached for each sample. Some information from the swelling experiments of the elastomers is shown in Table2.

Table 2 Swelling properties of the elastomers

Sample	<i>ρ</i> (g/cm ³)	V ₂	Mc (g/mol)
LCE ₁	0.55	0.73	92.753
LCE ₂	0.425	0.405	545.89

Photo-induced Bending and Unbending Behavior of LCE Film

The photo – actuation behaviour of the LCE film was investigated by shining UV and visible light over the mono-domain film. For photo-induced bending and unbending to occur, a relaxation of the polymer segment is necessary which can be achieved either by swelling the elastomer in a suitable solvent or by heating to above mesophase to isotropic transition temperature (or Tg) ^{17, 33}. In our experiment, the elastomeric film was heated to 75°C and was irradiated with UV light (254nm). Instantaneously, an asymmetric bending of the film was observed and this bending continued and reached maximum at an exposure time of about 1 min. Thereafter, there was no response upon further photo irradiation. The

film was reverted to the flat position (unbending) upon irradiation of the visible light (>540 nm). This bending and unbending of the film could be repeated by changing the wavelength of the irradiation light. The observed behaviour is due to the volume contraction caused by the photo-induced *trans to cis* transformation of the azobenzene unit. Moreover, it is worth mentioning here that, due to the high molar extinction co-efficient of the azobenzene units, a higher percentage of the light is absorbed by the surface molecules resulting in an unbalanced contraction between the surface and the bulk of the material which leads to the anisotropic bending of the film. Fig. 11 shows the photographs of bending and unbending behavior of LCE film upon UV and Vis irradiation. Videos displaying the photo - actuation upon irradiation of UV and visible light are provided in ESI (Video S1 and Video S2). As seen by the images/video, the elastomer converted light energy to specific mechanical energy and is suitable for light-driven actuators. Additionally the elastomer is also excellent candidates for shape memory devices.



Fig. 11 Images displaying the photo response of LCE film upon UV and Visible irradiation recorded at a temperature of 75°C (M to I temperature).

CONCLUSION

New liquid crystalline side-chain polysiloxane LCEs have been described which contain a same azo-containing non mesogenic monomer but different cross-linking units. The LCE₂ with a CL having a biphenyl core displayed the mesophase with a wider thermal range compared to the mesophase exhibited by LCE₁ containing a phenyl unit in the CL. Based on the POM and XRD results, the mesophase was characterized as an intercalated SmA phase (SmA_c). Both the elastomers showed photo induced isomerisation of the azomoiety having faster switching between the isomers and possess strong potential for application in optical devices. Remarkably, the mono-domain sample of the LCE showed a reversible photo - actuation in terms of

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asymmetric bending upon exposure to a UV light and unbending on irradiation with visible light with a faster response time.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from Science and Engineering Research Board, Department of Science and Technology, New Delhi: [Grant Number ECR/ 2015/000419] and DST PURSE-II, New Delhi for financial support. Authors also gratefully thank Alagappa Chettiar College of Engineering and Technology for help with TGA measurements and CeNS, Bangalore for providing DSC facility and RRI, Bangalore for providing XRD facility.

[†]ElectronicSupplementary Information (ESI) available: synthetic schemes, spectral data and DSC thermograms for the monomer & cross – linkers, ACD chemlab 3Dviewer for CL- C_2 , absorption spectra for monomer displaying photo – isomerisation, POM images of the mesophase displayed by the elastomersand videos of photo – actuation behaviour for LCE film.

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