

PHOTOINDUCED PHASE TRANSITION BEHAVIOR OF LIQUID CRYSTALLINE COPOLYMERS CONTAINING AZO CHROMOPHORE

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INTRODUCTION:

Photoresponsive polymers are being intensely investigated over last two decades, which can be attributed to both fundamental and applied significance. Presently the attention is being directed to these materials in view of their possible application in nonlinear optics and optoelectronics. It was demonstrated quite early that by covalent fixation of both photochromic group and the mesogenic group to the same polymer main chain high concentration of photochromic group can be attained. This has several advantages over guest-host system. Thereafter, a number of studies have been reported on synthesis of copolymers containing photochromic groups. A large number of studies have been concentrated on the photo-induced phase transition of liquid crystalline part due to trans-cis isomerization of azo groups. Trans form of azobenzene is rod-like and stable. Therefore, it fits into the liquid crystalline environment. On UV-irradiation the trans form isomerizes to bent cis form which is sterically obstructing. This incident induces transition from LC to isotropic phase. The number of studies on nonlinear optical properties of combined LC / photochromic dye is relatively small. It was proved that the polar order in a guest can be enhanced by the nematic ordering in a liquid crystal and is directly proportional to the degree of axial order in the medium. The polar orientation is found to be stable even at temperature above glass transition temperature. Further, studies were carried out using paired mesogens and enhancement in the interaction between the mesogens was observed.

In the present study mesogenic / azo copolymers were synthesized by using fixed mesogenic comonomer and varying azo containing comonomer. The spacer length was maintained at six methylene units. The comparative behavior of the copolymers was studied in terms of their liquid crystalline property, trans-cis isomerization and photoinduced phase transition.

EXPERIMENTAL

Synthesis of monomer

4-methoxyphenyl-4'-methacryloyloxy hexyloxy benzoate (MMHB) (M-I): It was synthesized by following the method of Horvath et. al. using 4-hydroxy benzoic acid as the starting material.

¹H-NMR (200 MHz, DMSO-d₆): δ(ppm) 8.01 (d, 2H), 7.04 (m, 6H), 5.99 (s, 1H), 5.63 (s, 1H), 4.08 (d, 4H), 3.74 (s, 3H), 1.85 (s, 3H), 1.39-1.72 (m, 8H).

4-nitrophenyl azophenyl-N-methylhexyl methacrylate (NAMM) (M-II): This monomer was synthesized in three steps by using method described in literature. In the final step tetrahydrofuran (THF) was used as solvent. Methacryloyl chloride was added under stirring at 60°C over a period of 30 minutes. After stirring for 4 hours the reaction mixture was cooled to 40°C and stirred for another 24 hours. The reaction mixture was cooled to room temperature and excess methylene chloride was added. Repeated extraction was carried out using water. The solution was dried over anhydrous sodium sulfate. The solvent was evaporated and the

residue recrystallized from ethanol.

¹H-NMR (200 MHz, DMSO-d₆): δ(ppm) 8.33 (d, 2H), 7.89 (m, 4H), 6.84 (d, 2H), 5.99 (s, 1H), 5.63 (s, 1H), 4.08 (t, 2H), 3.46 (t, 2H), 3.05 (s, 3H), 1.85 (s, 3H), 1.32-1.57 m, 8 H).

2-Methylene-succinic acid bis-(6-[methyl-[4-[(4-nitrophenylazo)-phenyl]-amino]-hexyl] ester (MSAE) (M-III):

4'-[(6-Hydroxyhexyl)methylamino]-4-nitroazobenzene (HMNA) was synthesized by following the synthetic route as in the case of M-II. It was then reacted with itaconic acid using Mitsunobu reaction. 2.86 gm (0.01 mole) HMNA was dissolved in 50 ml. THF. 6.55 gm (0.025 mole) triphenyl phosphine, dissolved in 10 ml. THF, was added. The solution was stirred under purging of argon gas at room temperature. A solution containing 4.04 gm (0.02 mole) diisopropyl azodicarboxylate and 0.72 gm (0.055 mole) itaconic acid in 10 ml THF was added dropwise over a period of 40 minutes. The progress of the reaction was checked by thin layer chromatography (TLC). The reaction was completed in 2 hours. The reaction was cooled in deep freezer and filtered. The residue was recrystallized from acetonitrile to get pure product.

¹H-NMR (200 MHz, DMSO-d₆): δ(ppm) 8.34 (d, 4H), 7.93 (m, 8H), 6.85 (d, 4H), 6.23 (s, 1H), 5.73 (s, 1H), 4.06 (m, 6H), 3.50 (m, 4H), 3.11 (s, 4H), 2.87 (s, 2H), 1.39-2.04 m, 16 H).

Synthesis of Copolymers: Equimolar mixture of M-I (mesogenic monomer) and M-II/M III (chromophore containing monomer) was dissolved in freshly distilled N-methyl pyrrolidone (NMP) to a total monomer concentration of 0.4 mole/l. Azobisisobutyronitrile (AIBN) (2 mole % with respect to total monomer) was added to the monomer solution. The solution was taken in glass ampoules and freed from dissolved gases by repeated freeze-thawing technique. The ampoules were placed in thermostated oil bath maintained at 65°C and the solution kept under stirring for 60 hours. The copolymer was precipitated into hot ethanol. The precipitated copolymers were purified by successive reprecipitation from THF into n-hexane and n-hexane/ethyl acetate(4:1,v/v). The pure copolymers were filtered and dried under reduced pressure at 60°C for 48 hours.

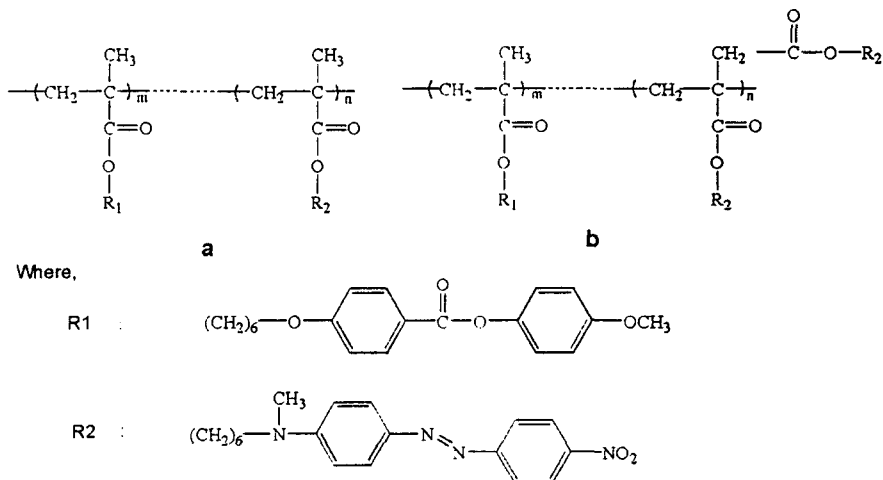


Figure 1: Structure of copolymers: (a) poly(MMHB-co-NAMM); (b) poly(MMHB-co-MSAE)

RESULTS AND DISCUSSION

UV-VIS absorption spectra: It is known that a cooperative motion exists between photoactive and non-photoactive mesogens. The effect of this cooperative motion on the birefringence of azo polymers were studied in detail by Natansohn et. al. To have an idea about the interaction between azo and mesogenic groups, present in the copolymers under study, the electronic spectra of the monomers and copolymers were taken. It can be seen that there is shift in absorption maxima (λ_{\max}) to higher wavelength as the polarity of the solvent is increased. Table II shows the λ_{\max} values of all the monomers in solution and polymers in solution and film respectively. The shift in absorption maximum of an azo dye may be due to two effects, such as association and dipole interaction of azo groups. Such shift was attributed by Whitten et. al. to solvatochromic effect. As regards dipole interaction, it is considered that azo dipoles are surrounded by solvent molecules. Highly polar solvent molecules have strong dipole-dipole interaction with the azo groups. Consequently, the shift in λ_{\max} is high. In the case of films the shift depends on the surrounding units. In both the copolymers MMHB units are present along with azo units. The ground state dipole moments of the monomers, calculated by using Hyperchem 5.0, are found to be: MMHB 1.180 D, NAMM 7.870 D, MSAE 12.667 D. MMHB molecules possess very low dipole moment. This approximates to a non-polar environment to azo units in the film of copolymer. So, the absorption maximum is expected to be around that in relatively less polar solvent such as dioxane. However, there is appreciable shift in the case of CP II, containing itaconate azo units (MSAE). The azo units are paired in this case and the dipole moment of this monomer is very high. Therefore, even in the environment of low polarity, it has some interaction and hence λ_{\max} shifts appreciably.

Table I: UV-VIS absorption maxima of monomers and copolymers

Sample	λ_{\max} (nm) in			
	Dioxane	Dioxane/DMAC 1:1 (vol/vol)	DMAC	Film(on glass slide)
NAMM	472	498	500	---
MMHB-co-NAMM	477	482	489	475
MSAE	471	495	499	---
MMHB-co-MSAE	477	489	500	486

Isomerization of azo group: Azo aromatic groups can undergo reversible trans-cis isomerization around the azo linkage when irradiated near its absorption maximum. Absorption spectra of CP I and CP II were taken in solutions and films respectively under irradiation at room temperature with Hg lamp. The absorption band having λ_{\max} at 488 nm is attributed to the $n-\pi^*$ transition, the first $\pi-\pi^*$ transition and an internal charge transfer transition. During irradiation the λ_{\max} value decreases due to conversion of trans isomer to cis isomer. The rate of decrease of λ_{\max} value is quite fast in solution whereas that in film is relatively slow. One isobestic point can be seen around 420 nm. λ_{\max} value slowly increases after discontinuing the irradiation which confirms the reversibility of isomerization in the present systems.

Photoinduced phase transition: During UV irradiation the azo unit isomerizes from trans to cis form. As the cis form destabilizes the LC phase, there is transition from LC phase to isotropic phase. Consequently there is change in birefringence. The change in transmittance of He-Ne laser was recorded during irradiation and after discontinuing the irradiation to respective

saturation values. Fig. 2 shows the representative curve of photoinduced birefringence (change in transmittance) as a function of irradiation time under the action of Hg lamp. Initially, the increase in birefringence proceeds rapidly and becomes smaller on continued irradiation. Finally a photostationary state is attained. The increase in the rate of growth can be due to reduced stability of the LC phase as it approaches the isotropization temperature. The increase in decay rate can be explained in terms of increased rate of cis-trans (reverse) isomerization at higher temperature. The rates of CP I are higher than the corresponding rates of CP II. The nematic phases being less ordered respond faster than the more ordered smectic phase. However, in the present investigation the nematic CP II is found to respond slower. Above observations can be explained in terms of dipole interaction. CP II is found to possess higher dipole interaction indicating the possibility of slower growth. At room temperature there is small residual birefringence after the relaxation in the case of CP I whereas no residual birefringence is observed in CP II. The absence of residual birefringence in CP II at room temperature may be due to the presence of paired mesogens. The bent cis form is thermally unstable and more so in the presence of paired mesogen.

Table II: Photoinduced phase transition parameters of copolymers

Samples	Birefringence parameters					
	Growth			Decay		
	k_{a-1} (sec^{-1})	k_{b-1} (sec^{-1})	τ_{resp} (sec)	k_{c-1} (sec^{-1})	k_{d-1} (sec^{-1})	τ_{relx} (sec)
CP I 25°C	0.0832	0.0647	35	0.1011	0.0035	19
55°C	0.0987	1.01×10^{-9}	20	0.1294	1.03×10^{-10}	17
CP II 25°C	0.0285	— ^a	62	0.0598	— ^a	36
65°C	0.0508	0.0487	38	0.0970	— ^a	21
80°C	0.0851	— ^a	22	0.1656	0.1277	11

^aSingle exponential fit

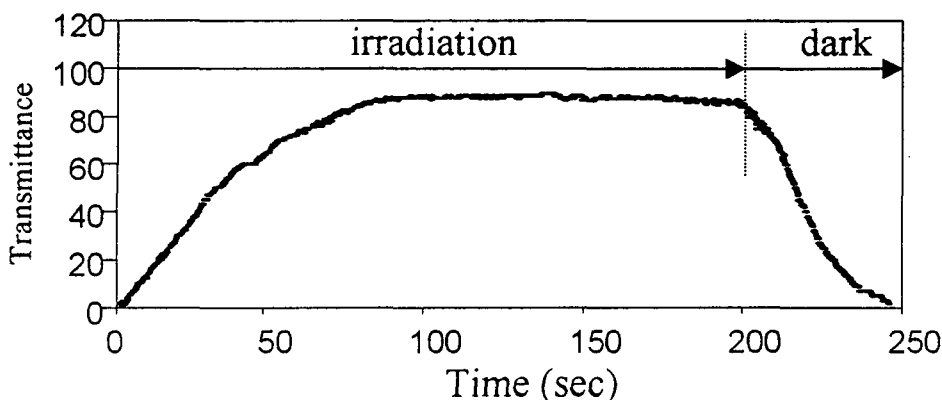


Figure 2: Growth and decay curve of transmittance due to the photoinduced phase transition for poly(MMHB-co-MSAE) under irradiation with high pressure Hg lamp (500 W, distance 24 cm at 45° angle), (probe beam He-Ne laser, $\lambda=632$ nm)