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Photochemical behaviours of star-like liquid crystal with azobenzene terminal groups

JIANQIANG LIU*
School of Physics and Microelectronics,Shandong University, Ji'nan, 250100, Shandong Province, People's Republic of China; Key Laboratory of Education Ministry on Colloid & Interface Chemistry, Ji'nan, 250100, Shandong Province, People's Republic of China
E-mail: jqliu@sdu.edu.cn

QIZHEN ZHANG, JINGZHI ZHANG
School of Chemistry and Chemical Engineering,Shandong University, Ji'nan, 250100, Shandong Province, People's Republic of China

WANGUO HOU
Key Laboratory of Education Ministry on Colloid & Interface Chemistry, Ji'nan, 250100, Shandong Province, People's Republic of China

The photochemical behaviours of a new star-like liquid crystal S6 with four hexyloxyazobenzene terminal groups were described in this paper. The molar absorption coefficient, quantum yield, photoisomerization, photo back-isomerization, thermal back-isomerization and activation energy of S6 in solution are studied by UV/Vis absorption spectra. The results indicate that the photochromism, photo and thermal back-isomerization of S6 in chloroform ($CHCl_3$) and tetrahydrofuran (THF) solutions are in accordance with the first order kinetics. The photochromism rate constants of S6 are 10^{-1} s^{-1}, it is 10^7 times larger than that of side-chain liquid crystalline polymers containing the same azobenzene moieties. These results indicate that the star structure does not significantly affect the photoisomerization activity of the azobenzene unit in its periphery. The k_t/k_c of S6 is less than that of azobenzene unit shows that the S6 has better photo-reversibility. So the star-like liquid crystal has many potential applications.

1. Introduction

Photochromism is a fascinating phenomenon and photochromic materials have recently attracted intense interest owing to their potential technological applications such as various photooptical devices and data recording media. Numerous polymers and low-molecular-mass compounds that exhibit different photoinduced transformations have been developed [1–7]. Recently, some advances in research dealing with the synthesis and study of optical properties of a series of photochromic LCs are considered [8–13]. Such as azobenzene systems, under UV irradiation, can undergo efficient and fully reversible photoisomerization reactions to provide versatile photoswitchable systems. We had successfully carried out the molecular architecture of the photochromic LC and got the star-like liquid crystal S6 containing four 4-hexyloxy-4′-hydroxyhexyloxy-azobenzene (HeA) units in its periphery, its phase behaviour was $Cr_{127}N_{144}I_{142}N_{116}Cr$ [14]. The structure of S6 was shown in Fig. 1, the star-like compound containing mesogenic and photochromic groups was structurally and functionally integrated system that showed simultaneously liquid crystalline and photochromic properties. The presence of the azo photochromic group provides its sensitivity to the light (see Fig. 1) and its photochemical behaviours are briefly studied by the UV/Vis absorption spectrum in the present paper.

2. Experimental

2.1. Materials

The synthesis and purification of S6 and HeA were described in Ref. [14, 15]. The compounds were characterized by EA, IR,^{1}H NMR, POM, DSC and XRD. Elemental analysis was carried out with a Perkin-Elmer 240 C auto elementary analyser. Infrared spectra was recorded on a Nicolet 5DX Fourier transform infrared photoacoustic spectral system (KBr/cm^{-1}).^{1}H NMR was carried out with a Japan JEOL FX-90Q (90 MHz, $CDCl_3$). Thermal phase transition behavior of the samples was examined by means of differential scanning

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*Author to whom all correspondence should be addressed.

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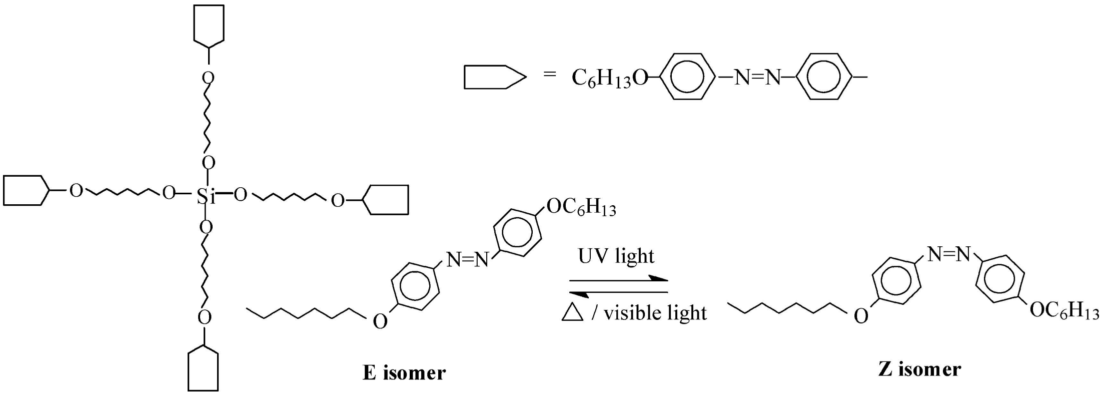

Figure 1 The structure and photoisomerization of star-like liquid crystal S6.

calorimetry (DSC, Perkin-Elmer 7 series thermal analysis system) and polarizing optical microscopic observation (POM, Seagull XPID polarizing optical microscope; Mettler FP80 and FP82 hot stage and controller). X-ray diffraction (XRD) pattern was recorded using D/max-γB diffractometer with Cu Kα radiation ($\lambda = 0.15405$ nm). All solvents in the experiment were refined before using.

2.2. Photochromism experiment

The photoirradiation was carried out by a 200 W high-pressure Hg-Xe lamp (Oriel) equipped with a glass filter and HP8451A UV/Vis spectrophotometer for ultraviolet irradiation [16]. A series of different concentration solutions of S6 in chloroform ($CHCl_3$) and tetrahydrofuran (THF) were prepared, they were scanned in the range of 300–600 nm. Then we can find the maximum absorption spectra is 360 nm, so $\lambda_{max} = 360$ nm. The absorptions were recorded at different time intervals until spectral variation was no longer evident. The solutions of S6 in $CHCl_3$ and THF in 1 cm path-length quartz cuvette were irradiated by ultraviolet light 360 nm at room temperature. The concentration of the solutions was adjusted to have an absorbance of about 0–1 at 360 nm. The intensity of UV irradiation were determined actinometrically and were equal to 1.89×10^{-7} J·s^{-1}·mol^{-1} ($\lambda_{ir} = 360$ nm) [17].

The 1.50×10^{-6}, 3.00×10^{-6}, 4.50×10^{-6}, 6.00×10^{-6} and 7.50×10^{-6} M S6 solutions were prepared in $CHCl_3$ and THF using the isolated S6 prepared as described earlier. The solutions were immediately subjected to UV/Vis absorption measurement and absorbance at $\lambda_{max} = 360$ nm of each solution was recorded with time. The plots between absorbance and molarity of the solution were then constructed in order to obtain the molar absorption coefficients ε of the compound in each solvent.

In the case of solutions of the compound, the process of *E*-*Z* isomerization is photochemically and thermally reversible; that is, under the action of visible light and annealing, back *Z*-*E* isomerization takes place. The solutions of S6 were irradiated by the 360 nm UV light for enough time ($t = 5$ min means $t = \infty$ here) and then immediately subjected to the 470 nm visible light or annealed in different temperature. Absorbance at different time was recorded to study the process of its photo and thermal back-isomerization.

3. Results and discussion

3.1. Molar absorption coefficients ε of S6

The UV absorption of S6 at various concentrations in various solvents was measured. Draw the absorbency of λ_{max} with the corresponding concentration, all the graphs gave straight line. The slope of the line is the molar absorption coefficient ε of S6 and ε in $CHCl_3$ and THF were 1.23×10^5 and 1.32×10^5 (dm^3·mol^{-1}·cm^{-1}), respectively. They are about four times higher than those of HeA, the ratio of ε is near that of azobenzene number [17]. So the absorption of S6 is stronger for the more azobenzene number it has. At the same time the polarity of solvent can increase the ε of S6 as the result of HeA in corresponding solutions. Those molar absorption coefficients obtained from the slopes of the graphs were summarized in Table I.

3.2. Quantum yield φ of S6

The quantum yield was determined using the formula $\varphi = \frac{\Delta A \times V}{\varepsilon \times L \times I_a \times t}$, where ΔA represents the absorption at the irradiation wavelength, I_a the irradiation intensity, ε the molar absorption coefficient at the irradiation wavelength, t the time of irradiation, V the volume and L the length of the cuvette. We can calculate the quantum yield φ of S6 in $CHCl_3$ and THF were 0.101 and 0.156, respectively. The φ of S6 is less than that of HeA for the steric influence [15, 18]. The photochemical quantum yield varies depending on the medium conditions and the polarity of solvent can increase the φ of S6. The differences in the reaction quantum yields can be referred to the different tendency of the formation of a highly polar state [19]. The result indicates that equilibrium of photoisomerization depends upon concentration and polarity of the solvent used.

3.3. Photoisomerization of S6

The solutions of S6 in $CHCl_3$ and THF were irradiated by ultraviolet light 360 nm at room temperature. The absorptions were recorded at different time intervals until spectral variation was no longer evident. The intensity of the UV absorption bands decreases with irradiation time in the 360 nm region but increases below 322 nm and above 424 nm. At the same time, the shoulder at about 440 nm gradually more resolved giving rise at the photostationary state to an

TABLE I ε, φ, k_p, k_t, k_c, k_t/k_c, k_h and E_A of S6 and azobenzene unit HeA

Sample	Solvent	$\varepsilon \times 10^{-4}$ /(dm^3·mol^{-1}·cm^{-1})	φ	k_p/(s^{-1})	k_t/(s^{-1})	k_c/(s^{-1})	k_t/k$_c$	$k_h \times 10^6$(s^{-1}) /T(K)	$E_A \times 10^{-4}$ /(J·mol^{-1})
S6	CHCl$_3$	12.3	0.101	0.408	0.146	0.0331	4.41	2167/287 4250/298 5120/303 5510/308	1.85
	THF	13.2	0.156	0.503	0.0416	0.00826	5.04	2.2/286 163/298 189/303 238/308	2.52
HeA	CHCl$_3$	3.27	0.528	0.514	0.0559	0.0117	4.78	694.4/289 1130/298 2090/303 2410/308	6.03
	THF	3.75	0.450	0.417	0.0324	0.00625	5.18	7.5/289 119/298 137/303 163/308	2.44

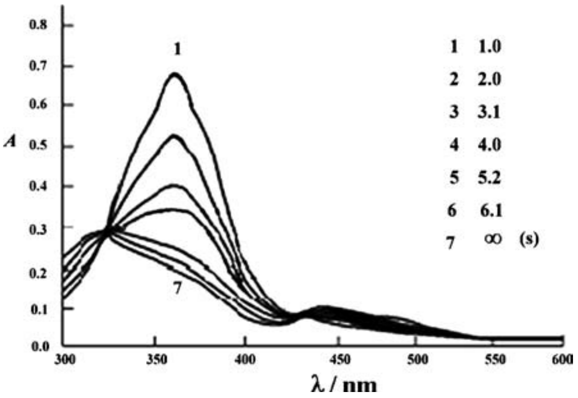

Figure 2 UV/vis spectrum of S6 in tetrahydrofuran solution.

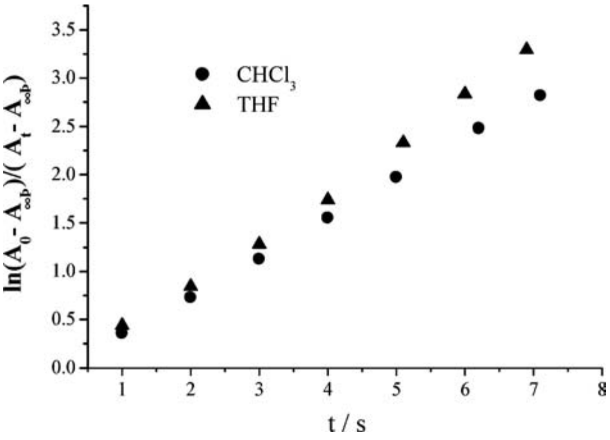

Figure 3 Photoisomerization of S6 in chloroform and tetrahydrofuran solutions.

absorption band with a distinct maximum at 440 nm (see Fig. 2). The occurrence of two distinct isobestic points at 424 and 322 nm as well as the similarity of the UV spectra of the irradiated samples at the photostationary state with that of *Z*-azobenzene indicate that only two absorbing species (*E* and *Z* isomers) are present and no side reactions such as photocrosslinking or photodegradation occur. Furthermore, the presence of two isobestic points (at 322 and 424 nm) during reversible isomerization processes clearly indicated the effective and reversible conversion of the azo unit. It also indicated that the isomerization was not accompanied by degradation, which would have resulted in a shift at two isobestic points. In all cases $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$, where A_0, A_t and A_∞ are the absorbances at 360 nm at zero time, *t* and infinite, respectively, shows a linear dependence on the irradiation time (see Fig. 3). They are in accordance with the first order kinetics and the slope is the photochromism rate constant k_p. k_p of S6 in CHCl$_3$ and THF were 0.408 and 0.503 (s^{-1}), respectively. The polarity of solvent can increase the k_p of S6. They were close to those of HeA (see Table I) and 10^7 times larger than those of side-chain liquid crystalline polymers containing the same azobenzene moieties in the corresponding solutions [20, 21]. These results indicate that the star structure does not significantly affect the photoisomerization rate, probably due to the presence of the flexible hexamethyl spacers.

3.4. Photo and thermal back-isomerization of S6

At first, the kinetics of the photo back isomerization was studied. In the formula $\ln[(A_\mathrm{e} - A_\infty)/(A_\mathrm{e} - A_\mathrm{t})] = (A_0 - A_\infty)/(A_e - A_\infty)\cdot k_t\cdot t$, A_0 is the absorbance at $\lambda_{\max} = 360$ nm at zero time, and A_∞ is the absorbance after 5 min irradiation at $\lambda_{\max} = 360$ nm ($t = \infty$) that can be regarded as the absorbance of the photostationary state. Then A_t and A_e are the absorbances at 470 nm at *t* time and infinite, respectively, which A_e is the absorbance of the equilibrium state of photo back-isomerization. k_t is rate constant of the *E* to *Z* isomers reaction and k_c is rate constant of the *Z* to *E* isomers reaction during the photo back-isomerization under the irradiation at $\lambda = 470$ nm visible light. The ratio of $k_\mathrm{t}/k_\mathrm{c}$ reflects the degree of photo back-isomerization, the value is more close to 1 means it is better to realize photoreversibility. To calculate the rate of this process, the values of $\ln[(A_\mathrm{e} - A_\infty)/(A_\mathrm{e} - A_\mathrm{t})]$ were plotted versus the time. We get the rate constant $\mathrm{k_t}$ from the slope of the line (see Fig. 4). Then following the term of the equilibrium state of photo back-isomerization: $k_\mathrm{c} = [(A_0 - A_\mathrm{e})/(A_\mathrm{e} - A_\infty)]\cdot k_\mathrm{t}$, we can get the rate constant k_c. They are in accordance with the first order kinetics and the values of $k_\mathrm{t}/k_\mathrm{c}$ in CHCl$_3$ and THF are 4.41 and 5.04, respectively (see Table I). They are all less than

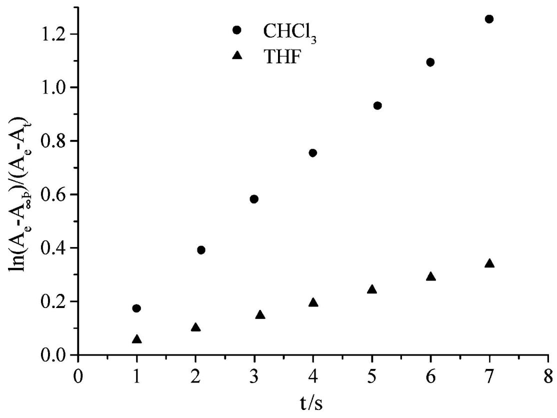

Figure 4 Photo back-isomerization for S6 in chloroform and tetrahydrofuran solutions.

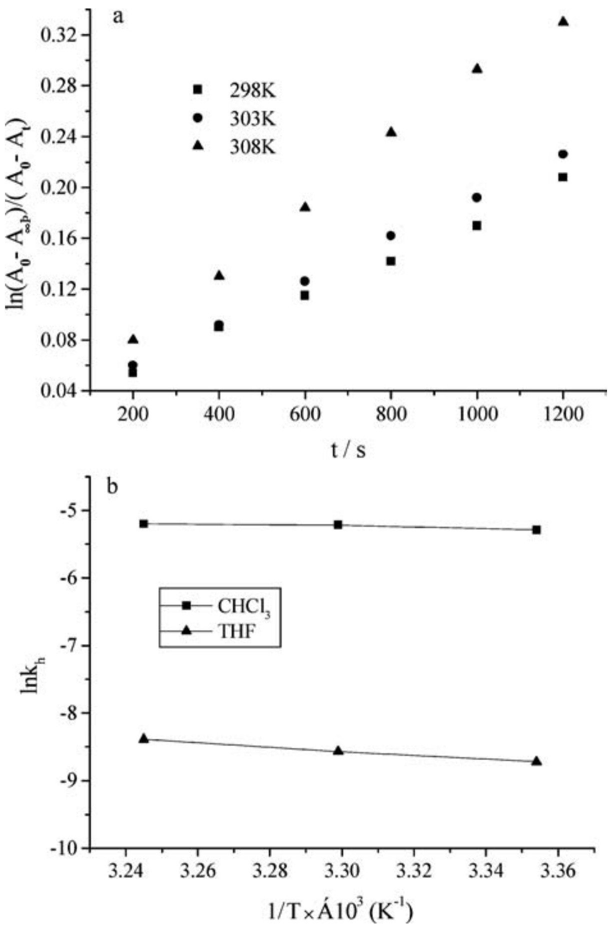

Figure 5 (a) Thermal back-isomerization for S6 in tetrahydrofuran solution at different temperatures and (b) Arrhenius plot for temperature dependence of rate constant of thermal *Z*/*E* process.

the k_t/k_c of azobenzene unit in the corresponding solvents, it shows that the S6 has better photo-reversibility.

Then the kinetics of the thermal back isomerization was studied at different temperatures and the value of the activation energy of the process was calculated. To this end, the solution of S6 was irradiated with UV light for 5 min and annealed in dark at different temperatures. Fig. 5a shows the temperature dependence of the *Z*/*E* isomerization rate. To calculate the rate constant k_h of this process, the values of $\ln[(A_0 - A_\infty)/(A_0 - A_t)]$ were plotted versus the time, where A_0 is the initial optical density and A_t and A_∞stand for the values of optical density at the time t and at the steady state, respectively. The slope of the graphs is the rate constant k_h of the thermal back isomerization. So, Table I presents the rate constants of the process. As is well seen, the *Z*/*E* isomerization rate strongly depends on the temperature and the polarity of solvent. Using the Arrhenius formula $\ln k_h = -\frac{E_A}{R\times T} + B$, we can calculate the activation energy of the thermal *Z*/*E* isomerization, the rate constants are plotted against the reciprocal temperature (Fig. 5b). E_A is calculated from the slope of this plot and listed in Table I, and it is found to be about 19.5 kcal/mol. The value of the activation energy is typical for azobenzene derivatives [22]. In conclusion, the thermal back isomerization of S6 in different solvents is in accordance with the first order kinetics. The rate and the most maximum absorption ($A_{\max}$) of thermal back isomerization depend on the temperature of the process, so we can say the higher temperature is beneficial to the stabilization of *E* isomerization. At the same time, the reaction rate and the $A_{\max}$ of thermal back isomerization in $CHCl_3$ are both far higher than those in THF, so the less polarity of solvent is beneficial to the stabilization of *E* isomerization, too.

4. Conclusion

Hence, in this work, the kinetics of *E*/*Z* and *Z*/*E* isomerization of terminal azobenzene groups of the star-like liquid crystal was studied in different solutions. The results indicate that the star structure does not significantly affect the photoisomerization activity of the azobenzene unit in its periphery and the S6 has better photo-reversibility. At the same time, the rate constants of the thermal back isomerization of S6 in different solvents were far small less than those of photochromism and photo back-isomerization of S6 in same solvent, so the effect of thermal back isomerization can be ignored in the common request. So the star-like liquid crystal has many potential applications and will become a new type photocontrolable switch and information functional material. Undoubtedly, the preparation of photoactive star-like liquid crystal presents an evident scientific and practical interest because the star-like molecules allows one to anticipate a fast optical response and the rearrangement of their branched structure under the action of external fields and, in particular, light irradiation. This aspect should be interesting for the development of fast-acting photosensitive materials, which can be easily handled. We also hope that switchable star-like molecules will have applications in transport systems based on the reversible perturbation of their ability to encapsulate and release small molecules [23, 24].

In another word, the star-like compounds can be looked on as the simplest dendrimer, we can bring it up to the multi-branched dendrimer by farther process. Further work in this direction will be focused on a comparative analysis of the kinetic features of photoisomerization and other photochemical behaviours for them of various generations, higher glass transition temperatures and bigger molecular mass.

Acknowledgments

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