

Synthesis and Characterization of High Molecular Weight Side Chain Liquid Crystalline/Photoactive Polymers

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ABSTRACT: Various liquid crystalline and photoactive azobenzene monomers were synthesized and attached to copoly(methyl methacrylate-glycidyl methacrylate) [copoly (MMA-GMA)] to get high molecular weight side chain liquid crystalline (LC)/photoactive copolymers. Further, spacers are generated *in situ* and reactive groups are obtained after the modification. All monomers and polymers were thoroughly characterized by FTIR, ^1H and ^{13}C NMR, UV-VIS spectrophotometry, gel permeation chromatography, thermogravimetric analysis, differential scanning calorimetry, and polarized optical microscopy. All side chain LC polymers showed higher thermal stability than

that of copoly(MMA-GMA). Three LC and one azo monomer exhibited characteristic nematic mesophase where as one LC monomer has shown nematic and sanded smectic-A texture. The rate of trans-cis isomerization of polymer was lower than that of the monomer and both monomers and polymers showed slow back isomerization. Present approach offers convenient way to synthesize high/ desired molecular weight photoactive LC polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2562–2573, 2009

Key words: liquid crystals; side chain liquid crystalline polymer; epoxy; photoactive polymers; azo polymers; synthesis

INTRODUCTION

Over last few decades side chain liquid crystalline (LC) polymers with photoactive chromophore have been subject of intensive research. In this domain, azo benzene containing side chain liquid crystalline polymers (SLCPs) are interesting in respect of easy synthesis, extreme response to incoming electromagnetic field,^{1–5} and wide spread usage in various fields such as nonlinear optics (NLO),⁶ photomechanical systems,^{7–10} photo switches, holographic data storage devices, and micropatterning.¹¹ Till now, many approaches have been used to introduce liquid crystalline (LC) and photoactive (AZO) units to polymer frame work. The first approach is the use of doping of chromophores into polymeric matrix (Guest-Host system).^{12,13} The main problem of this system is that the glass transition temperature of the host (polymer) decreases due to plasticization by guest (chromophore)¹⁴ and also the dye dispersed in the host polymer matrix is distributed nonhomogeneously, causing significant scattering losses.⁶ Second approach is utilization of the polymer system to which the chromophores are covalently attached as pendant side group or along main chain to the

polymer backbone. The latter approach helps in getting very high film homogeneity.⁶ Ikeda and coworkers^{7–10} reported that fabrication of freestanding film of a liquid-crystal networks, containing the azobenzene chromophore, has shown pronounced photomechanical effect under linearly polarized light due to photoselective volume contraction. Hoffman et al. reported photo switch based on azopolymers that serve as molecular antennae and actuators to reversibly turn the enzymatic activity on and off in response to a distinct light wavelength.¹⁵ Berg et al.^{16,17} developed rewritable photoactive biopolymer holography recording medium based on polypeptide and azobenzene units which has shown 80% diffraction efficiency. Natansohn and coworker and Shibaev et al. have reported side chain LC polymers with photoactive chromophore.^{18–21} Ding and Russell reported synthesis of side chain azo polymer and their photophysical study.²² Till now, synthesis of photoactive LC monomer followed by polymerization was found to be convenient approach to build up the azo benzene containing SLCPs. However, most of the time, this method fails to realize high molecular weight and use of comonomer complicates this strategy further. High molecular weight SLCPs are very much important for fabrication of robust nonlinear optical (NLO) and other optoelectronic devices. Recently, our group has reported synthesis of high molecular weight copoly (MMA-MA) which was further reacted with NLO active azo chromophore. Further, reactive functional

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groups are produced in the molecular architecture as an off-shoot of the reaction. This group can be utilized as and when required for additional modification/crosslinking of the polymer. In continuation of the work, we report the synthesis and characterization of various carboxyl group ended liquid crystalline and azo monomers. Epoxy group containing polymer was reacted with carboxyl ended LC/Azo molecules to get side chain liquid crystalline/photoactive copolymers. Our main aim of using GMA monomer is to produce spacers and active functional group (—OH) *in situ* during ring opening of epoxy. All LC and AZO monomers, SCLPs were characterized and photoresponsive property studied by UV/Vis spectroscopy.

EXPERIMENTAL

Synthesis of liquid crystalline/photoactive monomers and polymers materials

Disperse orange-3 (Aldrich, USA), thionyl chloride (Acros Organics, Belgium), bromobutane, *p*-amino benzoic acid, acetic acid, sodium sulfate (Sisco Research Laboratories, India), sodium nitrite, concentrated hydrochloric acid, sodium hydroxide (Merck, India), triphenyl phosphine (Loba chem, India), *p*-toluene sulfonic acid, sodium chloride (CDH, India), epichlorohydrin, sodium carbonate (s.d. Fine-Chem, India) were used without further purification. All the solvents used were of AR grade and freshly distilled before use.²³ Methyl methacrylate (MMA), glycidyl methacrylate, benzoyl peroxide (Acros organics, Belgium), terephthaloyl chloride (Fluka, Switzerland), 4-hydroxy benzoic acid (Merck), 4-methoxy phenol (Aldrich, Switzerland), cholesterol, dimethyl formamide (DMF) (Merck, India), Phenol (s.d. Fine Chem, India), and triethylamine (T. Baker Chem., India) were purified by standard procedures.

Characterization methods

Thin layer chromatography was performed with Merck, silica gel (with Zinc oxide) 60 F254 aluminum sheets. Elemental analysis was performed with a CHNS elemental analyzer (Perkin-Elmer, Series II 2400). Infrared spectra were taken in a Fourier transform infrared (FTIR) spectrophotometer (Perkin-Elmer 1600) using KBr pellets. The UV-Visible spectra were recorded on a Cary 500 Scan UV-VIS-NIR spectrophotometer by using DMSO as a solvent. Specific rotation of monomer (LCM-4) and LC polymer (SMGLCP-4 and SMGLAP-4/2) was measured by JASCO P-1020 polarimeter by using 1% monomer and polymer solution, respectively, in DMSO at 589 nm. ¹H (500 MHz) and ¹³C NMR (125 MHz) spectra were recorded on a Bruker 500-MHz FT-NMR spec-

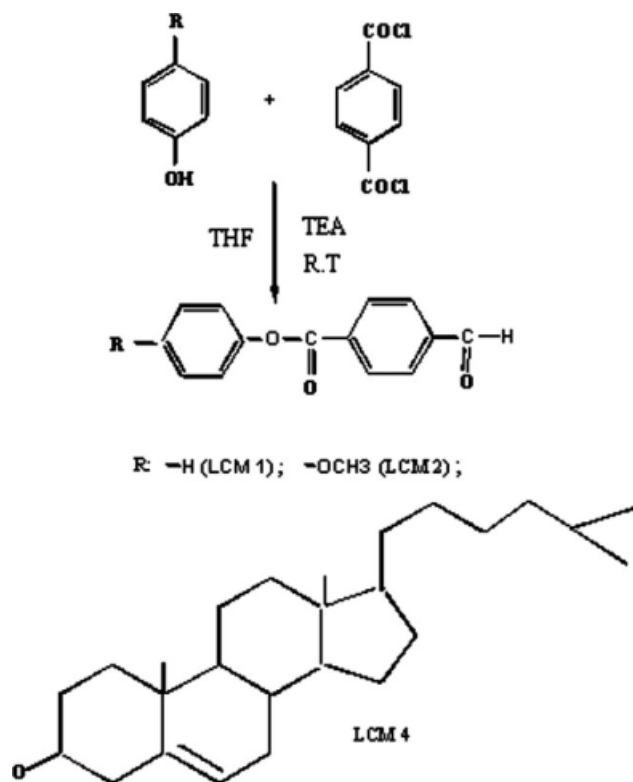
trometer with dimethyl sulfoxide-d₆ (DMSO-d₆) or CDCl₃ as the solvent and tetramethylsilane as an internal standard. Epoxy equivalent determination was carried out by following the methods of Durbetaki.²⁴ Inherent viscosities were measured with Ubbelohde viscometer at 30°C (0.5 g/dL) in DMSO. The molecular weight, molecular weight distribution, and polydispersity index of the polymer was determined with size exclusion chromatography (SEC) (Waters) in tetrahydrofuran as solvent using RI detector. The styragel columns HR 0.5, 1, and 4 covering molecular weight range of 1×10^2 to 5×10^5 were used at 35°C using a flow rate of 0.7 mL/min. Polystyrene standard was used for calibration. Differential scanning calorimeter (DSC) (TA instruments) was used to determine the thermal transitions. Heating/cooling rate used for all DSC analysis was 5°C/min and sample weight was around 10 mg. Thermo gravimetric analyzer (TGA) (TA instruments His Res TGA 2950) was used for thermal analysis at a heating rate of 20°C/min in N₂ atmosphere. A Leica DMLD, optical polarizing microscope with image analyzer equipped with LINKAM TMS 94 hot stage and LINKAM LNP controlling unit was used to observe the thermal transition and liquid crystalline state. Photoresponse study of polymers was carried out in DMSO solution at 30°C. The sample was irradiated with a medium pressure, 100 W mercury lamp (365 nm) by a discontinuous mode from a distance of 10 cm from the sample for various time intervals. The irradiated solution was subjected to spectral analysis.

SYNTHESIS

Synthesis of liquid crystalline/photoactive monomers

Synthesis of 4-Phenyl-4'-carboxy benzoate (LCM-1)

Synthesis of LCM-1 is given in Scheme 1. Recrystallized terephthaloyl chloride (30g, 0.144 mol), dissolved in 100 mL of tetrahydrofuran was taken in three-necked reaction flask fitted with a stirrer, a condenser, and dropping funnel. Phenol (4.98 g, 0.053 mol) and triethylamine (13 mL, 0.094 mol) dissolved in tetrahydrofuran (25 mL) was added drop wise to terephthaloyl chloride solution at 0°C. The reaction mixture was stirred for 16 h at room temperature. After completion of reaction triethylamine hydrochloride was removed by filtration. Sufficient distilled water was added to the stirred filtrate. The separated solid was filtered, washed repeatedly with water, and dissolved in ethyl acetate. Undissolved solid (terephthalic acid) was removed by filtration. The filtrate was washed with 5% sodium carbonate and sodium chloride solution, respectively. The organic layer was dried over anhydrous sodium



Scheme 1 Synthesis of LCM-1, 2, and 4.

sulfate, filtered, and solvent was removed under vacuum. Single product spot was confirmed by thin layer chromatography with ethyl acetate and heptane 1 : 1 (v/v) as an eluent. Yield 64%.

Synthesis of 4-Methoxyphenyl-4'-carboxy benzoate (LCM-2)

Synthesis of LCM-2 was carried out similarly as in the case of LCM-1 (Scheme 1) using 4-methoxy phenol and terephthaloyl chloride. Yield 68%.

Synthesis of 4-Butyloxyphenyl-4'-carboxy benzoate (LCM-3)

The synthesis of LCM-3 was carried out in three steps as shown in Scheme 2. In first step, the synthesis of 4-butyloxy benzoic acid was carried out by following the method described in literature.²⁵ In a typical recipe, *p*-hydroxy benzoic acid (34.53 g, 0.25 mol) was dissolved in 80 mL of THF. KOH (30.86 g, 0.55 mol) dissolved in 50 mL of water was added to it. A trace of KI was added as a catalyst and the mixture was refluxed. During refluxing 32.32 mL (0.3 mol) of bromobutane was added drop wise over 3 h. Subsequently, the reaction mixture was refluxed for 12 h and ethanol was distilled off at the end of the reaction. The remaining solution was then diluted with 200 mL of cold water and acidified

with HCl. The product, separated as a solid was washed four times with ethyl acetate and purified by recrystallization from acetone–water (75 : 25 v/v). Yield 78%. M.Pt. 155°C. The second step synthesis was carried out by following the method described in literature.²⁶ Butyloxy benzoic acid was converted in to corresponding acid chloride and further reacted with 4-hydroxy benzoic acid in presence of triethylamine dissolved in THF. Yield 60%.

Synthesis of 4-Cholesteroylphenyl-4'-carboxy benzoate (LCM-4)

Synthesis of LCM-4 was done similarly as in the case of LCM-1 [Scheme 2(b)]. In a typical recipe recrystallized terephthaloyl chloride (20.3 g, 0.1 mol) dissolved in 200 mL of chloroform was reacted with cholesterol (19.3 g, 0.05 mol) in presence of triethylamine (6.9 mL; 0.05 mol) dissolved in 100 mL of chloroform at 0°C. Yield 65%, Specific rotation, $[\alpha]_{589}^{25}$ [1% in DMSO]: -4.9° .

Synthesis of AZO monomers (AZO 1 and 2)

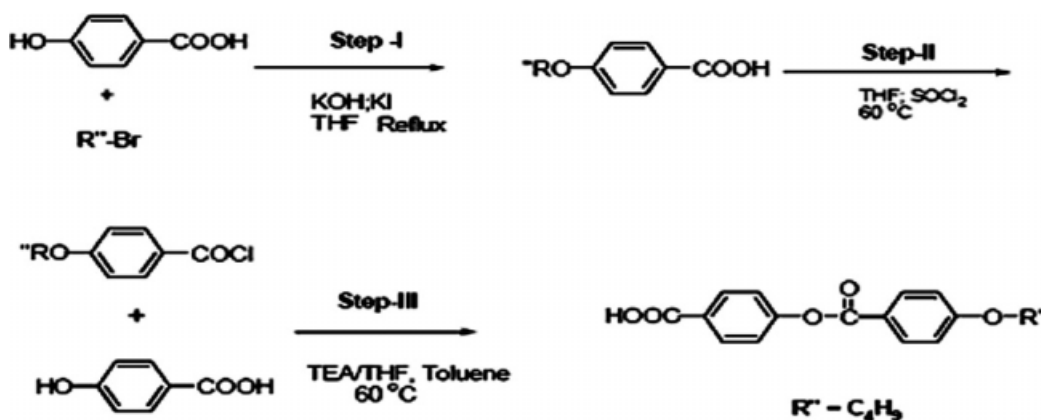
Synthesis 4-(4-Hydroxy-phenylazo)-benzoic acid (AZO-1). Synthesis of AZO-1 was done by following method reported in literature²⁷ by standard diazotization reaction from *p*-amino benzoic acid and phenol [Scheme 3(a)]. Yield 70%.

Synthesis of N-[4-(4-Nitro-phenylazo)-phenyl]-terephthalamic acid (AZO-2)

Synthesis of AZO-2 was carried out in the same way as the synthesis of LCM-1 [Scheme 3(b)]. In a typical recipe, recrystallized terephthaloyl chloride (20.3 g, 0.1 mol) dissolved in 200 mL of chloroform was reacted with 4-(4-nitrophenylazo)-phenyl amine (Disperse orange-3) (12.11 g, 0.05 mol) in presence of triethylamine (6.9 mL; 0.05 mol) dissolved in 100 mL of THF at 0°C. Yield 70%.

Synthesis of copoly(MMA-GMA)

A 20 wt % solution of methyl methacrylate and glycidyl methacrylate (80 : 20 w/w) in dry DMF was taken in three necked flask fitted with a nitrogen inlet and a condenser. The contents of the flask were flushed well with nitrogen for 30 min. Then 0.1% (by weight of monomers) of benzoyl peroxide dissolved in DMF was added. The polymerization reaction was carried out at 70°C for 1 h under nitrogen atmosphere. The contents of the flask were then poured into cold distilled water. The precipitated solid polymer was separated by filtration and reprecipitated twice from tetrahydrofuran/water. Copoly(MMA-GMA), thus obtained, was dried under



Scheme 2 Synthesis of LCM-3.

vacuum at 60°C for 24 h. The epoxy equivalent of the polymer, determined by following the method of Durbetaki, was found to be 608.²⁴ Yield 60%. The reaction scheme is shown in Scheme 4. The number average and weight average molecular weights (M_n and M_w), determined by SEC, were found to be 21,400 and 42,000, respectively.

Synthesis of side chain liquid crystalline/photoactive polymers (SLCPs)

The general reaction scheme for synthesis of LC and AZO polymer is shown in Scheme 4 and list of all polymers is shown in Table II.

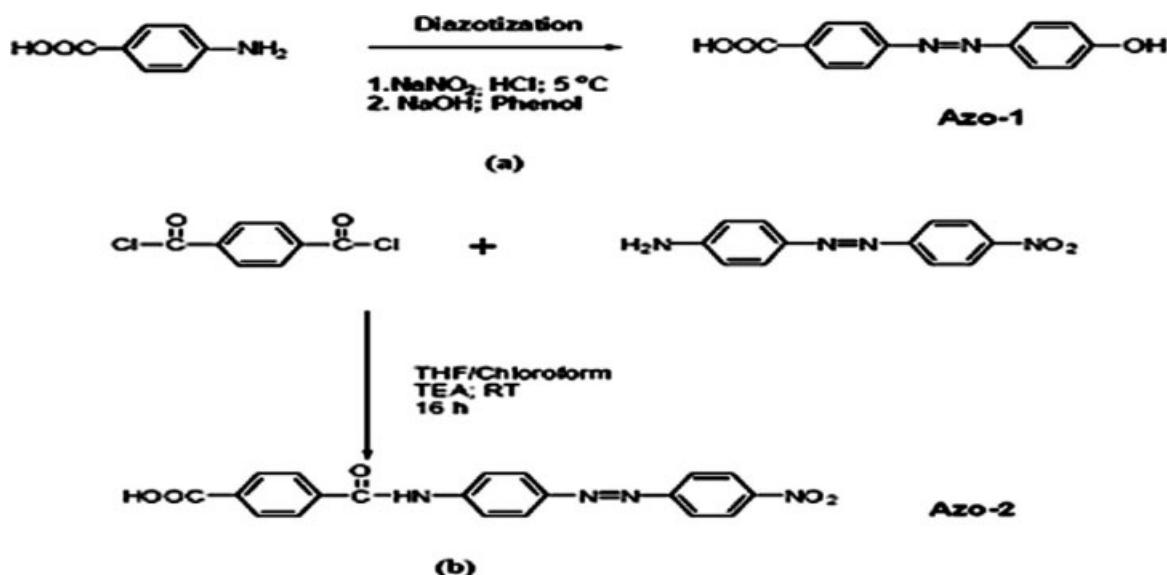
Synthesis of SMGLCP-1

The synthesis of liquid crystalline polymer SMGLCP-1 is shown in Scheme 4. Recrystallized LCM-1 (0.35 g, 0.0015 equiv) and copoly(MMA-

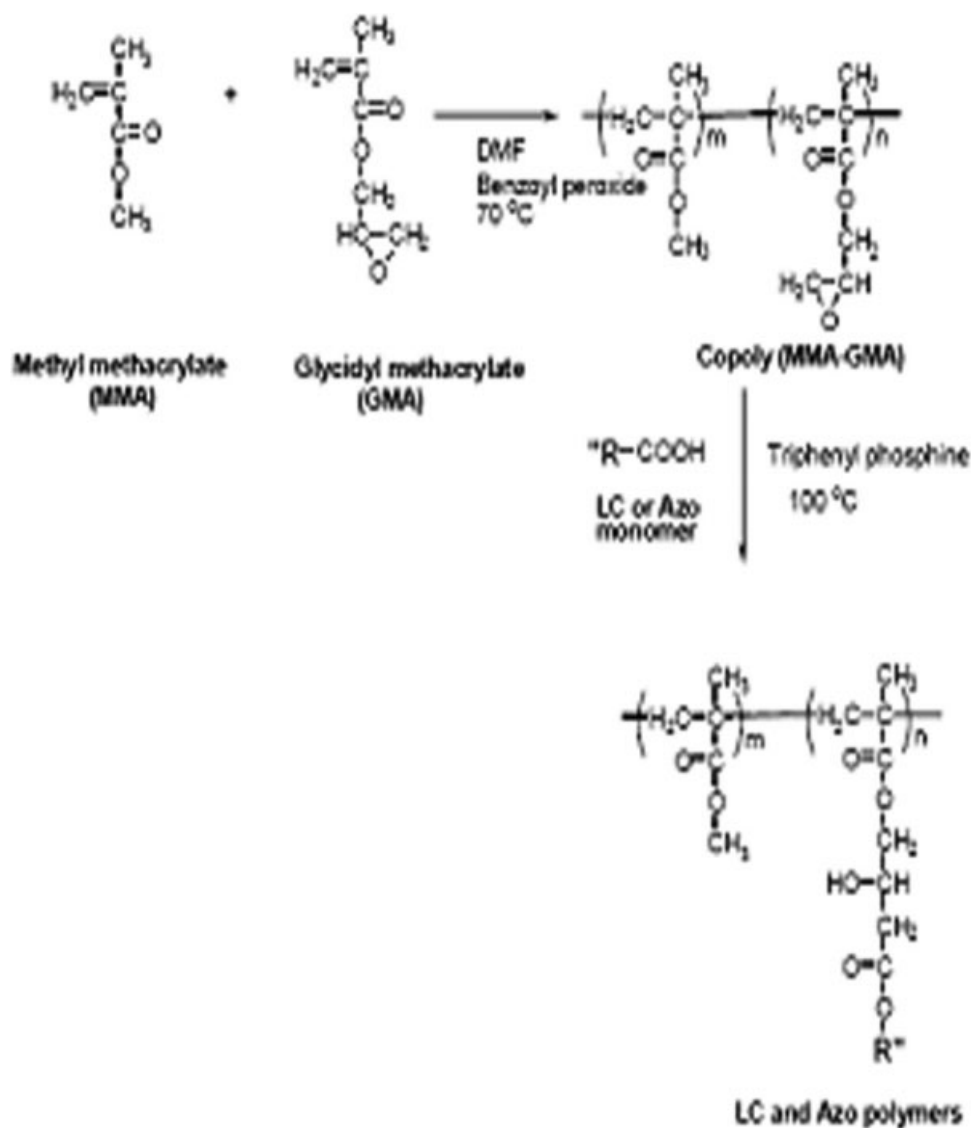
GMA) (0.91 g, 0.0015 equiv) were dissolved in 50 mL of DMF and taken into a cleaned and dried three-necked reaction flask. The reaction mixture was heated to 100°C in presence of triphenyl phosphine (0.01 g, 0.2%; w/v). The reaction mixture was stirred overnight at same temperature. After the reaction is over the liquid was poured into chilled distilled water. The precipitated solid was separated by filtration and purified by reprecipitation twice from DMF/water and dried under vacuum at 80°C. Yield 56%.

Synthesis of SMGLCP-2 and 3

The synthesis of liquid crystalline polymer SMGLCP-2 and SMGLCP-3 were carried out similarly as used for the synthesis of SMGLCP-1 (Scheme 4). Yield 55 and 60%.



Scheme 3 Synthesis of AZO-1 and AZO-2.



Scheme 4 Synthesis of copoly(MMA-GMA) and LC and azo polymers.

Synthesis of SMGLCP-4

The synthesis of liquid crystalline polymer was carried out by following the method as described for SMGLCP-1 using LCM-4 (Scheme 4). However, DMF/chloroform (1 : 1 v/v) was used in this case. The polymer was purified by reprecipitation twice from DMF/water. The resultant solid was dried under vacuum at 75°C for 24 h. Yield 60%.

Synthesis of AZO polymer

Synthesis of SMGAP-1

Synthesis of SMGAP-1 was carried out by following the method described for SMGLCP-1 (Scheme 4). Recrystallized AZO-1 (1.57 g, 0.0065 equiv) and copoly(MMA-GMA) (4 g, 0.0065 equiv) were reacted in DMF at 100°C in presence of triphenyl phosphine. The polymer was purified by reprecipitation twice

from DMF into ethanol/water mixture followed by filtration and drying in vacuum at 75°C. Yield 70%.

Synthesis of SMGAP-2

Synthesis of SMGAP-2 was carried out by following the method described in synthesis of SMGAP-1 (Scheme 4). Recrystallized AZO-2 (2.25 g; 0.0065 equiv) and the copoly(MMA-GMA) (4 g; 0.0065 equiv) were reacted at 100°C in presence of triphenyl phosphine. The polymer was purified by reprecipitation twice from DMF/chloroform mixture into ethanol/water and dried under vacuum at 75°C. Yield 70%.

Synthesis of SMGLAP-4/2

Synthesis of SMGLAP-4/2 was carried out by following the method as described for SMGAP-2

TABLE I
List of Monomers and Polymers Synthesized

Monomers	Structure	Polymer
4-Phenyl, 4' Carboxy benzoate (LCM 1)		SMGLCP-1
4-Methoxy phenyl, 4' Carboxy benzoate (LCM 2)		SMGLCP-2
4-Butoxy phenyl, 4' Carboxy benzoate (LCM 3)		SMGLCP-3
4-Cholesterylphenyl, 4' Carboxy Benzoate (LCM 4)		SMGLCP-4
4(4'-Hydroxyphenylazo)-benzoic acid (AZO 1)		SMGAP-1
N-[4(4'-nitrophenylazo)-phenyl]-terephthalamic acid (AZO 2) LCM 4/AZO 2		SMGAP-2 SMGLAP-4/2

(Scheme 4). AZO-2 (0.74 g; 0.00325 equiv), LCM-4 (1.74 g; 0.00325 equiv), and copoly(MMA-GMA) (4 g; 0.0065 equiv) were dissolved in 100 mL of DMF/chloroform mixture taken in a three-necked reaction flask. The mixture was slowly heated to 100°C under N₂ atmosphere. Triphenyl phosphine (0.2 g) was added into the reaction mixture. The hot reaction mixture was stirred overnight at same temperature and then cooled to room temperature and poured into excess chilled distilled water. The precipitated solid was separated by filtration and purified by redissolving in DMF/chloroform and reprecipitation into ethanol/water and dried in vacuum at 75°C. Yield 65%.

RESULTS AND DISCUSSION

Synthesis of photoactive and liquid crystalline monomers and polymers

In continuation of earlier study on synthesis of high/desired molecular weight photoactive polymers,²⁸ we made an attempt to synthesis photoactive LC via epoxy group available in high/desired molecular weight preformed polymer. This being a convenient route, for making high/desired molecular weight polymers, will be very useful for making high performance photoactive LC polymers. We tried to establish the feasibility of such synthetic route for LC, AZO polymers, and copolymers. Various liquid crystalline monomers (LCM-1 to -4) (Table I) were synthesized using various end groups. Two variants of photoactive azobenzene monomers (AZO-1 and AZO-2) were synthesized, one by standard diazotization method and another by reacting commercially available disperse orange-3 with terephthaloyl chloride (Schemes 1–3; Table I). The AZO-1 contains hydroxyl end group, but AZO-2

contains nitro end group. One more phenyl ring is present in AZO-2 as compared with AZO-1. The additional benzene ring enhances the LC properties of the azo monomer and red shift the λ_{\max} .²⁹ This helps in enhanced reorientation during holographic recording. The yield of the monomers is found to be in the range of 50–75%. Epoxy group containing polymer [copoly(MMA-GMA)] was prepared to hook the carboxyl ended LC and azo as side groups to get various high/desired molecular weight side chain LC and AZO polymers (Scheme 4). Conventional LC-AZO side chain liquid crystalline polymer synthetic strategy requires multistage monomer synthesis and further polymerization. Also, it is noted that the attainment of high molecular weight by this route is rarely possible. Therefore, in this study attempt was made to synthesize high molecular weight polymer with epoxy group, which was used to attach LC and azo groups by carboxyl-epoxy reaction. Synthesis route was restricted only to single polymer composition of about 20-mol % epoxy monomer (GMA). Side chain liquid crystalline co- and terpolymers based on copoly(MMA-GMA) and various liquid crystalline monomers (LCM-1 to -4) and photoactive azobenzene monomers (AZO-1 and AZO-2) were synthesized. SMGLCP-4 and SMGLAP-4/2 (Table I) polymers obtained by hooking LCM-4/Azo-2 monomers on to copoly(MMA-GMA) backbone do not exhibit any chirality due to steric hindrance from polymeric backbone.

Elemental analysis of monomers

Elemental analysis was carried out to ascertain the purity of the monomers used in this study. Table II shows the details of percentage of elements for various monomers. From the values it can be observed

TABLE II
Elemental Analysis of Monomers

Sr. No	% of Elements					
	Carbon		Hydrogen		Nitrogen	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
LCM-1	69.42	68.90	4.13	4.02	–	–
LCM-2	66.17	65.54	4.42	4.33	–	–
LCM-3	68.35	67.87	6.32	6.21	–	–
LCM-4	78.61	77.89	9.42	9.25	–	–
AZO-1	64.4	63.67	4.16	4.02	11.5	11.37
AZO-2	61.54	60.96	3.62	3.45	14.35	13.86

that experimental values fairly match with the theoretical value.

FTIR analysis of monomers and polymers

LC monomers (LCM-1 to -4)

From FTIR spectra of LCM-1 to -4 it is observed that the carboxyl group appears as broad peak around 3000 cm^{-1} (O–H str) and between 1720 and 1680 cm^{-1} (C=O). The peak at 1740 and 1200 cm^{-1} represent ester and ether linkage, respectively. The peaks at 1506 and between 2940 and 2800 cm^{-1} represent aromatic ring and aliphatic $-\text{CH}_2$, respectively. In case of LCM-4, the C=C unit from cholesteric molecule appears at 1604 cm^{-1} .

AZO 1 and 2

From the FTIR spectra of AZO-1, the peak at 3462 cm^{-1} indicate presence of hydroxyl group. The peak at 1791 cm^{-1} is attributed to presence of ester group in case of AZO-2. Azo moiety ($-\text{N}=\text{N}-$) of the monomers appear at 1425 and 1419 cm^{-1} , respectively. The amide group peak appears at 3421 and 1620 cm^{-1} and a peak at 1601 cm^{-1} is due to NO_2 group in AZO-2. The peaks at 1690 and 1681 cm^{-1} are due to C=O of carboxyl group of the monomers.

Polymers

Copolymer (MMA-GMA)

The peak at 1729 cm^{-1} is due to ester function, which indicates the presence of methacrylate moiety in the copolymer. Presence of epoxy group was confirmed by the appearance of peaks at 917 and 833 cm^{-1} . Peaks at 2996 and 2945 cm^{-1} represent aliphatic C–H units in the polymers.

LC/AZO polymers

It is observed from the spectral values of all LC polymers (SMGLCP-1 to SMGLCP-4) that the epoxy peak at 917 and 833 cm^{-1} are absent and a new peak at 3448 cm^{-1} , characteristics of $-\text{OH}$ group, is due to reaction between epoxy group of the copolymer and carboxylic acid group of the LC monomer. One additional peak at 1059 cm^{-1} is seen which can be attributed to ether linkage present in methoxy in SMGLCP-2 or butyloxy group in SMGLCP-3. In case of azopolymers (SMGAP-1, SMGAP-2, and SMGLAP-4/2), peak around 3528 – 3505 cm^{-1} is due to hydroxyl group. Amide group peaks of SMGAP-2 and SMGLAP-4/2 appear at 3500 and 1619 cm^{-1} , respectively. Further, epoxy peak at 912 cm^{-1} is absent in all polymers.

Nuclear magnetic resonance study (^1H and ^{13}C NMR) of monomers and polymers

LCM-1-4

Chemical shift values (δ values) of LCM-1 to -4 are given in Table III. The carboxylic acid proton appears at around 10.00 ppm. An aliphatic proton appears as a multiplet at 3.73 – 0.67 ppm for LCM-2 to LCM-4. In all cases, aromatic protons appear at 8.28 – 6.90 ppm. In ^{13}C NMR, the peak values (Table IV) at around 165 and 162 ppm are due to acid and ester groups, respectively. Alkoxy (LCM-2 to -3) and

TABLE III
 ^1H NMR δ Values for the Monomers and Polymers

Sample	OH	COOH	N–H	Aromatic protons	Aliphatic protons
LCM-1	–	10.40	–	8.28–7.16	–
LCM-2	–	10.00	–	8.30–6.84	3.73
LCM-3	–	10.80	–	8.00–6.50	4.00–0.96
LCM-4	–	10.05	–	8.26–7.00	2.40–0.67
AZO-1	10.59	11.20	–	8.24–8.20	–
AZO-2	–	10.95	9.60	8.40–6.90	–
Copoly(MMA-GMA)	–	–	–	–	3.20–1.60
SMGLCP-1	5.20	–	–	8.20–7.30	3.95–0.69
SMGLCP-2	5.15	–	–	8.03–6.32	4.30–0.58
SMGLCP-3	5.38	–	–	8.32–6.25	4.25–0.61
SMGLCP-4	5.50	–	–	8.38–7.90	4.98–0.50
SMGAP-1	5.20	–	–	8.27–8.16	4.76–0.50
SMGAP-2	5.60	–	9.80	8.60–7.5	3.90–0.74
SMGLAP-4/2	5.45	–	9.78	8.44–7.95	4.53–0.50

TABLE IV
 ^{13}C NMR δ Values for the Monomers and Polymers

Sample	Acid	Ester	Aliphatic carbons	Aromatic carbons	Amide
LCM-1	165.92	164.89	–	134.00–129.00	–
LCM-2	165.70	164.90	56.00	134.00–129.00	–
LCM-3	166.60	162.60	77.00–24.00	138.00–122.00	–
LCM-4	166.37	165.19	56.00–18.00	140.00–122.00	–
AZO-1	166.10	–	–	132.00–122.00	–
AZO-2	167.13	–	–	131.00–121.00	164.00
Copoly(MMA-GMA)	–	177.00	54.40–16.50	140.00–130.00	–
SMGLCP-4	–	176.00	65.60–16.20	–	–

cholesteric units (LCM-4) appear between 140 and 122 ppm.

AZO 1 and 2

The results of ^1H NMR spectroscopy of AZO-1 to -2 are summarized in Table III. It can be observed that the hydroxyl group proton of AZO-1 appears at 10.59 ppm and carboxylic acid protons around 11.00 ppm in both AZO-1 and 2. The secondary amine in AZO-2 appears at 9.60 ppm and aromatic protons in both AZO-1 and -2 resonate between 8.40 and 6.90 ppm. In ^{13}C NMR (Table IV), the carboxylic acid in AZO-1 and -2 appears at 167.10 and 166.10 ppm, respectively, and aromatic carbons appear at 132–121 ppm for both monomers.

Copoly(MMA-GMA)

From ^1H NMR spectrum copoly(MMA-GMA) (Table III) it is observed that aliphatic CH_2 protons of the polymer appear at 1.00–0.80 ppm. Methyl groups of

MMA and GMA units appear at 1.80 ppm. The double doublet between 2.90 and 2.80 is because of CH_2 unit in epoxy ring. Multiplet at 3.20 ppm is because of the CH units of the epoxy ring. The peaks due to glycidyl CH_2 appear as a double doublet around 4.30–4.40 ppm. ^{13}C NMR values of copoly(MMA-GMA) is given in Table IV. Ester carbon resonance is found at 177.20 ppm whereas the epoxide ring carbons appear between 52.00 and 44.00 ppm. The CH_3 and CH_2 units appear at 40.00 and 16.00 ppm, respectively.

SMGLCP-1-4

Table III shows the ^1H NMR δ values for side chain LC polymers (SMGLCP-1 to -4). A representative ^1H NMR spectrum for LC polymer (SMGLCP-4) is shown in Figure 1(a). The new peak at 5.60 ppm is due to hydroxyl group, which confirms the reaction between carboxyl group of LC monomers and epoxide ring of copoly(MMA-GMA). Appearance of new

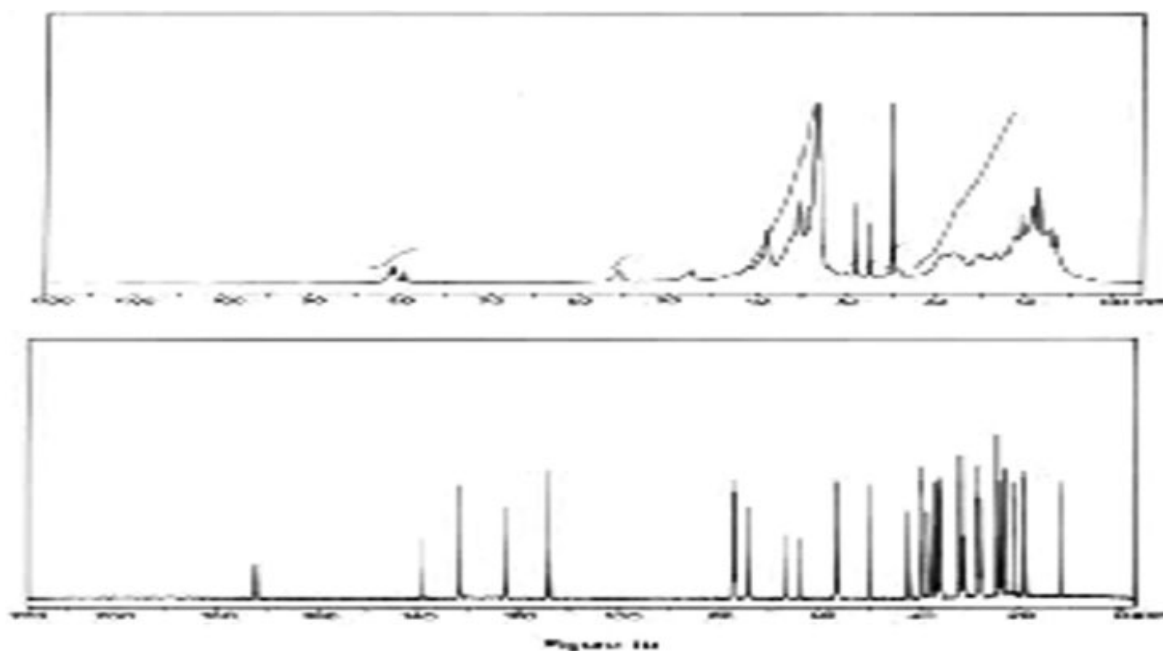


Figure 1 ^1H (a) and ^{13}C (b) NMR spectrum of SMGLCP-4.

TABLE V
Physicochemical Properties of Monomers and Polymers

Sample	η_{inh}^a (dL/g)	IDT ^b (°C)	Transition temperatures (°C)		
			T _g	DSC ^c	POM ^d
LCM-1	–	–		K 180 N 217 I	K 185 N 220 I
LCM-2	–	–		K 196 N 222 I	K 200 N 227 I
LCM-3	–	–		K 38 N 75 I	K 40 N 78 I
LCM-4	–	–		K 145 SmA 178 N 195 I	K 150 SmA 180 N 200 I
AZO-2	–	–		K 158 N 255 I	K 165 N 260 I
Copoly(MMA-GMA)	0.51	220	110	–	–
SMGLCP-1	0.52	320	100	K200 N 285 I	K 180 N 290 I
SMGLCP-2	0.58	360	85	K186N 270 I	K186 N 260 I
SMGLCP-3	0.56	275	75	K156 N 240 I	K 155 N 235 I
SMGLCP-4	0.58	270	120	K150SmA 225 N – ^e	K 140 SmA 190 N 240 I
SMGAP-1	0.54	295	108	K170 N 220 I	K145 N 250 I
SMGAP-2	0.60	320	105	K 155 N 283 I	K 170 N 280 I
SMGLAP-4/2	0.72	305	112	K 161SmA 275 – ^e	K 185 SmA 260 N 320 I

^a Inherent viscosity measured with a polymer solution (0.5 g/dL in DMSO) at 30°C.

^b IDT identified by TGA under N₂ atm at a heating rate of 20°C/min.

^c Transition temperature identified with DSC at a heating rate of 5°C/min under N₂.

^d Transition temperature identified with POM at a heating rate of 5°C/min under N₂.

^e Not identified as the isotropization is accompanied by degradation.

multiplet at 3.50 ppm, assigned to alkyl protons, is due to opening of epoxide ring. Aromatic resonances appear in their respective positions. The peaks due to aromatic proton appear at 8.30–6.25 ppm. ¹³C NMR values are given in Table IV and a representative spectrum (SMGLCP-4) is shown in Figure 1(b). It is observed that the peak due to carboxyl group of copoly(MMA-GMA) has completely vanished and ester linkage appeared at 176.00 ppm. Aromatic carbon peaks appear at 140.00–130.00 ppm. Peaks at 50.00–11.00 ppm are due to alkyl units such as CH, CH₂, and CH₃.

SMGAP-1, SMGAP-2, and SMGLAP-4/2

¹H and ¹³C NMR spectroscopy results of AZO polymers SMGAP-1 to -SMGLAP-4/2 are summarized in Tables III and IV. It can be seen that a new hydroxyl group appears for all azo polymers around 5.40 ppm due to opening of epoxy ring in copoly(MMA-GMA). Aromatic units resonate at 8.60–7.50 ppm. The peak due to amide unit in SMGAP-2 and SMGLAP-4/2 appears around at 9.80 ppm. Aliphatic units appear in the range of 4.76–0.74 ppm. Other ¹³C values for the polymers are found to be same as the other side chain LC polymers.

Solubility of polymers

All the synthesized polymers are found to be soluble in THF, DMF, chloroform, DMAC and DMSO, and insoluble in methanol and ethanol.

Viscosity measurement of polymers

Inherent viscosities of the polymers in DMSO are given in Table V. Inherent viscosity of copoly(MMA-GMA) is found to be 0.50 dL/g. For side chain LC polymers (SMGLCP-1 to SMGLCP-4), the value was found to be in the range of 0.52–0.56 dL/g in DMSO. Azo polymer SMGAP-1 has shown the value 0.54 dL/g in DMSO. For SMGAP-2 and SMGLAP-4/2, the viscosity values are found to be 0.60–0.70 dL/g in DMSO, which is slightly higher than other side chain LC polymers. This may be due to presence of secondary amine group in azopolymers, which has the ability to enter into hydrogen bonding leading to enhanced viscosity.

Thermogravimetric analysis of polymers

Initial degradation temperature (IDT) of the polymers is given in Table V. All side-chain LC polymers show higher IDT compared with copoly (MMA-GMA). After introducing the LC moiety into copoly(MMA-GMA) structure as a side group, the thermal stability has increased. This is due to introduction of rigid aromatic moiety to the aliphatic chain copolymer. Most of the polymers have shown thermal stability up to 280–300°C.

DSC study of monomers and polymers

DSC study of monomers

DSC results are summarized in Table V. LCM-1 shows crystalline to nematic LC transition at 180°C

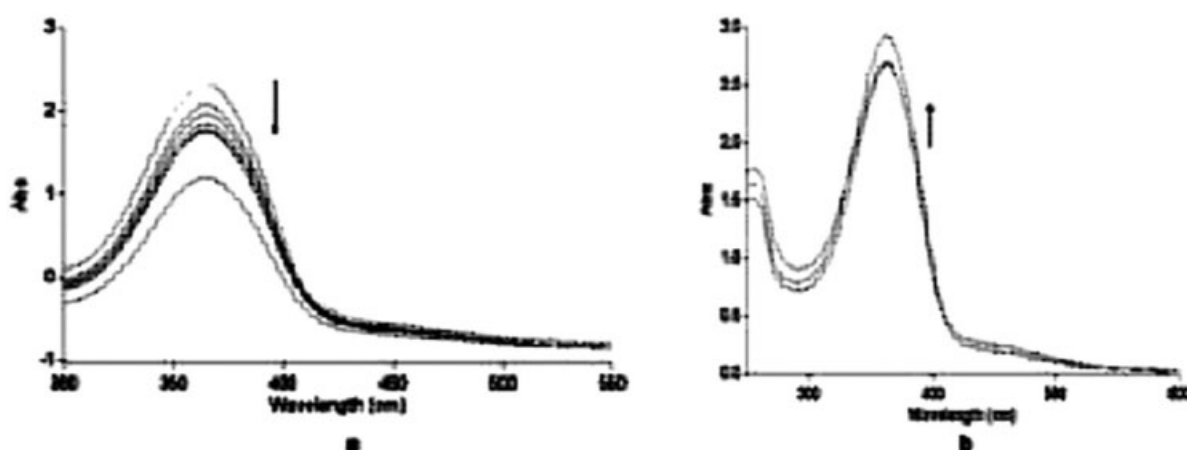


Figure 2 UV-Vis spectra of (AZO-1) during irradiation: trans-cis isomerization (365 nm) (a); cis-trans isomerization (Vis) (b).

and isotropization temperature at 217°C. LCM-2 and -3 show crystalline to mesophase transitions at 196°C and 38°C, respectively. More than two endotherms were observed for LCM-4 between 145 and 195°C. This indicates more than one mesogenic phases. AZO-1 is nonmesogenic in nature but AZO-2 show two thermal transitions between 158 and 255°C.

DSC study of polymers

The DSC results of polymers are summarized in Table V. It is observed that T_g of side chain LC polymers SMGLCP-1 to SMGLCP-3 decreases with increase in tail length. The T_g of SMGLCP-1 is 100°C and decreases to 75°C for SMGLCP-3. LC-isotropic transition also decreases in the same order. SMGLCP-4 shows the T_g (120°C) higher than that of other three side chain polymers. This may be due to presence of alicyclic ring as the bulky rigid tail. In case of azopolymers (SMGAP-1, SMGAP-2, and SMGLAP 4/2), the T_g values are found to be in the range of 105–112°C (Table V). SMGAP-1 and -2 show only two transitions whereas SMGLAP-4/2 shows three transition. This may be due to more than one LC phase in the latter.

Polarized optical microscopy study

LC monomers

Polarized optical microscopy (POM) study of LCM-1 to -4 and AZO-2 show characteristic LC phase (Table V). AZO-1 does not exhibit any characteristic mesophase. LC phases of monomers LCM-1 to -3 and AZO-2 are found to be nematic (thread like texture). LCM-4 has shown two different mesophases such as nematic (marbled texture) and smectic-A (sanded texture). The mesophase is found to similar to that

reported by Kumar et al.³⁰ Isotropization temperatures are also clearly observed for monomers and are given in Table V.

LC polymers

Side chain LCs

SMGLCP-1 to -3 has shown characteristic nematic LC phase at 180°C, 186°C, and 155°C, respectively, (Table V) and isotropization temperature is found to follow similar trend. SMGLCP-4 has two types of mesophase such as smectic-A (at 140°C) and nematic (190°C). This may be due to presence of cholesteric unit in the polymer. Azo polymers SMGAP-1 and -2 show the characteristic nematic mesophase at 145°C and 170°C, respectively. SMGLAP-4/2 shows both smectic-A (185°C) and nematic (260°C) mesophase. Here again, the presence of cholesteric units makes the difference. The additional benzene ring attached to azo unit also adds to mesogenic properties.³¹

Photoresponsive behavior study

Azobenzene monomers and LC-AZO polymers

On exposure to UV light, azobenzene monomers and polymers can be transformed from more stable trans form to less stable cis form by photoisomerization. Cis-trans back isomerization can take place either by a thermal process or by a photochemical process. These characteristics make them suitable for use in advanced photomechanical systems,^{7–10} photo switches, holographic data storage devices, and micropatterning.¹¹ In present study various chromophore combinations are made in the form of copolymer and their photoresponsive behavior was investigated. Figure 2(a,b) show the UV-Vis spectra

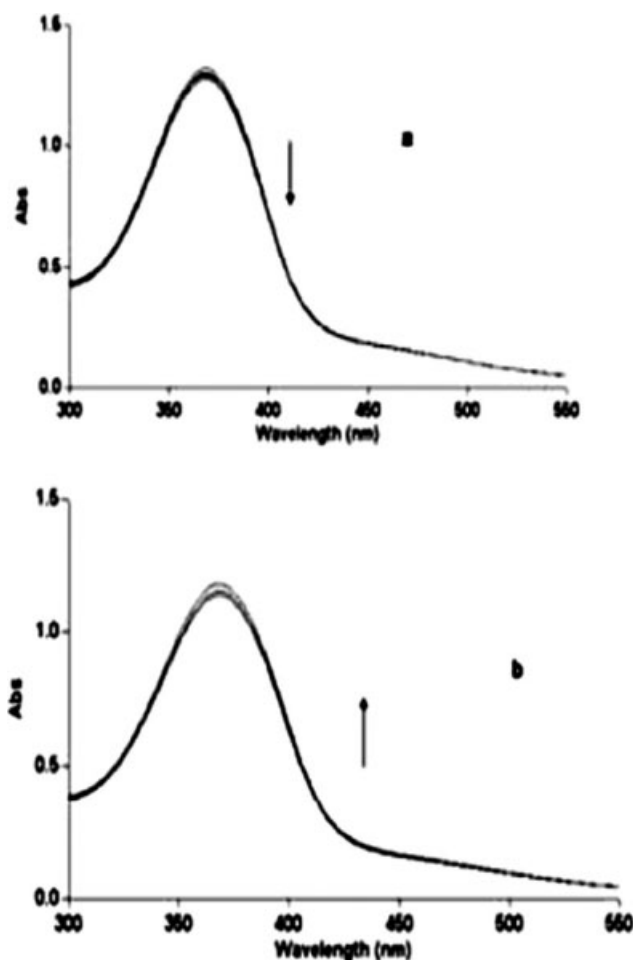


Figure 3 UV-Vis spectra of (SMGAP-1) during irradiation: trans-cis isomerization (365 nm) (a); cis-trans isomerization (Vis) (b).

of (AZO-1) during irradiation with UV and visible light at room temperature. A peak around 368 nm indicates λ_{max} due to π - π^* transition. Immediate decrease of peak height of trans isomer is observed [Fig. 2(a)]. The λ_{max} due to cis form is observed around 480 nm. Two "isobestic" points are observed around 325 nm and 415 nm. The irradiation was stopped and system was allowed to go for cis-trans (back isomerization) conversion by exposing to visible radiation at room temperature [Fig. 2(b)]. We can observe that the back isomerization is much slower compared to forward (trans-cis) isomerization. Similarly, the azo containing polymer (SMGAP-1) was studied under irradiation. We can see from Figure 3(a,b) that trans-cis isomerization is much slower compared to small azo molecules. This is expected as the mobility of chromophore in a polymer is much slower compared to small molecules. Also the back isomerization is slower than forward isomerization. Photoresponsive behavior of AZO-2 and polymers SMGAP-2 and SMGLAP-4/2 were found to follow similar trend.

CONCLUSIONS

A new synthetic strategy has been adopted to make high/desired molecular weight side chain liquid crystalline/crystalline/photoresponsive liquid crystalline copolymers. Spacers and additional functional groups were generated *in situ*. LC monomers (LCM-1 to -3) were built up using phenyl rings and ester linkage with various alkyl ends. Cholesteric LC monomer (LCM-4) was synthesized with bulky alicyclic ring attached to a phenyl ring through ester linkage. LC/AZO monomers were attached to copoly(MMA-GMA) by carboxyl-epoxy reaction to get side chain LC/photoactive copolymers. All side-chain LC polymers showed higher IDT compared with copoly(MMA-GMA) due to introduction of rigid aromatic moiety. LCM-4 has shown two different mesophase such as nematic and sanded smectic-A texture. All side-chain LC copolymers SMGLCP-1 to -3 show characteristic nematic LC phase. SMGLCP-4 has shown two types of mesophase such as smectic-A and nematic. Study of trans-cis isomerization and back isomerization indicated lower rate for polymer compared to that of the monomer.

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